

Review

Design of Efficient Molecular Catalysts for Synthesis of Cyclic Olefin Copolymers (COC) by Copolymerization of Ethylene and α -Olefins with Norbornene or Tetracyclododecene

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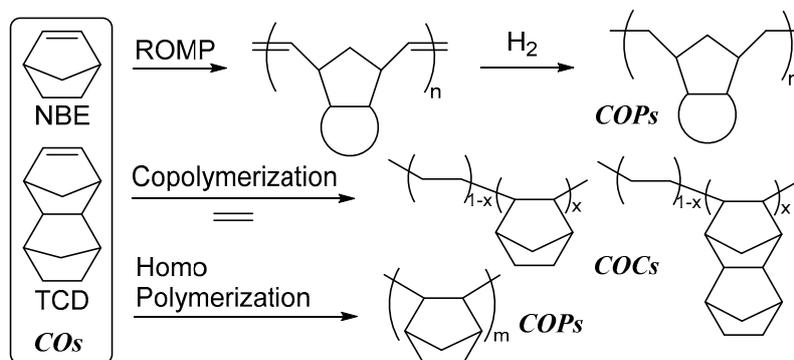
Abstract: Selected results for the synthesis of cyclic olefin copolymers (COCs)—especially copolymerizations of norbornene (NBE) or tetracyclododecene (TCD) with ethylene and α -olefins (1-hexene, 1-octene, 1-dodecene)—using group 4 transition metal (titanium and zirconium) complex catalysts have been reviewed. Half-titanocenes containing an anionic ancillary donor ligand, Cp'TiX₂(Y) (Cp' = cyclopentadienyl; X = halogen, alkyl; Y = anionic donor ligand such as aryloxo, ketimide, imidazolin-2-iminato, etc.), are effective catalysts for efficient synthesis of new COCs; ligand modifications play an important role for the desired copolymerization. These new COCs possess promising properties (high transparency, thermal resistance (high glass transition temperature), low water absorption, etc.), thus it is demonstrated that the design of an efficient catalyst plays an essential role for the synthesis of new fine polyolefins with specified properties.

Keywords: polymerization; titanium; zirconium; cyclic olefin copolymers; catalyst design; half-titanocene; homogeneous catalysis

1. Introduction

Polyolefins such as polyethylene (high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), etc.) and polypropylene, produced by metal-catalyzed olefin coordination polymerization, are important commercial synthetic polymers in our daily life, and the market capacity still increases every year (especially in China, India, and countries in the Middle East). Synthesis of new polymers with specified functions has been considered to be one of the most attractive targets, and precise control in the copolymerization is thus a feature that usually allows the alteration of the (physical, mechanical, and electronic) properties by varying the ratio of individual components. Design of molecular catalysts attracts considerable attention in terms of synthesis of new polymers; recent progress in the newly designed catalysts offers several new possibilities. Certain cyclic olefin copolymers (COCs) and cyclic olefin polymers (COPs) are amorphous materials with a promising combination of high transparency in the UV–vis region along with humidity- and thermal-resistance (high glass transition temperature, T_g), and extremely low water absorption (excellent water vapor barrier properties) [1–7]. Due to promising characteristics of COCs, these are used as (i) optical applications such as lenses, liquid crystal display light guide panels, and optical films; (ii) materials in medical and diagnostic equipment and electronic devices; and (iii) packaging applications, and many other uses [8,9]. In the practical production process, as shown in Scheme 1, methods such as ring-opening metathesis polymerization (ROMP) of multi-COs and subsequent hydrogenation (for COPs), coordination insertion copolymerization of ethylene with COs

(for COCs), or homopolymerization of COs (for COPs) are generally employed. The copolymerization approach seems to be more promising, because the desired properties (e.g., T_g) should be tuned by their compositions (e.g., CO content) as well as their microstructures (including tacticity, etc.) [1–7]. COCs are commercialized (as TOPAS[®], APEL[®], etc.) as ultrapure (applicable to advanced pharma packaging or food-contact films), crystal-clear (glass clear, amorphous), high-barrier (resistant to moisture, alcohols, acids) materials [8,9].

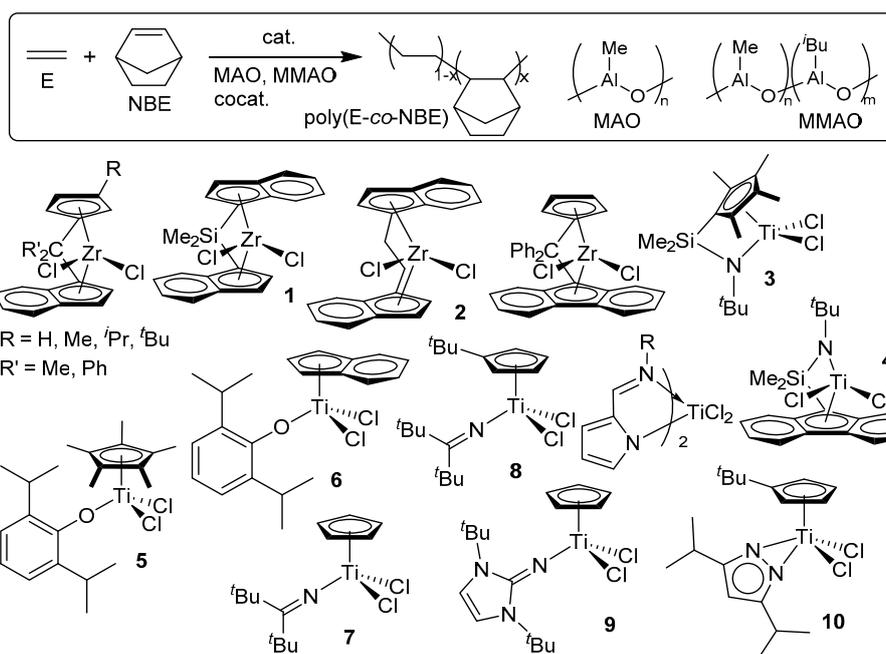


Scheme 1. Typical process for synthesis of COCs (cyclic olefin copolymers) and COPs (cyclic olefin polymers).

Many have reported on ethylene copolymerization with norbornene (NBE) using ordinary metallocenes [10–17], half-titanocenes [18–26], and others [27–30], however, successful examples of the efficient synthesis of random, high molecular weight copolymers with high T_g values (high NBE content) have been limited. Ethylene copolymers with tetracyclododecene (TCD, dimethano-octahydronaphthalene) are also known as promising materials [9], and are produced by using classical Ziegler-type vanadium catalyst systems (VOCl_3 , $\text{VO}(\text{OEt})\text{Cl}_2\text{-EtAlCl}_2\text{-Et}_2\text{AlCl}$, etc.) [31]. There have been reports on the copolymerizations using metallocene catalysts [3,32–35] and others [36], however, these catalysts have generally exhibited low catalytic activities and/or less efficient TCD incorporation. For examples, activities (TCD content) by $[\text{Et}(\text{Ind})_2]\text{ZrCl}_2$ [32], $[\text{Ph}_2\text{C}(\text{Ind})(\text{Cp})]\text{ZrCl}_2$ [33], $[\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})]\text{ZrCl}_2$ [33], $[\text{Me}_2\text{C}(3\text{-MeC}_5\text{H}_3)(\text{Flu})]\text{ZrCl}_2$ [3], $[\text{Me}_2\text{C}(3\text{-}^t\text{BuC}_5\text{H}_3)(\text{Flu})]\text{ZrCl}_2$ [3] were 25 kg-polymer/mol-Zr·h (35 mol %), 31 (85 mol % at 90 °C), 24 (68), 1.3 (40), 0.4 (44), and respectively. Design of molecular catalysts for synthesis of new polymers with specified functions is one of the most attractive targets in the field of catalysis, polymer chemistry, and organometallic chemistry [37–48]. In this minireview, reported examples of copolymerization of COs (NBE, TCD) with olefins (ethylene, propylene, 1-hexene, 1-octene, etc.), including our efforts using so-called *nonbridged* half-titanocene catalysts [39,41,45], $\text{Cp}'\text{TiX}_2(\text{Y})$ (Cp' = cyclopentadienyl; X = halogen, alkyl etc.; Y = anionic ancillary donor such as aryloxy, ketimide, imidazolin-2-iminato, etc.), have been summarized.

2. Copolymerization of Ethylene with Norbornene (NBE), Tetracyclododecene (TCD) by Titanium and Zirconium Complex Catalysts

As described in the introduction, many have reported on ethylene copolymerization with norbornene (NBE) [10–30], however, successful examples of the efficient synthesis of random, high molecular weight copolymers with high T_g values (high NBE content) have been limited. Selected complex catalysts employed for the copolymerization are shown in Scheme 2, and selected typical results are summarized in Table 1.



Scheme 2. Selected complex catalysts for copolymerization of ethylene with norbornene [1–30].

Table 1. Copolymerization of ethylene (E) with norbornene (NBE) by $[\text{Me}_2\text{Si}(\text{indenyl})_2]\text{ZrCl}_2$ (**1**), $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2$ (**3**), $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$ (Cp^* , **5**), indenyl (**6**)), $\text{Cp}^*\text{TiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ ($\text{Cp}^* = \text{Cp}$ (**7**), $^t\text{BuC}_5\text{H}_4$ (**8**)), $\text{Cp}^*\text{TiCl}_2[1,3\text{-}^t\text{Bu}_2(\text{CHN})_2\text{C}=\text{N}]$ (**9**), $(^t\text{BuC}_5\text{H}_4)\text{TiCl}_2(3,5\text{-}^i\text{Pr}_2\text{C}_3\text{HN}_2)$ (**10**)-MAO catalysts. ^a

Cat. (μmol)	Temp./ °C	Time/ min	E/atm	NBE ^b /M	$[\text{NBE}]_0/[\text{E}]_0$ ^c	Activity ^d	M_n ^e × 10 ⁻⁴	M_w/M_n ^e	NBE ^f /mol%	Ref.
1 (0.10)	25	10	4	0.2	0.41	28,860	23.1	2.02	10.8	24
1 (0.10)	25	10	4	1.0	2.04	4860	22.9	2.37	29.5	24
3 (0.50)	25	10	4	0.2	0.41	2460	21.1	1.88	9.6	24
3 (0.50)	25	10	4	1.0	2.04	2000	12.8	2.15	26.5	24
5 (0.2)	25	10	4	0.2	0.41	6540	57.9	1.61	8.2	24
5 (0.2)	25	10	4	1.0	2.04	2640	29.6	1.46	21.7	24
6 (0.2)	25	10	4	0.2	0.41	10,500	14.6	1.56	14.0	24
6 (0.5)	25	10	4	1.0	2.04	2300	5.87	1.82	35.2	24
7 (0.02)	25	10	4	0.2	0.41	21,600	70.6	1.85	17.8	24
7 (0.02)	25	10	4	1.0	2.04	40,200	71.9	2.92	40.7	24
7 (0.02)	25	20	4	1.0	2.04	60,150	53.4	2.11	41.5	24
7 (0.02)	25	30	4	1.0	2.04	59,700	61.3	2.18	41.0	24
7 (0.02) ^g	25	10	4	1.0	2.04	42,300	35.5	2.42	41.8	24
7 (0.02) ^h	25	10	4	1.0	2.04	50,400	35.1	2.31	42.9	24
7 (0.01) ⁱ	25	10	2	5.0	20.6	85,800	34.0	2.00	65.8	24
7 (0.01) ⁱ	25	10	2	10.0	41.2	31,500	44.4	2.01	73.5	24
7 (0.02)	40	10	4	1.0	2.45	48,900	62.0	2.37	45.9	24
7 (0.02)	60	10	4	1.0	3.02	194,000	47.5	2.20	51.2	24
7 (0.02)	80	10	4	1.0	3.94	133,000	33.8	2.34	61.7	24
8 (0.01)	25	10	4	1.0	2.04	68,400	62.4	2.78	38.2	6
8 (0.10) ^g	25	10	2	5.0	20.6	4980	14.2	1.94	64.8	6
9 (0.20)	25	10	4	1.0	2.04	6180	108	2.53	31.4	26
9 (0.20)	80	10	4	1.0	3.94	5780	80.0	2.35	36.9	26
9 (1.0)	50	10	2	5.0	27.3	1820	13.8	1.85	55.5	26
10 (0.25)	25	10	5	0.5	0.82	5170	126	2.32	37.2	26
10 (0.25)	25	10	5	1.0	1.63	3470	89.2	2.63	43.9	25

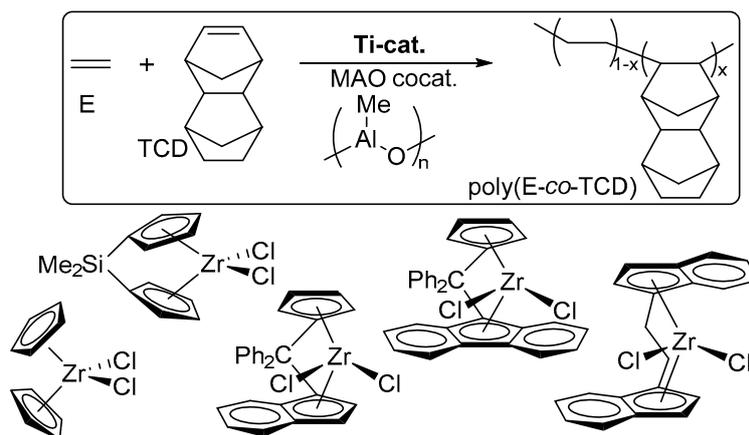
^a Conditions: toluene + norbornene (NBE) total 50 mL, ethylene 4 atm, methylaluminoxane (MAO) white solid 0.5–3.0 mmol; ^b NBE concentration charged (mmol/mL); ^c initial molar ratio; ^d activity in kg-polymer/mol-M-h ($M = \text{Ti, Zr}$); ^e gel permeation chromatography (GPC) data in *o*-dichlorobenzene vs polystyrene standards; ^f NBE content (mol %) estimated by ¹³C NMR spectra; ^g modified MAO (MMAO)-3A-T, Me/ⁱBu = 2.33, 3.0 mmol; ^h MMAO-3A-H, Me/ⁱBu = 2.67, 3.0 mmol; ⁱ toluene + NBE total 10 mL.

In the copolymerization of ethylene with NBE using metallocene (exemplified as **1**) and linked half-titanocene (**3**), the activity generally decreases upon increasing the NBE content (NBE concentration charged). Aryloxo-modified half-titanocenes (exemplified as **5** and **6**) have been known as effective catalysts in ethylene copolymerization, not only with α -olefin, but also with sterically encumbered olefins and cyclic olefins [39,41,45]; an efficient catalyst for the desired copolymerization can be tuned by the cyclopentadienyl fragment [39,41]. The indenyl-aryloxo analogue (**6**) showed efficient NBE incorporation with high catalytic activity, whereas the Cp*-aryloxo analogue (**5**) showed less efficient NBE incorporation than **6** [22,23], however, both the activity and the M_n value decreased upon increasing the NBE content. The Cp'-pyrazolato analogue (**10**) exhibited efficient NBE incorporation with rather low NBE concentration (Table 1) to yield ultrahigh molecular weight copolymers with unimodal molecular weight distributions, but the activity decreased upon increasing the NBE concentration [25].

We demonstrated that the Cp-ketimide analogue, CpTiCl₂(N=C^tBu₂) (**7**), exhibited remarkable catalytic activities, and a decrease in the activity was not observed, even after 30 min [24]. The activity increased upon increasing the initial NBE concentration, whereas, as described above, a decrease in activity was observed in other catalysts upon increasing NBE concentration. The NBE content in the copolymers was thus higher than those prepared by other catalysts under the same conditions. It is noteworthy that neither activity nor NBE incorporation were strongly affected by the Al cocatalyst employed (methylaluminumoxane (MAO), modified MAOs (MMAOs)), a fact that is in distinct contrast to that reported for the copolymerization by [Me₂Si(fluorenyl)(N^tBu)]TiMe₂ (**4**) in which both the catalytic activity and NBE incorporation are highly dependent upon the Al cocatalyst employed [21]. Both the activity (of **7**) and the NBE content in the copolymer increased at a higher temperature (40–80 °C), and the resultant copolymers possessed high molecular weights with unimodal molecular weight distributions ($M_n = 3.38 \times 10^5$ to 6.20×10^5 , $M_w/M_n = 2.20$ – 2.37) [24]. The efficient synthesis of high molecular weight copolymers with high NBE content (58.8–73.5 mol %) is possible upon increasing the NBE concentration at low ethylene pressure (2 atm). This may also be explained by the fact that **7** showed remarkable catalytic activity for NBE homopolymerization. The resultant polymers possessed uniform compositions, confirmed by differential scanning calorimetry (DSC) thermograms as well as gel permeation chromatography (GPC) traces, and a linear relationship between glass transition temperatures and NBE content in the resultant poly(ethylene-*co*-NBE)s was observed [22–25].

The Cp'-imidazolin-2-iminato analogue exhibits remarkable catalytic activities for ethylene (co)polymerization [49–51], and ethylene/NBE copolymerization by CpTiCl₂[1,3-^tBu₂(CHN)₂C=N] (**9**) afforded ultrahigh molecular weight copolymer with efficient NBE incorporation and a catalytic activity that did not decrease at 80 °C [26]; both the activity and the M_n value decreased upon increasing the NBE concentration under low ethylene pressure. Although the observed activities by **9** were lower than those by **7**, **9** seems to be a promising candidate as an efficient catalyst that affords high molecular weight polymers at high temperature. In contrast to the imidazolin-2-iminato analogue [26], the Cp'-imidazolidin-2-iminato analogue showed less efficient NBE incorporation in the ethylene/NBE copolymerization [52]. In these catalysts, a significant effect of the ligand substituents on both the catalytic activity and the comonomer incorporation was observed.

As described above, ethylene copolymers with tetracyclododecene (TCD, dimethano-octahydronaphthalene) and poly(ethylene-*co*-TCD)s are promising materials, possessing higher glass transition temperatures compared to poly(ethylene-*co*-NBE)s with the same cyclic olefin content; catalyst(s) development/design for the efficient copolymerization (high catalytic activity and efficient TCD incorporation) has thus been a promising target in the field of catalysis and polymer chemistry. These are produced by using classical Ziegler-type vanadium catalyst systems (VOCl₃, VO(OEt)Cl₂·EtAlCl₂·Et₂AlCl, etc.) [9,31]. In contrast to many reports of the ethylene/NBE copolymerization [1–30], there have been reports for the copolymerization using metallocene catalysts (Scheme 3) [3,32–35] and others [36], however, these catalysts generally exhibited low catalytic activities and/or less efficient TCD incorporation [35].



Scheme 3. Reported metallocene catalysts for copolymerization of ethylene with tetracyclododecene (TCD) [3,32–35].

More recently, we realized that the ketimide-modified half-titanocenes, which are effective catalysts for ethylene copolymerization with NBE [24], especially the (^tBuC₅H₄)TiCl₂(N=C^tBu₂) (**8**)-MAO catalyst, exhibited remarkable catalytic activities and efficient comonomer incorporation in ethylene/TCD copolymerization, affording high molecular weight polymers with uniform molecular weight distributions (Table 2) [53]. The activity of **8** was significantly higher than that of the Cp analogue (**7**), whereas the activity of the Cp analogue (**7**) was much higher than that of **8** for α -olefin/TCD copolymerization [54]. The resultant polymers prepared by **7**- or **8**-MAO catalysts possess high molecular weights with uniform molecular weight distributions. The resultant polymers possess sole glass transition temperatures (T_g), suggesting that these are poly(ethylene-*co*-TCD)s with uniform compositions.

Table 2. Copolymerization of ethylene with tetracyclododecene (TCD) by Cp'TiCl₂(N=C^tBu₂) (Cp' = Cp (**7**), ^tBuC₅H₄ (**8**)), CpTiCl₂[1,3-^tBu₂(CHN)₂C=N] (**9**), Me₂Si(C₅Me₄)(N^tBu)]TiCl₂ (**3**)-MAO catalysts ^a.

Ti/ μ mol	TCD ^b /mol/L	temp./ $^{\circ}$ C	Activity ^c	M_n ^d $\times 10^{-5}$	M_w/M_n ^d	T_g ^e (T_m ^e)/ $^{\circ}$ C	TCD ^f /mol%
3 (0.05)	1.0	25	13,900	14.3	1.58	56	-
7 (0.4)	1.0	25	1510	2.33	1.56	-	-
7 (0.8)	2.0	25	1650	1.92	1.41	150	-
8 (0.02)	1.0	25	43,700	5.88	1.60	108	25.6
8 (0.02)	2.0	25	23,900	6.38	1.50	153	32.8
8 (0.02)	2.0	40	27,800	6.43	1.67	170	33.5 ^g
8 (0.02)	2.0	60	33,300	6.53	1.72	177	35.3
8 (0.02)	3.0	25	16,800	6.43	1.61	171	33.6 ^g
8 (0.02)	4.0	60	22,400	6.08	1.61	203	36.7
9 (0.2)	1.0	25	6680	4.68	1.77	160 (108) ^g	-

^a Polymerization conditions: toluene and TCD total 30 mL, ethylene 6 atm, 10 min, d-MAO (prepared by removing toluene and AlMe₃ from the ordinary MAO) 3.0 mmol; ^b initial monomer concentration;

^c activity = kg-polymer/mol-Ti-h; ^d GPC data in *o*-dichlorobenzene vs polystyrene standards; ^e measured by differential scanning calorimetry (DSC) thermograms; ^f estimated from ¹³C NMR spectra; ^g estimated on the basis of the plots of T_g and TCD content.

In contrast, attempted copolymerizations by the imidazolin-2-iminato analogues, CpTiCl₂[1,3-^tBu₂(CHN)₂C=N] (Cp' = ^tBuC₅H₄, Cp (**9**)), afforded polymers possessing melting temperature (ca. 110 $^{\circ}$ C, probably corresponding to polyethylene with low TCD content) and/or glass transition temperature (ca. 160 $^{\circ}$ C, corresponding to ethylene/TCD copolymer containing moderate TCD content). These suggest that the resultant polymers are a mixture of at least two compositions and that the catalytically active species are not uniform during the polymerization.

The linked half-titanocene (**3**) exhibited high catalytic activity under the same conditions, affording a high molecular weight copolymer with low TCD content (estimated by the T_g value).

Note that the activity of the **8**-MAO catalyst increased at higher temperature (activity of **8**: 23,900 kg-polymer/mol-Ti·h (25 °C) < 27,800 (40 °C) < 33,300 (60 °C)) upon increasing the TCD content in the copolymers. As observed in poly(ethylene-*co*-NBE)s, a linear relationship between the TCD content and glass transition temperature (T_g) was observed, suggesting that the resultant copolymers possess uniform composition. Since the reported metallocene catalysts showed low catalytic activities (and/or had less efficient TCD incorporations), and ordinary Ziegler-type vanadium catalyst systems are generally sensitive to polymerization temperature, the present catalyst would be a promising candidate (as a *thermally robust* catalyst) for efficient synthesis of ethylene/TCD copolymers (highly transparent, thermal-resistant materials).

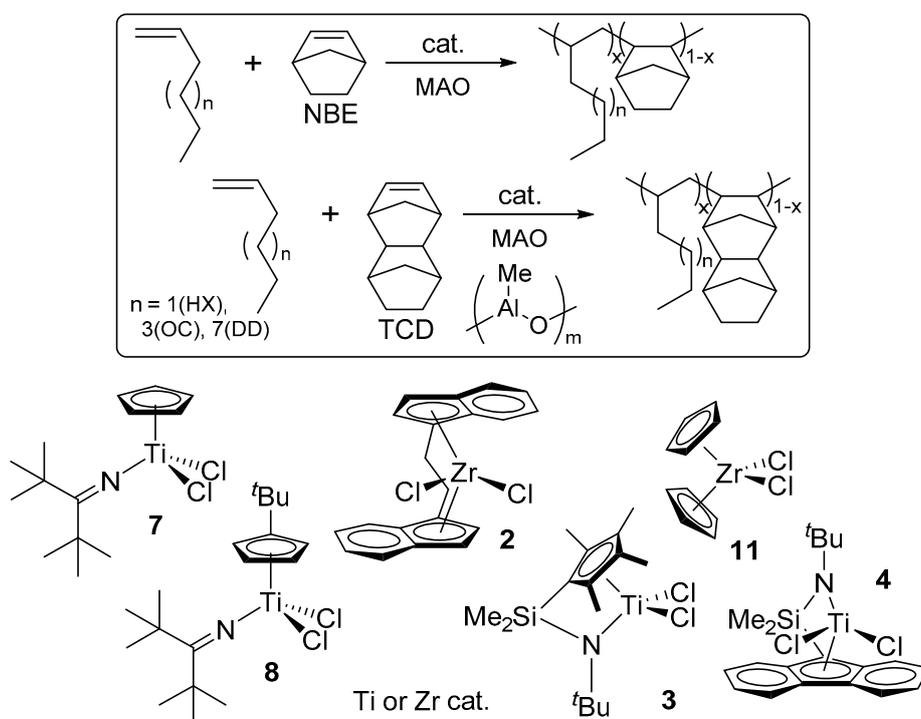
3. Copolymerization of α -Olefin with Norbornene (NBE) or Tetracyclododecene (TCD) by Half-Titanocene Catalysts

As described in the introduction, reported examples for copolymerization of NBE with α -olefin have been limited [54–64], probably due to the difficulty of α -olefin insertion after NBE incorporation by linked-metallocene catalysts, as pointed out in a previous review by Tritto et al. [5]. In fact, both the catalytic activity and the M_n values decreased upon increasing the α -olefin content in the NBE/1-octene copolymerization using $[\text{H}_2\text{C}(\text{Me}_2\text{C}_5\text{H}_2)_2]\text{ZrCl}_2$ [58]. As one exception, the fluorenyl-based half-titanocenes, exemplified by $[\text{Me}_2\text{Si}(\text{fluorenyl})-(\text{N}^t\text{Bu})]\text{TiMe}_2$, (**Flu-CGC**, **4**) reported by Shiono et al. afforded copolymers of NBE not only with propylene [60,61], but also with α -olefin (1-hexene, 1-octene, and 1-decene) [62,63], and the resultant copolymers possessed narrow molecular weight distributions because of the nature of livingness, as observed in the NBE [64,65] and the propylene polymerizations [66]. Both the activity (especially) and the α -olefin content were affected by the ligand substituents and cocatalyst employed [60–63]. Examples of copolymerization of TCD with α -olefins have not been reported, so far [67].

We recently reported that the ketimide-modified half-titanocenes, $\text{CpTiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ (**7**), which are effective catalysts for ethylene/NBE copolymerization [24], showed high catalytic activity with efficient NBE incorporation in the copolymerization of NBE with α -olefins (1-hexene and 1-octene), affording high molecular weight polymers with uniform molecular weight distributions and compositions (Scheme 4) [54]. Selected results are summarized in Table 3.

As shown in Table 3, the copolymerizations of NBE with 1-hexene (HX), 1-octene (OC), and 1-dodecene (DD) by **7**- or **8**-MAO catalysts afforded high molecular weight copolymers with unimodal molecular weight distributions and with uniform compositions confirmed by DSC thermograms (observed as a sole glass transition temperature (T_g)). Moreover, the T_g values increased upon increasing the NBE content, as estimated by ^{13}C NMR spectra. The copolymerization of NBE with HX by $(^t\text{BuC}_5\text{H}_4)\text{TiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ (**8**)-MAO catalyst proceeded with moderate catalytic activity that is comparable to that of the reported **Flu-CGC** (**4**)- $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ catalyst [62], and the activity increased upon increasing the NBE concentration charged. The Cp analogue (**7**) showed >10 times higher activity and better NBE incorporation than the $^t\text{BuC}_5\text{H}_4$ analogue (**8**) under the same conditions, and the T_g values (corresponding to NBE contents in the resultant copolymers) were not affected by the kind of Al cocatalyst employed (MAO or MMAO). Good correlation between T_g values and NBE content in poly(NBE-*co*-HX)s was observed, irrespective of the cyclopentadienyl fragment (Figure 1a); this would be in distinct contrast to that reported previously (exemplified by **4**), in which the plots (slope) are affected by substituents on the fluorenyl ligand as well as by the cocatalyst employed [62,63]. Similarly, the copolymerization of NBE with OC by **7**- or **8**-MAO catalysts proceeded with high catalytic activities, and both the activity and the NBE incorporation by **7** were higher than that by **8** under the same conditions. The activity of **7** (on the basis of polymer yields) was not strongly affected by the initial NBE/OC feed ratios, whereas the activity of **8** increased upon increasing the initial NBE concentration charged under certain conditions. Similar trends (for both

the activities and NBE incorporations) were observed in the copolymerization of NBE with DD. Good linear relationships between T_g values and NBE content in poly(NBE-*co*-HX)s (Figure 1a) and poly(NBE-*co*-OC)s (Figure 1b) were observed, irrespective of kind of titanium catalysts (7 and 8) employed. The T_g values were affected by the α -olefin employed; T_g values with the same NBE content increased in the following order: poly(NBE-*co*-DD) < poly(NBE-*co*-OC)s < poly(NBE-*co*-HX)s (Figure 1b). Moreover, the NBE incorporation was not strongly affected by the nature of α -olefin employed, and relatively linear correlations between NBE content in the copolymers and NBE/ α -olefin feed molar ratios were observed, irrespective of kind of α -olefins employed, especially under high NBE/ α -olefin feed ratio conditions. Synthesis of high molecular weight copolymers of (long chain) α -olefins with various NBE content (with uniform molecular weight distributions and compositions) can be achieved by adopting these catalyses. The activity of 7 increased at high temperature, especially at 50 °C, and no significant differences in the T_g values (NBE content) in the resultant copolymers were observed by varying the temperature (25–70 °C). This would suggest that there has not been a significant temperature dependence observed for the NBE incorporation, as has been observed in ethylene/ α -olefin copolymerization by ordinary *ansa* metallocene catalysts [68,69].



Scheme 4. Copolymerization of norbornene (NBE) and tetracyclododecene (TCD) with α -olefin (1-hexene, 1-octene, and 1-dodecene) [54].

The copolymerization of TCD with HX by the Cp-ketimide analogue (7) afforded the copolymers with unimodal molecular weight distributions, with uniform compositions confirmed by DSC thermograms (Table 3) [54]. The copolymerizations with OC or DD by 7 afforded copolymers with high T_g values. In contrast, 8 showed low activity in the copolymerization with HX, OC, and DD. The attempted copolymerizations of TCD with HX by [Me₂Si(C₅Me₄)(N^tBu)]TiCl₂ (3)-MAO catalyst afforded a negligible amount of polymers in most cases; low molecular weight oligomer ($M_n = 5300$) with low TCD content (estimated by DSC thermogram, $T_g = 9.8$ °C) was obtained under specified conditions. The copolymerizations with HX, OC, and DD by [Et(indenyl)₂]ZrCl₂ (2) or Cp₂ZrCl₂ (11) yielded a small amount of oligomer under certain conditions; this is in distinct contrast to that observed for CpTiCl₂(N^tBu₂) (7).

Table 3. Copolymerization of norbornene (NBE) or tetracyclododecene (TCD) with 1-hexene (HX), 1-octene (OC), and 1-dodecene (DD) by [Et(indenyl)₂]ZrCl₂ (**2**), Cp₂ZrCl₂ (**11**), [Me₂Si(C₅Me₄)(N^tBu)]TiCl₂ (**3**), Cp'TiCl₂(N=C^tBu₂) (Cp' = Cp (**7**), ^tBuC₅H₄ (**8**))-MAO catalysts. ^a

Catalyst (μmol)	MAO/mmol	α-olefin	CO	CO Feed ratio ^b /%	Time/min	Activity ^c	M _n ^d × 10 ⁻⁴	M _w /M _n ^d	CO cont. ^e /mol %	T _g ^f /°C
7 (0.04)	3.0	HX	NBE	12	30	7500	4.18	1.64	20.0	78
7 (0.04)	3.0	HX	NBE	21	30	9620	3.61	1.58	37.2	126
7 (0.03)	3.0	HX	NBE	44	60	12,900	4.09	1.72	64.5	211
7 (0.02)	3.0	HX	NBE	57	60	12,500	3.94	1.61	69.2	246
7 (0.10)	3.0	OC	NBE	14	60	6140	4.57	1.67	13.0	31
7 (0.05)	3.0	OC	NBE	25	20	8240	3.33	1.63	39.6	99
7 (0.03)	3.0	OC	NBE	50	60	7890	4.18	1.67	67.5	192
7 (0.03)	3.0	OC	NBE	63	60	6220	4.79	3.24	77.6	235
7 (0.10)	3.0	DD	NBE	32	60	4490	3.84	1.67	37.3	56
7 (0.03)	3.0	DD	NBE	59	60	4580	5.42	1.75	76.1	157
7 (0.03)	3.0	DD	NBE	70	60	4150	8.26	3.19	84.1	212
8 (0.20)	3.0	OC	NBE	50	60	1720	6.49	1.69	37.0	102
8 (0.20)	3.0	OC	NBE	63	60	930	6.34	1.68	49.2	135
8 (0.30)	3.0	DD	NBE	59	60	1370	6.68	1.76	43.0	64
8 (0.20)	3.0	DD	NBE	70	60	1650	6.61	1.64	55.0	100
2 (20)	10	HX	TCD	75	10	49	0.73	1.18	-	-
2 (20)	10	OC	TCD	75	20	26	0.76	1.22	-	-
2 (20)	10	DD	TCD	75	20	21.5	0.71	1.25	-	-
11 (20)	10	HX	TCD	75	120	1.0	1.4	1.27	-	98
11 (20)	10	OC	TCD	75	120	0.9	1.5	1.28	-	83
3 (10)	6.0	HX	TCD	50	30	31	5.3	1.41	-	9.8
3 (10)	10	OC	TCD	75	60	6	3.6	1.37	-	6.3
7 (0.20)	1.0	HX	TCD	50	15	4590	17.6	1.70	41.6	205
7 (0.20)	1.5	HX	TCD	75	15	2870	12.2	1.76	62.8	271
7 (0.30)	1.5	OC	TCD	75	15	2030	9.9	1.93	55.5	235
7 (0.40)	1.0	OC	TCD	83	15	1410	1.03	1.74	67.6	259
7 (0.40)	1.5	DD	TCD	75	15	1830	13.0	1.67	60.5	165
8 (0.50)	1.0	HX	TCD	50	15	307	-	-	-	-
8 (0.60)	1.5	OC	TCD	75	15	120	-	-	-	-
8 (1.0)	1.5	DD	TCD	75	15	62	-	-	-	-

^a Conditions: toluene 1.0 mL, TCD 2.0 mL (13.4 mmol), 25 °C; ^b cyclic olefin (CO: NBE, TCD) initial feed molar ratio; ^c activity = kg-polymer/mol-M·h; ^d GPC data in tetrahydrofuran (THF) vs polystyrene stds; ^e estimated from ¹³C NMR spectra; ^f Measured by differential scanning calorimetry (DSC) thermograms.

The activity in the TCD/HX copolymerization decreased upon increasing the TCD concentration, with increasing TCD content in the copolymer (Table 4) [54]. The resultant copolymers possessed rather high molecular weights with unimodal molecular weight distributions ($M_n = 12,000$ – $27,600$, $M_w/M_n = 1.20$ – 1.76), and the TCD content (estimated by ¹³C NMR spectra) increased upon increasing TCD concentration with an increasing glass transition temperature (T_g); synthesis of the copolymers with high T_g (e.g., 286 °C) could be thus attained by adopting this catalysis. The activity was also affected by MAO (Al/Ti molar ratio), especially under high TCD concentration conditions, and no significant differences in either the molecular weights or T_g values of the copolymers were observed. Similarly, the copolymerizations of TCD with OC or DD afforded copolymers possessing rather high molecular weights with unimodal molecular weight distributions ($M_n = 9900$ – $25,600$, $M_w/M_n = 1.61$ – 1.93); the TCD content increased upon increasing TCD concentration with an increase in the T_g values. Moreover, the TCD incorporation by the 7-MAO catalyst was not strongly affected by the nature of the α-olefin employed (HX, OC, or DD) under high TCD/α-olefin feed conditions; relatively linear correlations were observed between TCD content in the copolymers and TCD/α-olefin feed molar ratios.

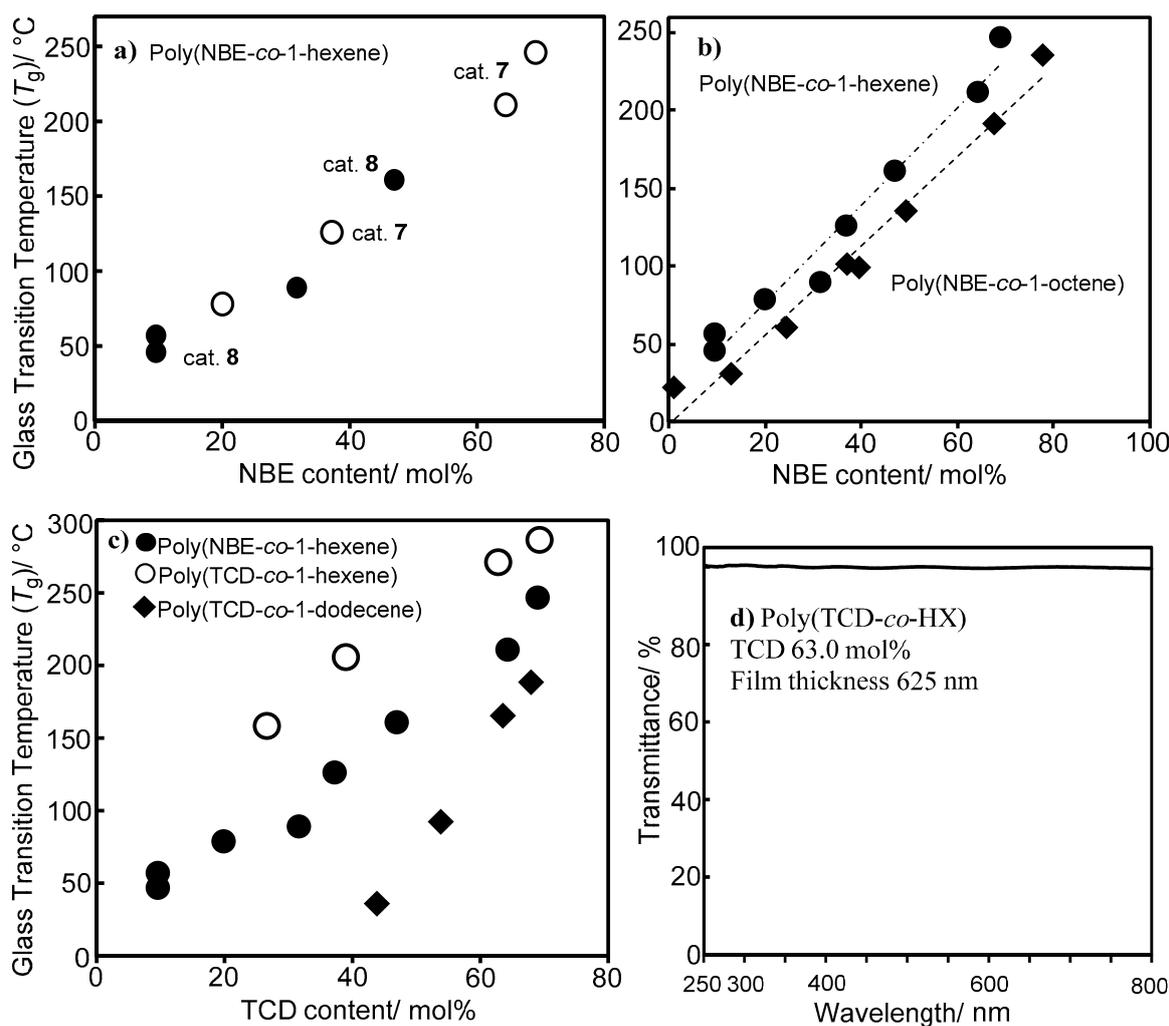


Figure 1. Plots of glass transition temperature (T_g) vs NBE content (mol %) in (a) poly(NBE-co-1-hexene)s by $\text{Cp}^*\text{TiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ ($\text{Cp}^* = \text{Cp}$ (7, \circ) or $^t\text{BuC}_5\text{H}_4$ (8, \bullet)-MAO catalysts; (b) poly(NBE-co-1-hexene)s (marked with \bullet) and poly(NBE-co-1-octene)s (marked with \blacklozenge); (c) plots of T_g values vs TCD content (mol %) in poly(TCD-co-1-hexene)s and poly(TCD-co-1-dodecene)s; (d) plots of transmittance vs wavelength in poly(TCD-co-1-hexene) [54].

Table 4. Copolymerization of tetracyclododecene (TCD) with 1-hexene (HX), 1-octene (OC), or 1-dodecene (DD) by $\text{CpTiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ (7)-MAO catalyst ^a.

Catalyst (μmol)	MAO / mmol	α -olefin	TCD Feed Ratio ^b / %	temp. / °C	Activity ^c	M_n ^d $\times 10^{-4}$	M_w/M_n ^d	TCD cont. ^e / mol %	T_g ^f / °C
7 (0.20)	1.0	HX	50	25	4590	17.6	1.70	41.6	205
7 (0.20)	1.0	HX	75	25	2560	1.42	1.66	-	-
7 (0.20)	1.5	HX	75	25	2870	12.2	1.76	62.8	271
7 (0.20)	1.5	HX	75	50	2550	1.18	1.73	-	282
7 (0.20)	1.5	HX	75	70	1670	1.01	1.71	-	289
7 (0.20)	1.0	OC	50	25	4210	1.83	1.61	44.4	172
7 (0.30)	1.5	OC	75	25	2030	9.9	1.93	55.5	235
7 (0.40)	1.0	OC	83	25	1410	1.03	1.74	67.6	259
7 (0.40)	1.5	DD	75	25	1830	13.0	1.67	60.5	165

^a Conditions: toluene 1.0 mL, TCD 2.0 mL (13.4 mmol), 15 min; ^b TCD initial feed molar ratio;

^c activity = kg-polymer/mol-M-h; ^d GPC data in THF vs polystyrene stds; ^e estimated from ^{13}C NMR spectra;

^f measured by DSC thermogram.

Fairly good linear relationships between the T_g values and the TCD content in poly(TCD-*co*-HX)s, poly(TCD-*co*-OC)s, and poly(TCD-*co*-DD)s were observed (Figure 1c), and the T_g values in the resultant copolymers are affected by the α -olefin employed. It is clear that the T_g values in poly(TCD-*co*-HX)s, [poly(TCD-*co*-OC)s, and poly(TCD-*co*-DD)s] are higher than those in poly(NBE-*co*-HX)s [poly(NBE-*co*-OC)s, and poly(NBE-*co*-DD)s] with the same α -olefin content (Figure 1c). Synthesis of high molecular weight copolymers of (long chain) α -olefins with various TCD content (with uniform molecular weight distributions and compositions) can be achieved by using these catalysts. Moreover, the resultant copolymers, poly(TCD-*co*-HX)s and poly(TCD-*co*-OC)s, show high transparency as thin films (Figure 1d), demonstrating a possibility that these polymers are promising materials with high transparency as well as with high glass transition temperatures ($T_g > 230$ °C).

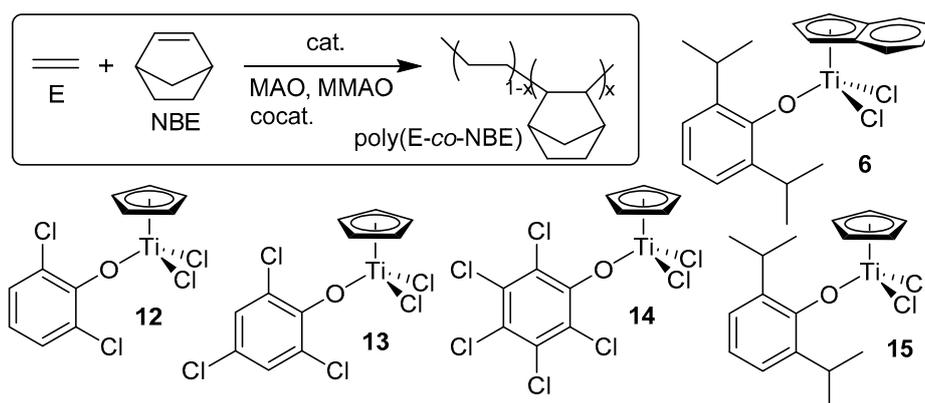
4. Efficient Norbornene (NBE) Incorporation in Ethylene/NBE Copolymerization by Half-Titanocene Catalysts Containing Chlorinated Aryloxo Ligands

As shown in Table 5, the Cp-chlorinated phenoxy analogues, CpTiCl₂(OAr) (Ar = 2,6-Cl₂C₆H₃ (**12**), 2,4,6-Cl₃C₆H₂ (**13**), or C₆Cl₅ (**14**)), showed higher catalytic activity (2010–3090 kg-polymer/mol-Ti·h) than the reported (Ind)TiCl₂(O-2,6-*i*Pr₂C₆H₃) (**6**) and CpTiCl₂(O-2,6-*i*Pr₂C₆H₃) (**15**) under the same conditions in the presence of the MAO cocatalyst (Scheme 5) [70]. The activities of **12–14** were also higher than those of the indenyl analogues. The resultant polymers are poly(ethylene-*co*-NBE)s possessing rather high molecular weights ($M_n = 45,400$ – $82,500$) with uniform molecular weight distributions ($M_w/M_n = 1.29$ – 1.63), and their compositions are uniform, as confirmed by DSC thermograms. These are similar observations to those of copolymerization by the **6**-MAO catalyst, but the resultant polymer prepared by **15** possessed bimodal molecular weight distributions, as previously observed in ethylene/1-hexene copolymerization [71], suggesting that several catalytically active species are present in the solution.

Table 5. Copolymerization of ethylene with norbornene (NBE) by Cp'TiCl₂(OAr) (Cp' = Cp, Ar = 2,6-Cl₂C₆H₃ (**12**), 2,4,6-Cl₃C₆H₂ (**13**), C₆Cl₅ (**14**), or 2,6-*i*Pr₂C₆H₃ (**15**); Cp' = indenyl, Ar = 2,6-*i*Pr₂C₆H₃ (**6**))-MAO catalysts ^a.

Cat. (μ mol)	NBE Feed/mol/L	Temp./°C	Activity ^b	T_g ^c /°C	M_n ^d $\times 10^{-4}$	M_w/M_n ^d	NBE cont. ^e /mol %
12 (0.3)	1.0	25	2470	153	5.47	1.55	49.6
12 (0.5)	2.0	25	2010	164	6.78	1.63	-
12 (0.5)	2.0	40	2390	176	5.60	1.56	-
13 (0.3)	1.0	25	3090	142	7.41	1.50	45.3
13 (0.3)	1.0	40	4140	151	6.50	1.37	-
13 (0.3)	1.0	60	3930	160	2.75	1.79	-
13 (0.5) ^f	2.0	25	3060	156	8.25	1.37	53.3
13 (0.3)	2.0	50	2350	176	3.50	1.65	58.8
14 (0.3)	1.0	25	2320	128	6.01	1.49	42.3
14 (0.6) ^f	2.0	25	2030	150	6.94	1.40	-
15 (2.5)	2.0	25	319	-	bimodal	-	-
6 (2.0)	2.0	25	492	114	2.52	1.29	-
7 (0.04)	2.0	25	20,400	127	57.3	1.78	-
CGC (3) (0.10)	1.0	25	4860	-	22.9	2.37	29.5
DSBI (1) (0.50)	1.0	25	2000	-	12.8	2.15	26.5

^a Conditions: toluene + NBE total 50 mL, MAO white solid (prepared by removing AlMe₃, toluene from TMAO, MAO: methylaluminoxane) 3.0 mmol, ethylene 4 atm, 25 °C; ^b activity in kg-polymer/mol-Ti·h; ^c glass transition temperature (T_g) measured by DSC; ^d GPC data in *o*-dichlorobenzene vs polystyrene standards; ^e NBE content estimated by ¹³C NMR spectra; ^f time 6 min. CpTiCl₂(N=C^{*i*}Bu₂) (**7**), CGC: [Me₂Si(C₅Me₄)(N^{*i*}Bu)]TiCl₂ (**3**); DSBI: [Me₂Si(indenyl)₂]ZrCl₂ (**1**).



Scheme 5. Copolymerization of ethylene with norbornene with half-titanocenes containing chlorinated aryloxy ligands [70].

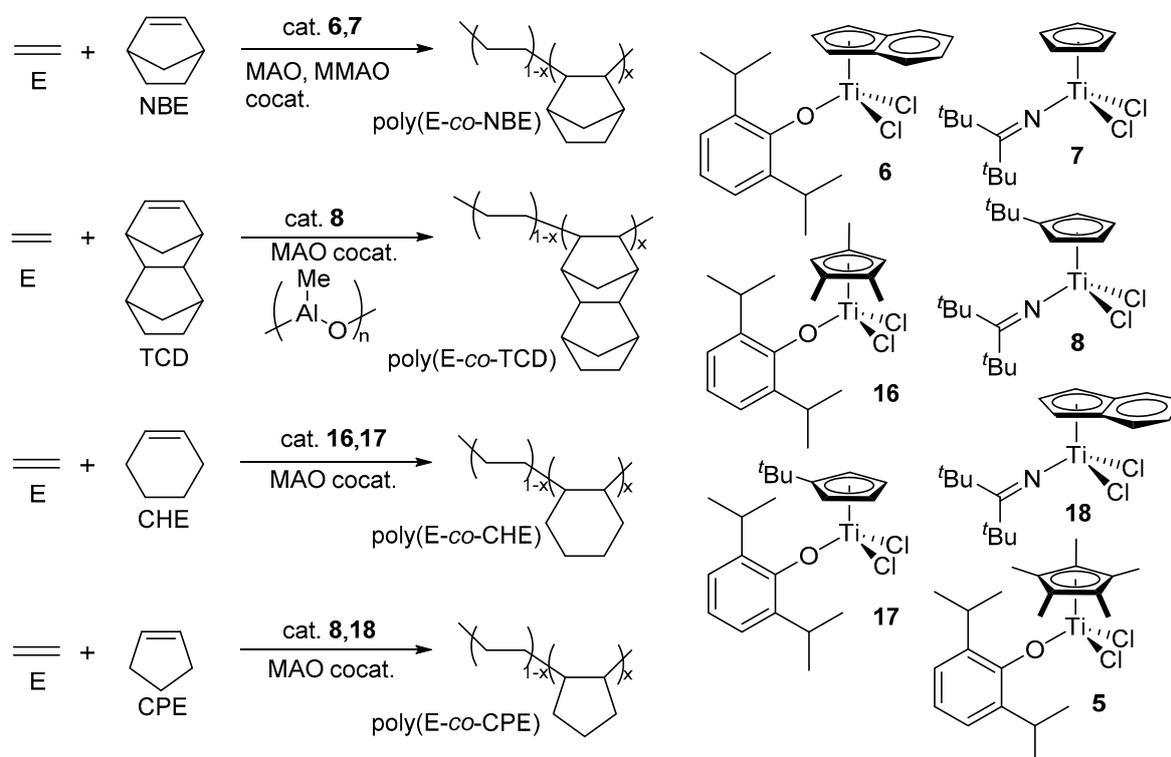
Note that the NBE content in the resultant copolymers (estimated by glass transition temperature (T_g)) prepared by **12–14** are higher than those prepared by the others under the same conditions; the NBE content by **12** and **13** (NBE content 49.6 and 45.3 mol %, respectively) is much higher than $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2$ (CGC, **3**, 29.5 mol%), $[\text{Me}_2\text{Si}(\text{indenyl})_2]\text{ZrCl}_2$ (DSBI, **1**, 26.5 mol%), and $\text{CpTiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ (**7**) under the same conditions. Although the activities of **12** and **13** were lower than that of **7** (but at a higher or similar level compared to CGC and DSBI), the results thus clearly indicate that the chlorinated phenoxy-modified Cp analogues, especially **12** and **13**, showed the most efficient NBE incorporation compared with the others under these conditions. The 2,4,6- $\text{Cl}_3\text{C}_6\text{H}_2$ analogue (**13**) showed higher catalytic activity than that of the 2,6- $\text{Cl}_2\text{C}_6\text{H}_3$ analogue (**12**), whereas **12** showed better NBE incorporation than **13** under the same conditions (e.g., run 1 vs run 4). The activity (on the basis of polymer yields) of **13** at 40–60 °C was higher than that conducted at 25 °C; the activity of **12** at 40 °C was higher than that conducted at 25 °C. A linear relationship between the NBE content in the resultant copolymers and glass transition temperature (T_g) was observed.

As far as we know, this is the first demonstration that an introduction of electron-withdrawing substituents leads to more efficient comonomer incorporation in ethylene/cyclic olefin copolymerization. This fact would be in distinct contrast to the catalyst design in ordinary olefin (ethylene and styrene) polymerization, in which stabilization of the active site by more electron-donating substituents is important, leading to the high activity. The results from this study demonstrate a possibility that control of π -donation (which would affect the ability of accepting π -electrons from olefins) plays a role for the efficient incorporation of (sterically encumbered) cyclic olefins in this catalysis.

5. Summary and Outlook

We have shown that efficient incorporations of norbornene (NBE) and tetracyclododenece (TCD) have been achieved in the copolymerization with ethylene, 1-hexene (HX), 1-octene (OC), and with 1-dodecene (DD) by using $\text{Cp}'\text{TiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ ($\text{Cp}' = \text{Cp}$ (**7**), $t\text{BuC}_5\text{H}_4$ (**8**))-MAO catalysts. The resultant copolymers possess rather high molecular weights, unimodal molecular weight distributions, and uniform compositions as confirmed by DSC thermograms. This is, as far as we know, the first demonstration for the synthesis of TCD/ α -olefin copolymers, in addition to preparation of a series of random poly(NBE-co- α -olefin)s with various NBE content. Moreover, the efficient synthesis of poly(ethylene-co-TCD)s has also been attained in this catalysis. These copolymers possess a high glass transition temperature (thermal resistance) with high transparency and should show unique properties (e.g., humidity resistance). It is thus highly expected that these polymers are promising materials as a new class of cyclic olefin copolymers (COCs).

As described in the introduction, design of molecular catalysts that precisely control the copolymerization has attracted considerable attention for the synthesis of new polymers with specified functions. The ligand design plays an essential role, and we demonstrated in so-called *nonbridged* half-titanocene catalysts— $\text{Cp}'\text{TiX}_2(\text{Y})$ ($\text{Cp}' = \text{cyclopentadienyl}$; $\text{X} = \text{halogen, alkyl etc.}$; $\text{Y} = \text{anionic ancillary donor such as aryloxy, ketimide, imidazolin-2-iminato, etc.}$)—that efficient catalysts for the desired copolymerization can be tuned by the ligand modification on both the cyclopentadienyl fragment and nature (and substituents) of the anionic donor ligand employed, as demonstrated in the ethylene copolymerization with NBE [22–24], TCD [53], cyclohexene [72], cyclopentene [73], 2-methyl-1-pentene [74], and the others [39,41,45], as summarized in Scheme 6. We thus believe that the results demonstrated here are promising in terms of the synthesis of new polymers, and provides a better understanding not only for the polymer design (combination of monomers), but also for the catalyst design for efficient synthesis.



Scheme 6. Ethylene copolymerization with cyclic olefins by modified half-titanocene catalysts [22–24,39,41,45,53,72–74].

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Author Contributions: W.Z. wrote the initial draft and K.N. revised for submission. Some experiments cited as references were conducted by W.Z. Authorship must be limited to those who have contributed substantially to the work reported.

Conflicts of Interest: The authors declare no competing financial interest.

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