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MINI REVIEW

Development of half-titanocene catalysts for synthesis of cyclic olefin copolymers

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ABSTRACT

Certain cyclic olefin copolymers (COCs) are known as promising amorphous materials with high transparency in the UV-vis region, thermal and humidity resistance, low dielectric constant, low water absorption, and dimensional stability. This short review focuses on the synthesis of (new) cyclic olefin copolymers by designed (nonbridged) half-titanocene catalysts, which enabled to proceed synthesis of the amorphous polymers by ethylene/propylene copolymerization not only with norbornene (NBE), and tetracyclododecene (TCD), but also with so called low strained cyclic olefins (cyclopentene, cyclohexene, cycloheptene, and cyclooctene). Their thermal properties (glass transition temperature, T_g values) are affected by structure of the cyclic olefin employed and the contents, whereas linear relationships between T_g values and the contents were observed in all cases. **Polyolefins J (2023) 10: 59-70**

Keywords: Cyclic olefin copolymers; titanium catalyst; half-titanocene; norbornene; cyclic olefin.

INTRODUCTION

Olefin polymerization by early transition metal catalysts is the core technology for industrial production of polyolefins. Synthesis of the new copolymers that are not able to be prepared by conventional catalysts (Ziegler-Natta, metallocene catalysts, etc.) has been a long-term interest. This is because that (thermal, physical, mechanical, electronic) properties of the resultant copolymers were modified by the individual components. Functional polyolefins with specified properties should be more sustainable than those prepared from rather complicated monomers required several steps from fossil oil, especially in terms of better materials recycling (monomer unifications) and chemical recycling (no or much less additional functional groups, less additive). Design and development of the molecular catalysts for the purpose (highly active, better comonomer incorporations) has thus been a promising subject for successful synthesis [1-15].

It has been known that the ligands (steric and electronic) as well as the basic geometry (structural

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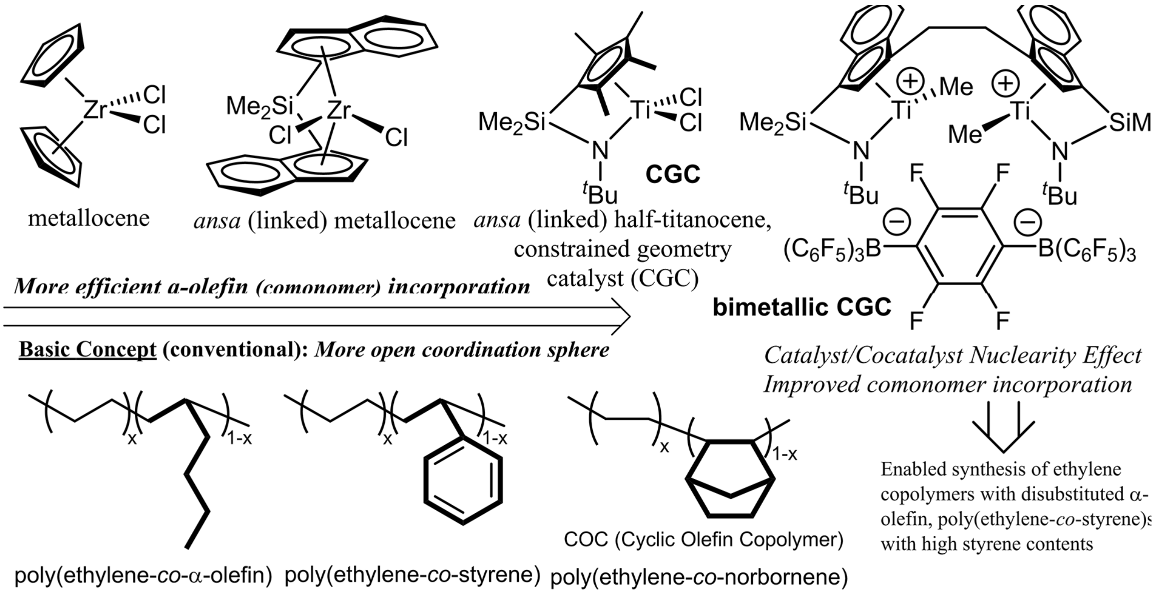
features) in the catalysts play an important role in catalysis. As shown in Scheme 1, it has been proposed that *ansa* (bridged) metallocenes showed better α-olefin incorporation than the unbridged ones in the ethylene/α-olefin copolymerization, and the *ansa* (cyclopentadienyl)(amide)titanium catalysts, exemplified as $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (called **CGC**, constrained geometry catalyst) [3], exhibited the more efficient α-olefin incorporation [3,16-18]. These facts were explained as due to a concept that the bridge constrains the structure to provide a more open coordination space for the coordination of α-olefins (rather steric bulk compared to ethylene). Indeed, the CGC demonstrated a capability of (rather) efficient styrene incorporation in the ethylene/styrene copolymerization [6,7], but showed invariably of the incorporation (<50 mol%) [2,6,7,19]. Later, the bimetallic catalysts (**bimetallic CGC**) enabled synthesis of the copolymer with high styrene content (76 mol%) [19-21]; the catalyst also enabled the synthesis of ethylene copolymers with disubstituted α-olefins [20,21].

Half-titanocenes modified with anionic ancillary donor ligands of type, $Cp'TiX_2(Y)$ (Y = phenoxide, ketimide, phosphinimide, iminoimidazolide, amidinate etc., Scheme 2), first were demonstrated by us with phenoxide [22,23], and the synthesis of the new ethylene copolymers by incorporations of various olefins (sterically encumbered olefins, cyclic olefins, aromatic vinyl monomers, the others) was demonstrated [5-7, 16-38]. In particular, both the phenoxide (**1**) and the ketimide (**2**) analogues have been known as successful examples. Later, the η^1-amidinate analogue (**3**) demonstrated the industrial production of chlorine-free synthetic rubber (EPDM, ethylene propylene diene terpolymer) without deep cooling, which is commonly employed in the conventional (Ziegler type) vanadium catalyst systems in industry [13].

Certain cyclic olefin copolymers (COCs) are promising amorphous materials with high transparency in the UV-vis region, high thermal resistance, low water absorption (humidity resistance), low dielectric constants, and dimensional stability; some of the ethylene-based copolymers have been commercialized (as TOPAS®, APEL®) [39,40] as ultra-pure, crystal-clear, and high barrier materials (especially for optical and medical applications). The copolymerization approach enables modification of their compositions (cyclic olefin contents, etc.) and microstructures (including tacticity, etc.). Although we can see many reports for the ethylene copolymerization with highly strained norbornene (NBE) by ordinary metallocene catalysts, half-titanocene catalysts, and the others (Scheme 2) [41-48], however, the successful examples for the efficient synthesis of random, high molecular weight copolymers with high NBE contents (high glass transition temperature (T_g values)) still have been limited by the ketimide analogue (**2a**) and the modified linked half-titanocenes (shown below) [49-51]. Moreover, the successful examples in the synthesis of amorphous copolymers by incorporation of low strain



Scheme 1. Selected group 4 transition metal complex catalysts for olefin polymerization (metallocene, *ansa*-half-titanocene called constrained geometry catalyst, **CGC**).

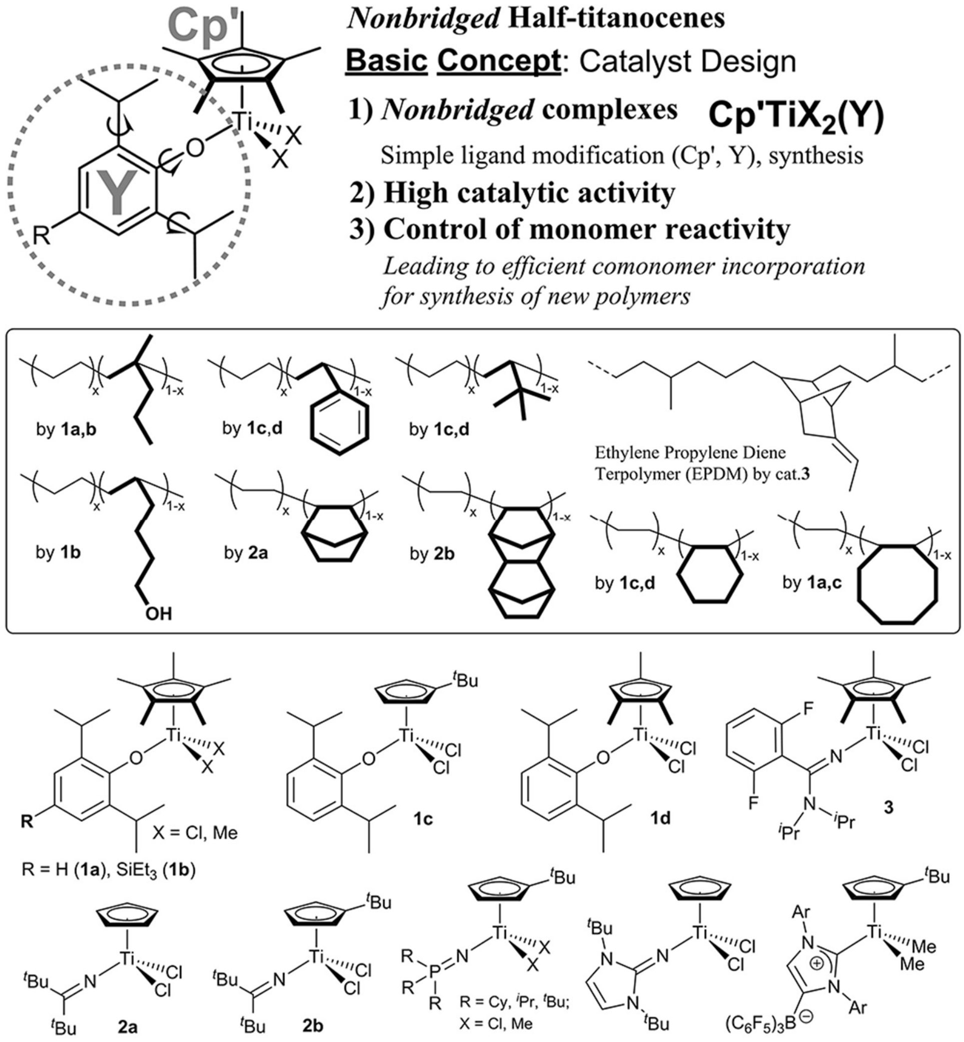
monomers (cyclopentene, cycloheptene, cyclooctene etc.) still have been limited, as described below.

This short review (perspective) thus introduces successful reports for the synthesis of various COCs that were very difficult to prepare by conventional catalysts. These research efforts could provide important information on the basic design of cyclic olefin copolymers (monomer design) as well as catalysts.

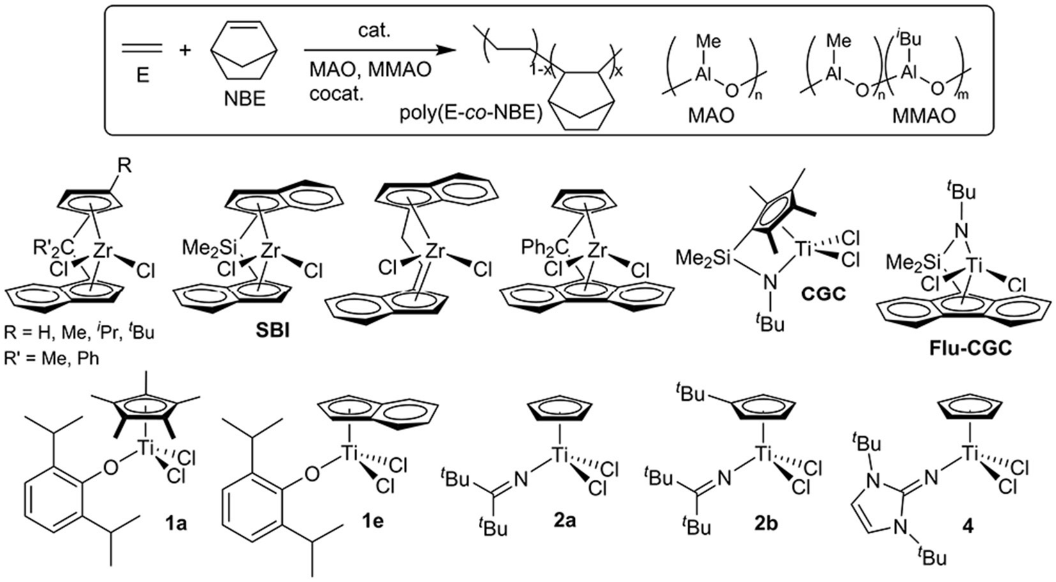
ETHYLENE COPOLYMERIZATION WITH NORBORNENE (NBE), AND TETRACYCLODODECENE (TCD)

In the ethylene/NBE copolymerization by ordinary metallocene (exemplified as **SBI-Zr**, Scheme 3) and **CGC**, both the activity and the molecular weight (M_n values) in the resultant copolymers decreased with increase in the NBE contents (NBE concentration charged, Table 1) [41,42,47]. In contrast, the fluorenyl analogue (**Flu-CGC**) enabled to proceed the NBE living polymerization in the presence of appropriate Al cocatalyst (dried MAO prepared by removing $AlMe_3$ from the commercially available MAO in toluene solution, or MMAO) [50,52,53]. The catalyst exhibited more efficient NBE incorporation than **CGC**, which enabled to afford not only the ethylene copolymers with high NBE contents [50], but also synthesis of NBE copolymers with propylene [53], α-olefin (1-hexene, 1-octene, etc.) [54,55], and later the gradient NBE copolymers with 1-alkene (1-octene, 1-decene, and 1-dodecene) [56]. Effect of the fluorenyl substituent plays a role toward the activity [55].

Efficient synthesis of the ethylene/NBE copolymers with efficient NBE incorporation was



Scheme 2. Nonbridged half-titanocenes: Basic concept for the catalysts design and selected examples of catalysts, and copolymers.



Scheme 3. Ethylene copolymerization with norbornene (NBE).

also demonstrated by the ketimide-modified half-titanocene, CpTiCl$_2$(N=C^{t}Bu$_2$) (**2a**) to afford the high molecular weight random copolymers with high NBE contents (Table 1) [51]. No significant decrease in the activity (the catalyst deactivation) were observed even after 30 min. The activity rather increased by increasing in the initial NBE concentration charged, showing a unique contrast to the ordinary catalysts (metallocene, linked half-titanocenes like **CGC**) except **Flu-CGC**. The activities and the NBE incorporation were not strongly affected by the Al cocatalyst employed (MAO, MMAOs), whereas the effect of the Al cocatalyst was apparently observed by **Flu-CGC** [50,53,54]. The activity by **2a** increased at 60ºC, and the significant decrease in the activity was not observed at 80ºC [51]. The efficient synthesis of high molecular weight copolymers with high NBE contents (58.8-73.5 mol%) could be achieved and the copolymer compositions were uniform (confirmed by DSC thermograms, GPC traces). As shown in Figure 1, a relationship between the T_g values in the copolymer increased linearly with an increase in the NBE content [45,47,51]. Later, the syntheses of poly(NBE-co-α-olefin)s, and poly(TCD-co-α-olefin)s (TCD = tetracyclododecene, dimethanoocta-hydronaphthaline) with high T_g values (α-olefin = 1-hexene, 1-octene, 1-dodecene) were

Table 1. Ethylene (E) copolymerization with norbornene (NBE) by [Me$_2$Si(indenyl)$_2$]ZrCl$_2$ (**SBI**), [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (**CGC**), (indenyl)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1e**), CpTiCl$_2$(N=C^{t}Bu$_2$) (**2a**), CpTiCl$_2$[1,3-^{t}Bu$_2$(CHN)$_2$C=N] (**4**) – MAO catalysts (references 51,58).$^{(a)}$

Cat. (μmol)	Temp./ºC	E/atm	NBE$^{(b)}$/M	$[NBE]_0/[E]_0$$^{(c)}$	Activity$^{(d)}$	$M_n$$^{(e)}$	$M_w/M_n$$^{(e)}$	NBE$^{(f)}$/mol%
SBI (0.10)	25	4	0.2	0.41	28860	231,000	2.02	10.8
SBI (0.10)	25	4	1.0	2.04	4860	229,000	2.37	29.5
CGC (0.50)	25	4	0.2	0.41	2460	211,000	1.88	9.6
CGC (0.50)	25	4	1.0	2.04	2000	128,000	2.15	26.5
1e (0.2)	25	4	0.2	0.41	10500	146,000	1.56	14.0
1e (0.5)	25	4	1.0	2.04	2300	58,700	1.82	35.2
2a (0.02)	80	4	1.0	3.94	133000	338,000	2.34	61.7
2a (0.02)	60	4	1.0	3.02	194000	475,000	2.20	51.2
2a (0.02)	40	4	1.0	2.45	48900	620,000	2.37	45.9
2a (0.02)	25	4	1.0	2.04	40200	719,000	2.92	40.7
2a (0.02)$^{(g)}$	25	4	1.0	2.04	59700	613,000	2.18	41.0
2a (0.01)$^{(h)}$	25	2	5.0	20.6	85800	340,000	2.00	65.8
2a (0.01)$^{(h)}$	25	2	10.0	41.2	31500	444,000	2.01	73.5
4 (0.20)	25	4	1.0	2.04	6180	108,0000	2.53	31.4
4 (0.20)	80	4	1.0	3.94	5780	800,000	2.35	36.9

$^{(a)}$Conditions: toluene and NBE total 50 mL, ethylene 4 atm, MAO (white solid) 0.5-3.0 mmol, 10 min. $^{(b)}$Initial NBE concentration in mmol/mL. $^{(c)}$Initial NBE/E molar ratio. $^{(d)}$Activity in kg-polymer/mol-M·h (M = Ti, Zr). $^{(e)}$GPC data in *o*-dichlorobenzene *vs* PS stds. $^{(f)}$NBE content (mol %) estimated by ^{13}C NMR spectra. $^{(g)}$Time 30 min. $^{(h)}$Toluene+NBE total 10 mL.

also demonstrated by **2a**, and the NBE/1-octene copolymerization in the presence of 1,7-octadiene by the tert-BuC_5H_4 analogue (**2b**) gave the polymer containing terminal olefinic double bond in the side chain [57]. Linear relationships between the T_g values and the NBE or TCD contents were observed [57].

The half-titanocene containing imidazolin-2-iminato ligand, $CpTiCl_2[1,3\text{-}^tBu_2(CHN)_2C{=}N]$ (**4**), showed rather high catalytic activities with efficient NBE incorporation in the copolymerization to give ultrahigh molecular weight copolymers [58]. Although the observed activities by **4** were lower than those by **2a**, the catalyst could exhibit a promising possibility of the thermally robust, efficient catalyst for synthesis of the ultrahigh molecular weight polymers. Significant effect of the ligand substituents toward both the catalytic activity and the comonomer incorporation could be thus demonstrated.

The ethylene/TCD copolymers are promising materials possessing higher T_g values compared to the ethylene/NBE copolymers with the same cyclic olefin contents. Classical Ziegler-type vanadium catalyst systems [$VOCl_3$, $VO(OEt)Cl_2$ – $EtAlCl_2{\bullet}Et_2AlCl$ etc.] have been employed in industry under deep cooling conditions [59]. In contrast to many reports for the ethylene/NBE copolymerization [1-30], there were reports for the copolymerizations using metallocene catalysts (Scheme 4) [60-64], which generally exhibited low catalytic activities and/or less efficient TCD incorporation. Recently, the efficient copolymerization to afford high molecular weight polymers with uniform compositions was demonstrated by $(^tBuC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**2b**) in the presence of MAO cocatalyst (Table 2) [65]. The Cp analogue, $CpTiCl_2(N{=}C^tBu_2)$ (**2a**), which is effective catalyst for efficient α-olefin/TCD and ethylene/NBE copolymerizations [51-57], however showed low catalytic activities. The activity by **2b** increased at high temperature with increase in the TCD contents in the copolymers. The resultant polymers possess high molecular weights with unimodal molecular weight distributions, and a linear relationship between the T_g values and the TCD contents was seen (Figure 1). As described above, the ordinary metallocene catalysts exhibited low catalytic activities with less efficient TCD incorporations, and conventional vanadium catalyst systems are generally conducted under deep cooling conditions, the catalyst (**2b**) would thus provide a promising possibility of development of thermally robust catalysts in the copolymerization.

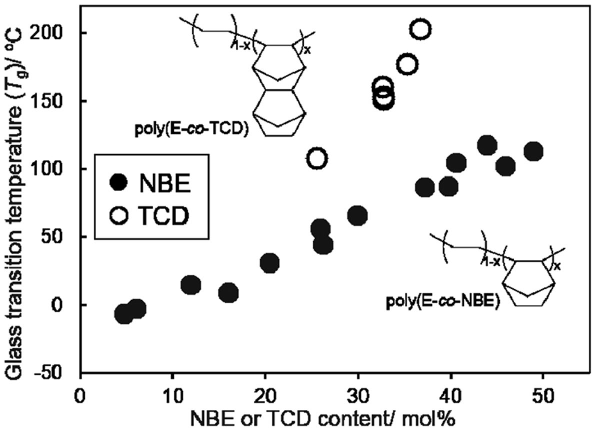


Figure 1. Plots of glass transition temperature (T_g) vs norbornene (NBE) or tetradecane (TCD) contents in the ethylene (E) copolymers, poly(E-*co*-NBE)s, and poly(E-*co*-TCD)s [49,51].

SYNTHESIS OF THE OTHER CYCLIC OLEFIN COPOLYMERS

Structure of cyclic olefin should play a role toward the properties (thermal and mechanical properties, transparency, dielectric constant, etc.). For example, ethylene copolymers with *exo*-1,4,4a,9,9a,10-hexahydro-9,10(1’,2’)-benzeno-l,4-methanoanthracene showed better mechanical property in film (elongation-at-break, stress-strain behavior) compared to the copolymers with BE with the similar T_g value [66]. As described in the introduction, the reports for the ethylene copolymerization with so called low strained cyclic olefins, especially cyclohexene (CHE) [67], cycloheptene (CHP) [68-70], and *cis*-cyclooctene (COE) [68-71] were limited until recently, whereas there are reports in the copolymerization with cyclopentene (CPE) [68,72-76]. The copolymerization with CHP, and COE by the linked half-titanocene catalysts afforded low molecular weight oligomers even under the specified conditions [68], and the synthesis of high molecular weight amorphous copolymers thus seemed very difficult until recently [70].

The ethylene/CPE copolymers prepared by ordinary zirconocene (metallocene) catalysts possessed a microstructure with 1,3- (and 1,2-) CPE insertion, and subsequent ethylene was inserted after isomerization of inserted CPE [72,73], whereas the copolymerization by titanium catalysts proceeded via 1,2-CPE insertion [68,74-76]. The copolymerization

Table 2. Ethylene copolymerization with tetracyclododecene (TCD) by Cp'$TiCl_2(N{=}C^tBu_2)$ [Cp' = Cp (**2a**), $^tBuC_5H_4$ (**2b**)], $CpTiCl_2[1,3\text{-}^tBu_2(CHN)_2C{=}N]$ (**4**), $Me_2Si(C_5Me_4)(NtBu)]TiCl_2$ (**CGC**)–MAO catalysts (reference 65).(a)

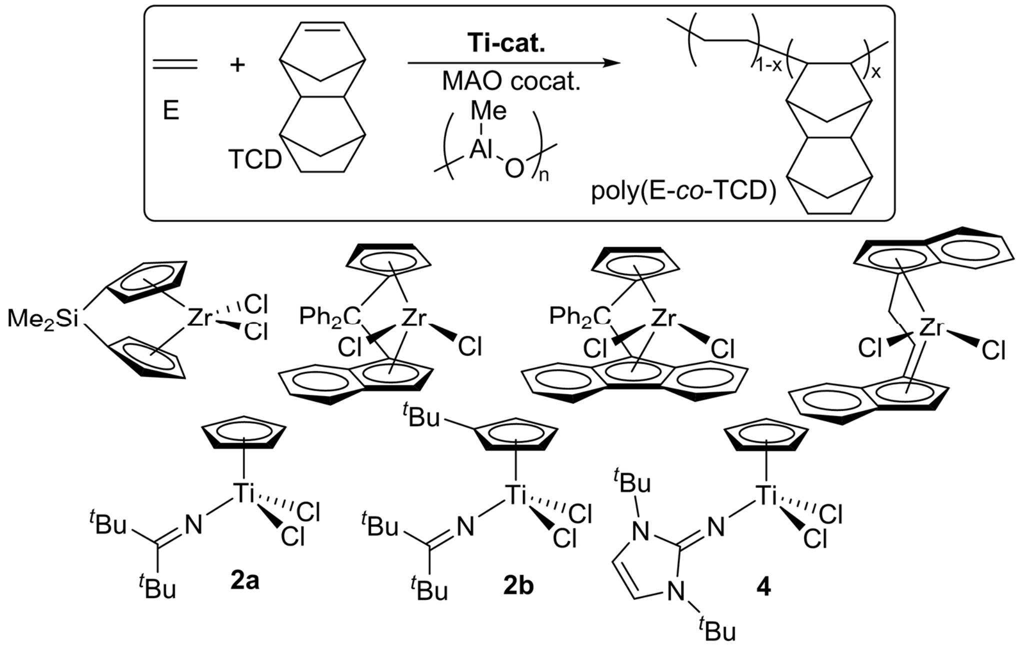
Ti/μmol	TCD(b)/mol/L	Temp./°C	Activity(c)	M_n(d)×10^{-5}	M_w/M_n(d)	T_g(e) (T_m(e))/°C	TCD(f)/mol%
CGC (0.05)	1.0	25	13900	14.3	1.58	56	
2a (0.8)	2.0	25	1650	1.92	1.41	150	
2b (0.02)	1.0	25	43700	5.88	1.60	108	25.6
2b (0.02)	2.0	25	23900	6.38	1.50	153	32.8
2b (0.02)	2.0	40	27800	6.43	1.67	170	33.5g
2b (0.02)	2.0	60	33300	6.53	1.72	177	35.3
2b (0.02)	3.0	25	16800	6.43	1.61	171	33.6g
2b (0.02)	4.0	60	22400	6.08	1.61	203	36.7

(a)Polymerization conditions: toluene and TCD total 30 mL, ethylene 6 atm, 10 min, d-MAO (prepared by removing toluene and $AlMe_3$ from the ordinary 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* polystyrene stads. (e)By DSC thermograms. (f)Estimated by ^{13}C NMR spectra. (g)Estimated on the basis of the plots of T_g and TCD content.

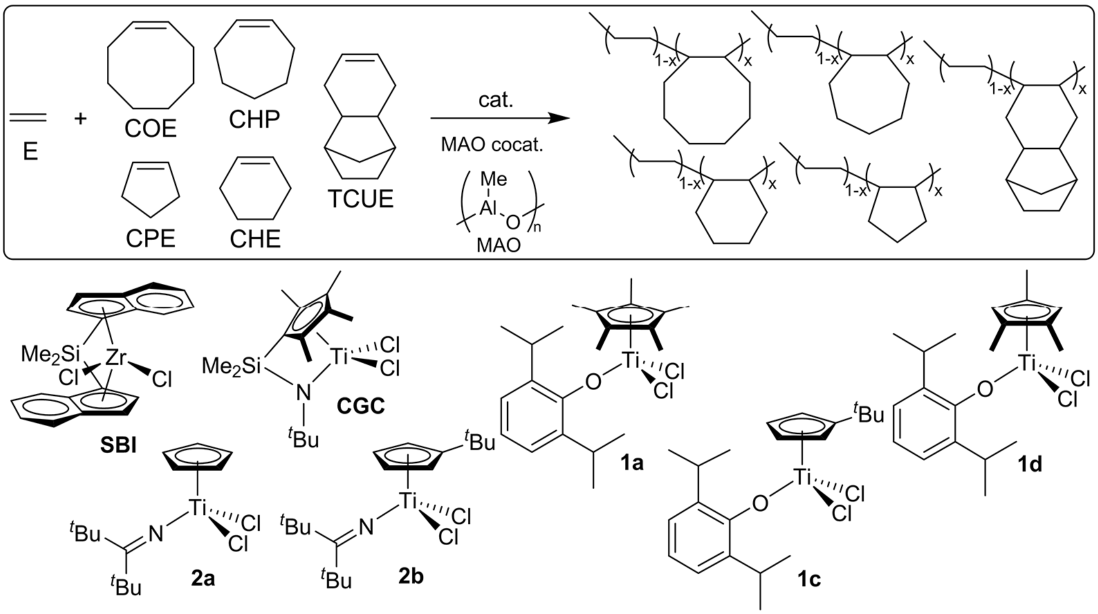
with efficient CPE insertion as well as with high activity was demonstrated by the $^tBuC_5H_4$-ketimide analogue (**2b**) to afford high molecular weight copolymers (CPE content <43.6 mol%) [76]. A linear relationship between the CPE content and the T_g value was also demonstrated [75]. Cp'$TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ [Cp' $^tBuC_5H_4$ (**1c**), $1,2,4\text{-}Me_3C_5H_2$ (**1d**)] proceeded the copolymerization with CHE with 1,2-insertion, whereas the other catalysts (metallocenes, **CGC, 1a, 2, 4**) did not incorporate CHE under the similar conditions [67]. The catalysts enabled synthesis of the ethylene copolymers with 4-methyl-1-cyclohexene (with 1,2-insertion) and 1-methylcyclopentene(with 1,2- and 1,3-insertion) [77].

The ethylene/COE copolymerization by **1a** gave high molecular weight amorphous copolymers with efficient 1,2-COE incorporations (M_n = 1.08-12.6×10^5), whereas the ketimide analogue (**2a**) showed rather less COE incorporations compared to **1a** but showed higher activities to afford ultrahigh molecular weight copolymers [70]. The copolymerization with CHP by **1a** gave ultrahigh molecular weight amorphous copolymers (M_n = 1.32-3.08×10^6) with exclusive 1,2-CHP insertion. In contrast, **CGC** and **SBI-Zr** gave (semi)crystalline copolymers with less COE incorporations (Scheme 5); the resultant polymers by **SBI-Zr** possessed broad molecular weight distributions with 1,3-insertion [70]. The ketimide analogue (**2a**) showed notable activities in the copolymerization with tricyclo[6.2.1.0(2,7)]undeca-4-ene (TCUE) to produce high molecular weight copolymers (M_n = 6.4–22.0×10^5, TCUE content 9.4-40.7 mol%) [70].

As observed in the ethylene copolymers with NBE,



Scheme 4. Reported catalysts for ethylene/tetracyclododecene copolymerization.



Scheme 5. Ethylene copolymerization with (low strained) cyclic olefins [67,70,75,76].

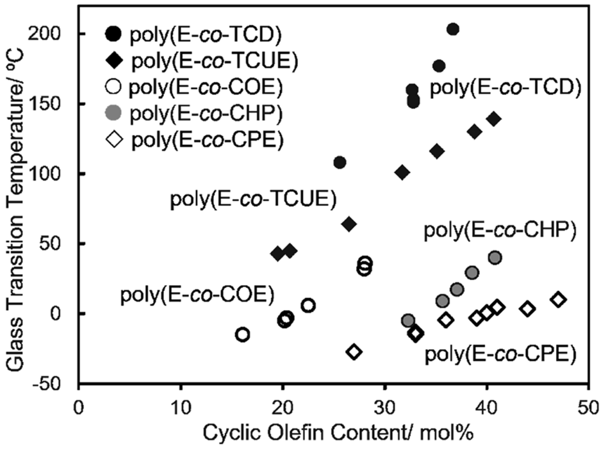
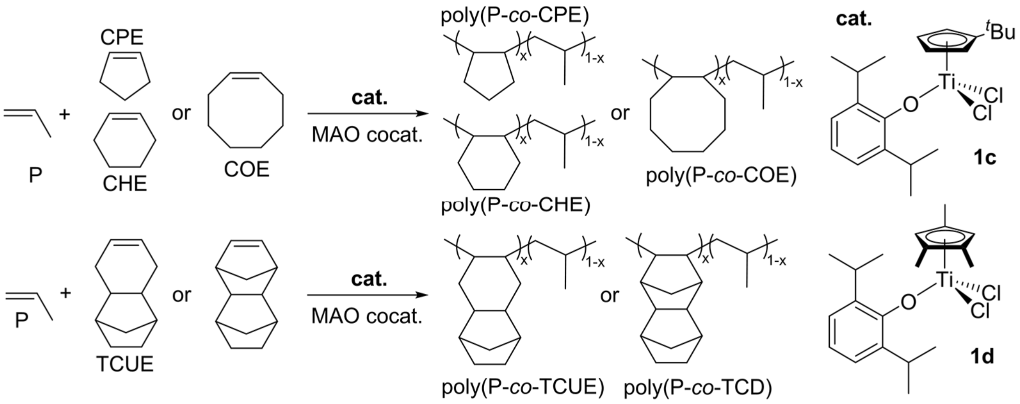


Figure 2. Relationships between T_g values and cyclic olefin content in the ethylene-cyclic olefin copolymers: Effect of monomer structure toward their thermal property [70].

TCD (Figure 1), and with CPE, linear relationships between their T_g values and the cyclic olefin contents were demonstrated in all cases (Figure 2). It is clear that their T_g values were affected by the ring size; placing an additional ring into cyclohexene leads to an increase in the T_g value [70].

More recently, synthesis of the amorphous propylene copolymers with CPE, CHE, CHP, COE, TCUE, and with TCD were demonstrated (Scheme 6) [37]. Linear plots of the T_g values versus the cyclic olefin contents were seen in all cases, suggesting that the cyclic structure affects the T_g values (except the copolymers with CPE, COE); the T_g values in the propylene copolymers were higher than those in the ethylene copolymers in the region of low cyclic olefin content (up to 25 mol%) [37].



Scheme 6. Propylene copolymerization with (low strained) cyclic olefins [37].

CONCLUDING REMARKS AND OUTLOOK

As described in the introduction, olefin polymerization by transition metal catalysis is the core technology for the polyolefins process, and the development of new ethylene copolymers that have not been incorporated by conventional catalysts has been a long-term subject. In this manuscript, recent development for synthesis of cyclic olefin copolymers (COCs) has been reviewed including our recent reports. It is clear that design of the molecular catalysts plays a key role for the success. Additionally, analysis of catalytically active species (the structural and electronic nature) has been the central subject for understanding the catalysis mechanism, and we recently use solution synchrotron XAS (X-ray absorption spectroscopy) analysis such as XANES (XANES = X-ray Absorption Near Edge Structure) for analysis of the oxidation state and the basic geometry and their coordination atoms to the centered metal through EXAFS (EXAFS = Extended X-ray Absorption Fine Structure) [78,79]. The method should provide information of the oxidation state, the geometry, coordinated atom and the distance through the spectra. We hope that we could introduce clear picture for designing new COCs and more efficient molecular catalysis through this paper.

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CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

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