IPPI

Polyolefins Journal, Vol. 10, No. 2 (2023)
DOI: 10.22063/POJ.2023.3308.1250

MINI REVIEW

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

Kotohiro Nomura

Department of Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo, 1920397, Japan

Received: 14 January 2023, Accepted: 27 January 2023

## 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].

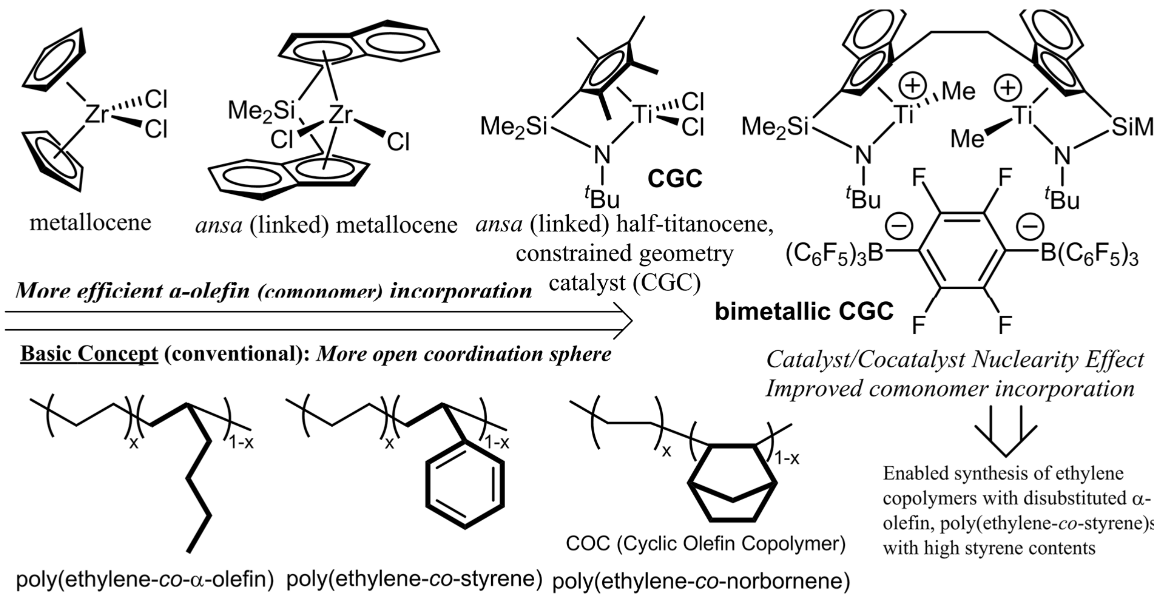
It has been known that the ligands (steric and electronic) as well as the basic geometry (structural

*Corresponding Author - E-mail: ktnomura@tmu.ac.jp

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 $\eta^1$-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**).

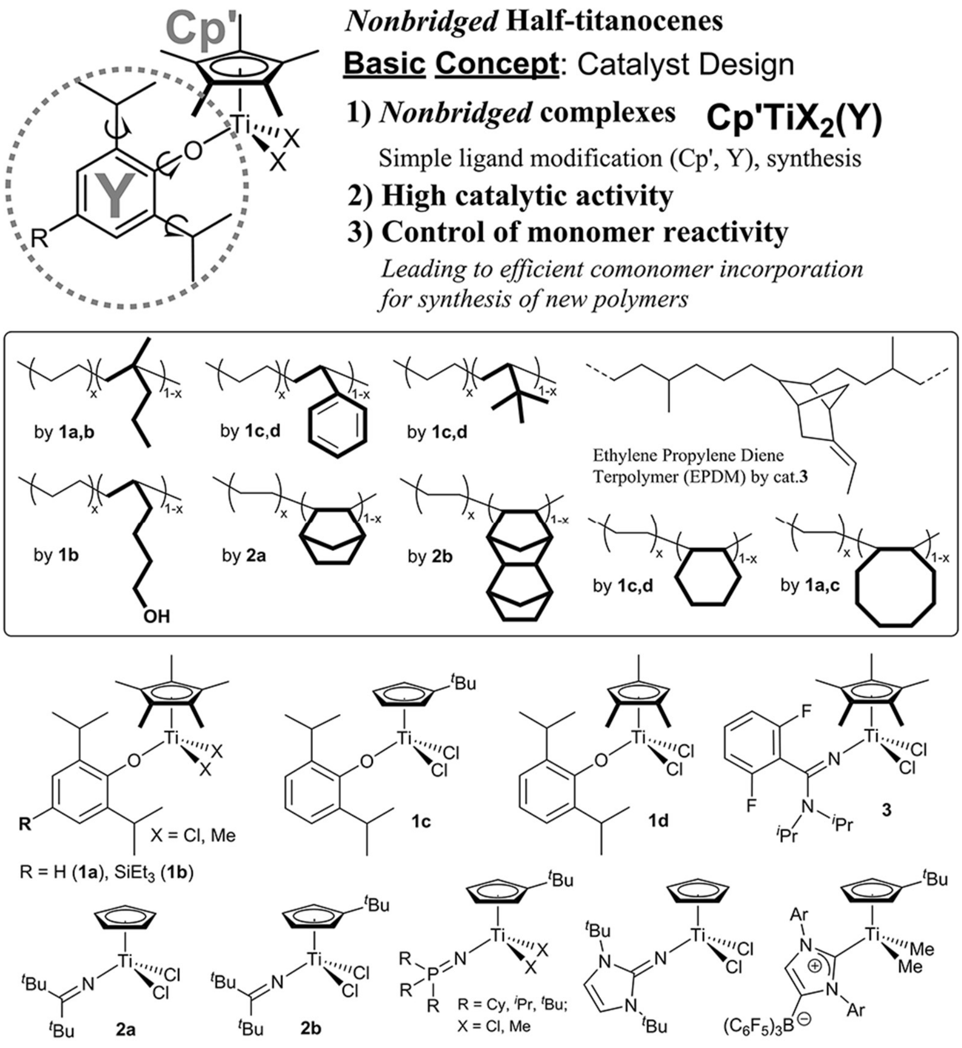
monomers (cyclopentene, cycloheptene, cyclooctene etc.) still have been limited, as described below.

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.

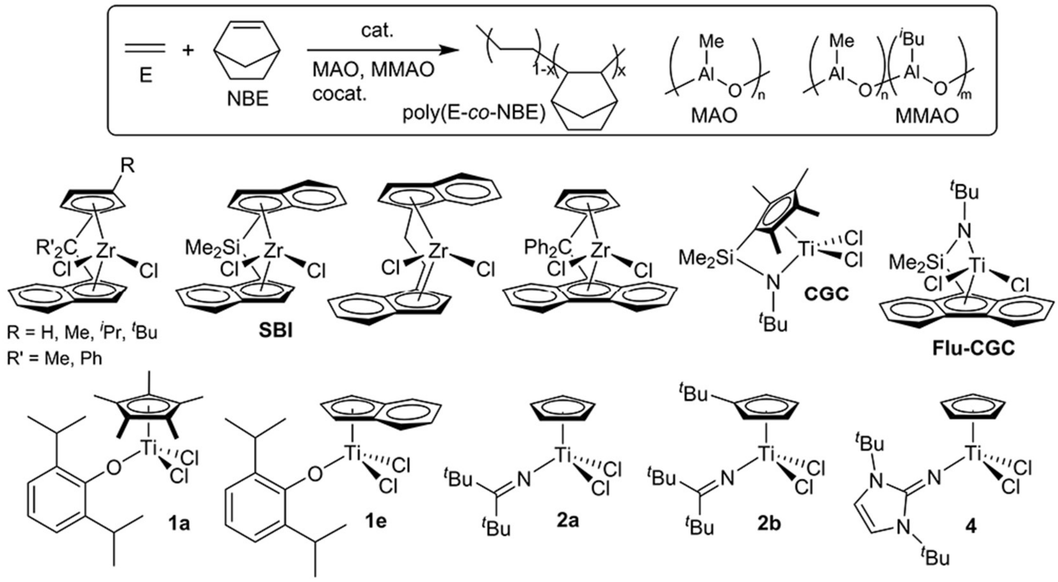
## ETHYLENE COPOLYMERIZATION WITH NORBORNENE (NBE), AND TETRACYCLODODECENE (TCD)

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, $CpTiCl_2(N{=}C^tBu_2)$ (**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 $[Me_2Si(indenyl)_2]ZrCl_2$ (**SBI**), $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**CGC**), (indenyl)$TiCl_2$(O-2,6-$^iPr_2C_6H_3$) (**1e**), $CpTiCl_2(N{=}C^tBu_2)$ (**2a**), $CpTiCl_2[1,3\text{-}^tBu_2(CHN)_2C{=}N]$ (**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 [$VOCl_3$, $VO(OEt)Cl_2$ – $EtAlCl_2$•$Et_2AlCl$ 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 $(^tBuC_5H_4)TiCl_2(N{=}CtBu_2)$ (**2b**) in the presence of MAO cocatalyst (Table 2) [65]. The Cp analogue, $CpTiCl_2(N{=}CtBu_2)$ (**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.

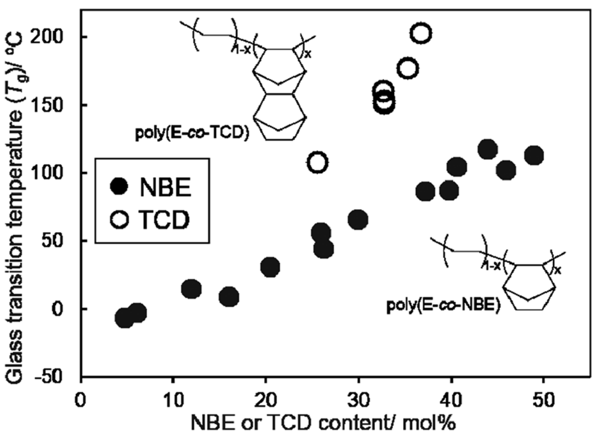



**Figure 1**. Plots of glass transition temperature ($T_g$) vs norbornene (NBE) or tetradecane (TCD) contents in the ethylene (E) copolymers, poly(E-*co*-NBE)s, and poly(E-*co*-TCD)s [49,51].

## 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$^t$$Bu_2$) [Cp' = Cp (**2a**), $^t$Bu$C_5H_4$ (**2b**)], Cp$TiCl_2$[1,3-$^t$$Bu_2$$(CHN)_2$C=N] (**4**), $Me_2Si(C_5Me_4)$(NtBu)]$TiCl_2$ (**CGC**)–MAO catalysts (reference 65).[a]

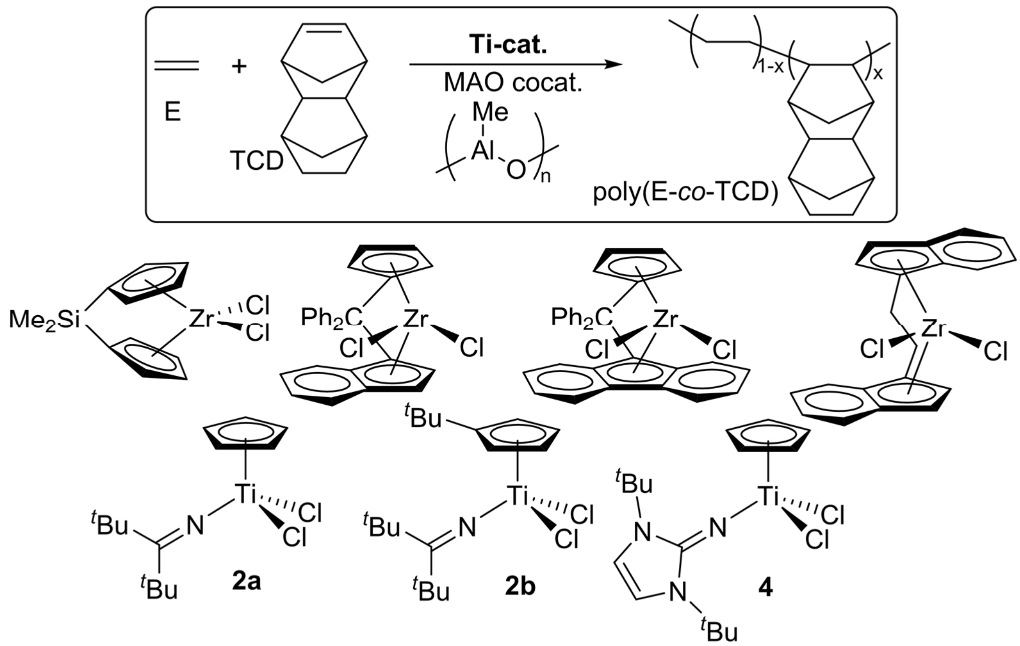
| Ti/μmol | TCD[b]/mol/L | Temp./°C | Activity[c] | $M_n$[d]×10$^{-5}$ | $M_w/M_n$[d] | $T_g$[e] ($T_m$[e])/°C | TCD[f]/mol% |
|---|---|---|---|---|---|---|---|
| **CGC** (0.05) | 1.0 | 25 | 13900 | 14.3 | 1.58 | 56 | |
| **2a** (0.8) | 2.0 | 25 | 1650 | 1.92 | 1.41 | 150 | |
| **2b** (0.02) | 1.0 | 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 | 33.5[g] |
| **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 | 33.6[g] |
| **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.

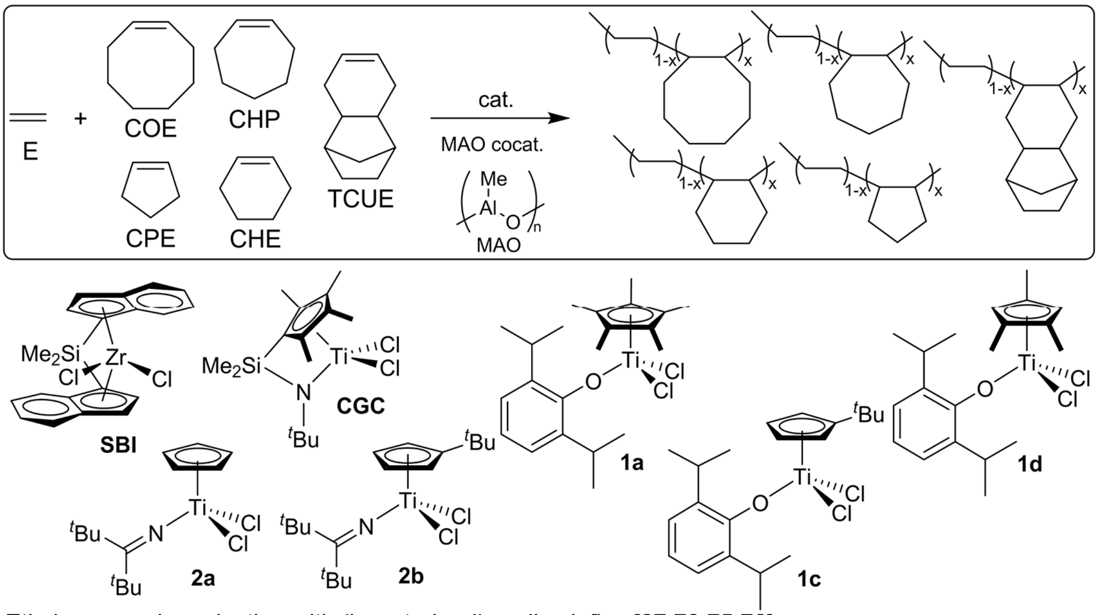
with efficient CPE insertion as well as with high activity was demonstrated by the $^t$Bu$C_5H_4$-ketimide analogue (**2b**) to afford high molecular weight copolymers (CPE content <43.6 mol%) [76]. A linear relationship between the CPE content and the $T_g$ value was also demonstrated [75]. Cp'$TiCl_2$(O-2,6-$^i$$Pr_2C_6H_3$) [Cp' $^t$Bu$C_5H_4$ (**1c**), 1,2,4-$Me_3C_5H_2$ (**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].

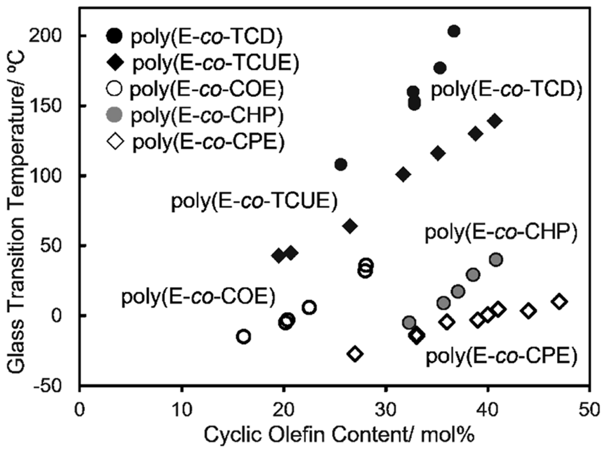
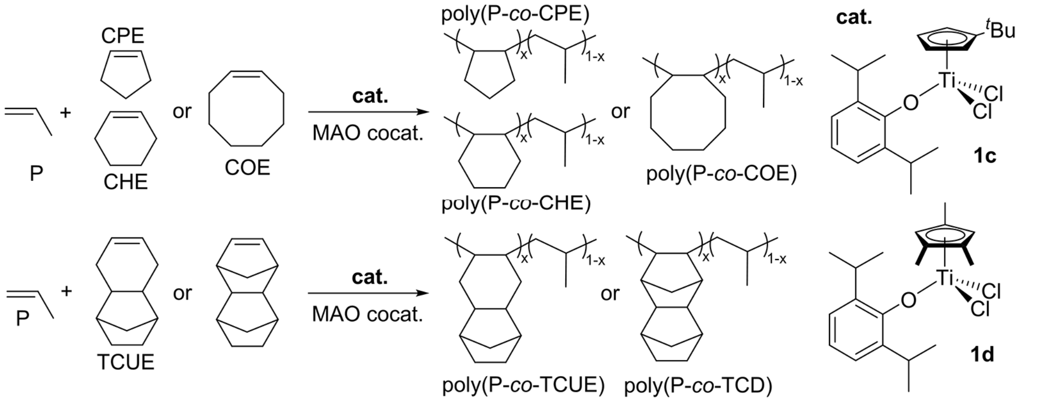



**Figure 2**. Relationships between $T_g$ values and cyclic olefin content in the ethylene-cyclic olefin copolymers: Effect of monomer structure toward their thermal property [70].

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.

## ACKNOWLEDGEMENTS

The projects by KN were partly supported by Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS, No. 15H03812, 18H01982, 21H01942).

## CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

## REFERENCES

1. Kaminsky W (1994) Olefinpolymerisation mittels metallocenkatalysatoren. Angew Makromol Chem 223: 101-120
2. Kaminsky W (1996) New polymers by metallocene catalysis. Macromol Chem Phys 197: 3907-3945
3. McKnight AL, Waymouth RM (1998) Group 4 *ansa*-cyclopentadienyl-amido catalysts for olefin polymerization. Chem Rev 98: 2587-2598
4. Gibson VC, Spitzmesser SK (2003) Advances in non-metallocene olefin polymerization catalysis. Chem Rev 103: 283–316
5. Nomura K, Liu J, Padmanabhan S, Kitiyanan B (2007) Nonbridged half-metallocenes containing anionic ancillary donor ligands: New promising candidates as catalysts for precise olefin polymerization. J Mol Catal-A 267: 1-29
6. Nomura K (2009) Half-titanocenes containing anionic ancillary donor ligands as promising new catalysts for precise olefin polymerization. Dalton Trans 2009: 8811-8823
7. Nomura K, Liu J (2011) Half-titanocenes for precise olefin polymerisation: Effects of ligand substituents and some mechanistic aspects. Dalton Trans 40: 7666-7682
8. Redshaw C, Tang Y (2012) Tridentate ligands and beyond in group IV metal α-olefin homo-/co-polymerization catalysis. Chem Soc Rev 41: 4484-4510
9. Osakada K (2014) Organometallic Reactions and Polymerization, Springer-Verlag
10. Hoff R, Mathers RT (2018) Handbook of Transition Metal Polymerization Catalysts, 2nd ed., Wiley.
11. Stürzel M, Mihan S, Mülhaupt R (2016) From multisite polymerization catalysis to sustainable materials and all-polyolefin composites. Chem Rev 116: 1398-1433
12. Baier MC, Zuideveld MA, Mecking S (2014) Post-metallocenes in the industrial production of polyolefins. Angew Chem Int Ed 53: 9722-9744
13. van Doremaele G, van Duin M, Valla M, Berthoud A (2017) On the development of titanium $\kappa^1$-amidinate complexes, commercialized as Keltan ACETM technology, enabling the production of an unprecedented large variety of EPDM polymer structures. J Polym Sci Pol Chem 55: 2877-2891
14. Yuan S-F, Yan Y, Solan GA, Ma Y, Sun W-H (2020) Recent advancements in N-ligated group 4 molecular catalysts for the (co)polymerization of ethylene. Coord Chem Rev 411: 213254
15. Nomura K (2023) Catalysis for a Sustainable Environment: Reactions, Processes and Applied Technologies, Wiley, in press
16. Suhm J, Schneider MJ, Mülhaupt R (1998) Influence of metallocene structures on ethene

copolymerization with 1-butene and 1-octene. J Mol Catal-A 128: 215-227
17. Suhm J, Schneider MJ, Mülhaupt R (1997) Temperature dependence of copolymerization parameters in ethene/1-octene copolymerization using homogeneous rac-$Me_2Si$(2-MeBenz[e]Ind)$_2ZrCl_2$/MAO catalyst. J Polym Sci Pol Chem 35: 735-740
18. Kakinuki K, Fujiki M, Nomura K (2009) Copolymerization of ethylene with α-olefins containing various substituents catalyzed by half-titanocenes: Factors affecting the monomer reactivities. Macromolecules 42: 4585-4595
19. Li H, Marks TJ (2006) Nuclearity and cooperativity effects in binuclear catalysts and cocatalysts for olefin polymerization. Proc Nat Acad Sci USA 103: 15295-15302
20. Delferro M, Marks TJ (2011) Multinuclear olefin polymerization catalysts. Chem Rev 111: 2450-2485
21. McInnis JP, Delferro M, Marks TJ (2014) Multinuclear group 4 catalysis: Olefin polymerization pathways modified by strong metal–metal cooperative effects. Acc Chem Res 47: 2545-2557
22. Nomura K, Naga N, Miki M, Yanagi K, Imai, A (1998) Synthesis of various non-bridged Cp-aryloxy titanium(IV) complexes of the type CpTi(OAr)$X_2$, and the catalytic alkene polymerization. – Important role of substituents on both aryloxy and cyclopentadienyl groups. Organometallics 17: 2152-2154
23. Nomura K, Naga N, Miki M, Yanagi K (1998) Olefin polymerization by (cyclopentadienyl)(aryloxy)titanium(IV) complexes−cocatalyst systems. Macromolecules 31: 7588-7597
24. Nomura K, Oya K, Komatsu T, Imanishi Y (2000) Effect of cyclopentadienyl fragment on monomer reactivities and monomer sequence distributions in ethylene/a-olefin copolymerization by nonbridged (cyclopentadienyl)(aryloxy)titanium(IV) complexes – MAO catalyst systems. Macromolecules 33: 3187-3189
25. Nomura K, Okumura H, Komatsu T, Naga N (2002) Ethylene/styrene copolymerization by various (cyclopentadienyl)(aryloxy)titanium(IV) complexes - MAO catalyst systems. Macromolecules 35: 5388-5395
26. Nomura K, Itagaki K, Fujiki M (2005) Efficient incorporation of 2-methyl-1-pentene in copolymerization of ethylene with 2-methyl-1-pentene catalyzed by nonbridged half-titanocenes. Macromolecules 38: 2053-2055
27. Nomura K, Itagaki K (2005) Efficient incorporation of vinylcylohexane in ethylene/vinylcyclohexane copolymerization catalyzed by nonbridged half-titanocenes. Macromolecules 38: 8121-8123
28. Nomura K, Liu J, Fujiki M, Takemoto A (2007) Facile, efficient functionalization of polyolefins via controlled incorporation of terminal olefins by repeated 1,7-octadiene insertion. J Am Chem Soc 129: 14170-14171
29. Liu J, Nomura K (2008) Efficient functional group introduction into polyolefins by copolymerization of ethylene with allyltrialkylsilane using nonbridged half-titanocenes. Macromolecules 41: 1070-1072
30. Itagaki K, Nomura K (2009) Efficient synthesis of functionalized polyolefin by incorporation of 4-vinylcyclohexene in ethylene copolymerization using half-titanocene catalysts. Macromolecules 42: 5097-5103
31. Kitphaitun S, Yan Q, Nomura K (2020) Effect of SiMe3, SiEt3 para-substituents for exhibiting high activity, introduction of hydroxy group in ethylene copolymerization catalyzed by phenoxide-modified half-titanocenes. Angew Chem Int Ed 59: 23072-23076
32. Aoki H, Nomura K (2021) Synthesis of amorphous ethylene copolymers with 2-vinylnaphthalene, 4-vinylbiphenyl and 1-(4-vinylphenyl) naphthalene. Macromolecules 54: 83-93
33. Kawamura K, Nomura K (2021) Ethylene copolymerization with limonene, β-pinene: New bio-based polyolefins prepared by coordination polymerization. Macromolecules 54: 4693-4703
34. Kitphaitun S, Chaimongkolkunasin S, Manit J, Makino R, Kadota J, Hirano H, Nomura K (2021) Ethylene/myrcene copolymer as new bio-based elastomers prepared by coordination polymerization using titanium catalysts. Macromolecules 54: 10049-10058
35. Kitphaitun S, Takeshita H, Nomura K (2022) Analysis of ethylene copolymers with long chain α-olefins (1-dodecene, 1-tetradecene, 1-hexadecene): A transition between main chain crystallization and side chain crystallization. ACS Omega 7: 6900-6910
36. Kitphaitun S, Fujimoto T, Ochi Y, Nomura

K (2022) Effect of borate cocatalysts toward activity and comonomer incorporation in ethylene copolymerization by half-titanocene catalysts in methylcyclohexane. ACS Org Inorg Au 2: 386-391
37. Okabe M, Nomura K (2023) Propylene cyclic olefin copolymers with cyclopentene, cyclohexene, cyclooctene, tricyclo[6.2.1.0(2,7)] undeca-4-ene, and with tetracyclododecene: The synthesis and effect of cyclic structure on thermal properties. Macromolecules 56: 81-91
38. Guo L, Makino R, Shimoyama D, Kadota J, Hirano H, Nomura K (2023) Synthesis of ethylene/ isoprene copolymers containing cyclopentane/ cyclohexane units as unique elastomers by half-titanocene catalysts. Macromolecules: 10.1021/ acs.macromol.2c02399
39. http://www.topas.com/products/topas-coc-polymers (TOPAS®)
40. https://jp.mitsuichemicals.com/en/special/apel/index.htm (APEL®)
41. Cherdron H, Brekner M-J, Osan F (1994) Cycloolefin copolymer: A new class of transparent thermoplastics. Angew Makromol Chem 223: 121-133
42. Kaminsky W, Beulich I, Arndt-Rosenau M (2001) Copolymerization of ethene with cyclic and other sterically hindered olefins. Macromol Symp 173: 211-226
43. Dragutan V, Streck R (2000) Catalytic polymerization of cycloolefins: Ionic, Ziegler-Natta and ring-opening metathesis polymerization, Elsevier
44. Tritto I, Boggioni L, Ferro DR (2006) Metallocene catalyzed ethene- and propene co-norbornene polymerization: Mechanisms from a detailed microstructural analysis. Coord Chem Rev 250: 212-241
45. Nomura K (2008) Nonbridged half-titanocenes containing anionic ancillary donor ligands: promising new catalysts for precise synthesis of cyclic olefin copolymers (COCs). Chin J Polym Sci 26: 513-523
46. Li X, Hou Z (2008) Organometallic catalysts for copolymerization of cyclic olefins. Coord Chem Rev 252: 1842-1869
47. Zhao W, Nomura K (2016) Design of efficient molecular catalysts for synthesis of cyclic olefin copolymers (COC) by copolymerization of ethylene and α-olefins with norbornene or tetracyclododecene. Catalysts 6: 175
48. Boggioni L, Tritto I (2017) State of the art of cyclic olefin polymers. MRS Bull 38: 245-251
49. Nomura K, Tsubota M, Fujiki M (2003) Efficient ethylene/norbornene copolymerization by (aryloxo)(indenyl)titanium(IV) complexes−MAO catalyst system. Macromolecules 36: 3797-3799
50. Hasan T, Ikeda T, Shiono T (2004) Ethene−norbornene copolymer with high norbornene content produced by *ansa*-fluorenylamidodimethyltitanium complex using a suitable activator. Macromolecules 37: 8503-8509
51. Nomura K, Wang W, Fujiki M, Liu J (2006) Notable norbornene (NBE) incorporation in ethylene–NBE copolymerization catalysed by nonbridged half-titanocenes: better correlation between NBE incorporation and coordination energy. Chem Commun 2659-2661
52. Hasan T, Nishii K, Shiono T, Ikeda T (2002) Living polymerization of norbornene via vinyl addition with *ansa*-fluorenylamidodimethyltitanium complex. Macromolecules 35: 8933-8935
53. Cai Z, Nakayama Y, Shiono, T (2006) Living random copolymerization of propylene and norbornene with *ansa*-fluorenylamidodimethyltitanium complex: Synthesis of novel syndiotactic polypropylene-b-poly(propylene-ran-norbornene). Macromolecules 39: 2031-2033
54. Shiono T, Sugimoto M, Hasan T, Cai Z, Ikeda T (2008) Random copolymerization of norbornene with higher 1-alkene with *ansa*-fluorenylamidodimethyltitanium catalyst. Macromolecules 41: 8292-8294
55. Cai Z, Harada R, Nakayama Y, Shiono T (2010) Highly active living random copolymerization of norbornene and 1-alkene with *ansa*-fluorenylamidodimethyltitanium derivative: Substituent effects on fluorenyl ligand. Macromolecules 43: 4527-4531
56. Yuan H, Kida T, Kim H, Tanaka R, Cai Z, Nakayama Y, Shiono T (2020) Synthesis and properties of gradient copolymers composed of norbornene and higher α-olefins using an *ansa*-fluorenylamidodimethyltitanium-[Ph3C][B(C6F5)4] catalyst system. Macromolecules 53: 4323-4329
57. Zhao W, Nomura K (2016) Copolymerizations

of norbornene, tetracyclododecene with α-olefins by half-titanocene catalysts: Efficient synthesis of highly transparent, thermal resistance polymers. Macromolecules 49: 59-70

58. Apisuk W, Trambitas A G, Kitiyanan B, Tamm M, Nomura K (2013) Efficient ethylene/norbornene copolymerization by half-titanocenes containing imidazolin-2-iminato ligands and MAO catalyst systems. J Polym Sci Pol Chem 51: 2575-2580

59. Mitsui Chemicals Co., Synthesis of ethylene/TCD copolymers by vanadium catalyst systems [$VOCl_3$, $VO(OEt)Cl_2$ – $EtAlCl_2$•$Et_2AlCl$ etc.] in the presence of halogenated Al alkyl cocatalyst, JP2001-106730; JP2006-22266; JP2008-248171

60. Kaminsky W, Bark A (1992) Copolymerization of ethene and dimethanooctahydro-naphthalene with aluminoxane containing catalysts. Polym Int 28: 251-253

61. Kaminsky W, Engehausen R, Kopf J (1995) A tailor-made metallocene for the copolymerization of ethene with bulky cycloalkenes. Angew Chem Int Ed Engl 34: 2273-2275

62. Goodall BL, McIntosh LH, Rhodes LF (1995) New catalysts for the polymerization of cyclic olefins. Macromol Symp 89: 421-432

63. Kaminsky W, Beulich I, Arndt-Rosenau M (2001) Copolymerization of ethene with cyclic and other sterically hindered olefins. Macromol Symp 173: 211-226

64. Donner M, Fernandes M, Kaminsky W (2006) Synthesis of copolymers with sterically hindered and polar monomers. Macromol Symp 236: 193-202

65. Apisuk W, Ito H, Nomura K (2016) Efficient synthesis of cyclic olefin copolymers with high glass transition temperatures by ethylene copolymerization with tetracyclododecene (TCD) using (tert-$BuC_5H_4$)$TiCl_2$(N=$CtBu_2$) – MAO catalyst. J Polym Sci Pol Chem 54: 2662-2667

66. Hong M, Cui L, Liu S, Li Y (2012) Synthesis of novel cyclic olefin copolymer (COC) with high performance via effective copolymerization of ethylene with bulky cyclic olefin. Macromolecules 45: 5397-5402

67. Wang W, Fujiki M, Nomura K (2005) Copolymerization of ethylene with cyclohexene (CHE) catalyzed by nonbridged half-titanocenes containing aryloxo ligand: Notable effect of both cyclopentadienyl and anionic donor ligand for efficient CHE incorporation. J Am Chem Soc 127: 4582-4583

68. Lavoie AR, Waymouth RM (2004) Catalytic syntheses of alternating, stereoregular ethylene/cycloolefin copolymers. Tetrahedron 60: 7147-7155

69. Naga N (2005) Copolymerization of ethylene with cycloolefins or cyclodiolefins by a constrained-geometry catalyst. J Polym Sci Pol Chem 43: 1285-1291

70. Harakawa H, Okabe M, Nomura K (2020) Synthesis of cyclic olefin copolymers (COCs) by ethylene copolymerisations with cyclooctene, cycloheptene, and with tricyclo[6.2.1.0(2,7)]undeca-4-ene: Effect of cyclic monomer structures on thermal properties. Polym Chem 11: 5590-5600

71. Buchmeiser MR, Camadanli S, Wang D, Zou Y, Decker U, Kühnel C, Reinhardt I (2011) A catalyst for the simultaneous ring-opening metathesis polymerization/vinyl insertion polymerization. Angew Chem Int Ed 50: 3566-3571

72. Kaminsky W, Spiehl R (1989) Copolymerization of cycloalkenes with ethylene in presence of chiral zirconocene catalysts. Makromol Chem 190: 515-526

73. Naga N, Imanishi Y (2002) Copolymerization of ethylene and cyclopentene with zirconocene catalysts: Effect of ligand structure of zirconocenes. Macromol Chem Phys 203: 159-165

74. Lavoie AR, Ho MH, Waymouth RM (2003) Alternating stereospecific copolymerization of cyclopentene and ethylene with constrained geometry catalysts. Chem Commun 864-865

75. Fujita M, Coates GW (2002) Synthesis and characterization of alternating and multiblock copolymers from ethylene and cyclopentene. Macromolecules 35: 9640-9647

76. Liu J, Nomura K (2007) Highly efficient ethylene/cyclopentene copolymerization with exclusive 1,2-cyclopentene incorporation by (cyclopentadienyl)(ketimide)titanium(IV) complex - MAO catalysts. Adv Synth Catal 349 : 2235-2240

77. Harakawa H, Patamma S, Boccia AC, Boggioni L, Ferro DR, Losio S, Nomura K, Tritto I (2018) Ethylene copolymerization with 4-methylcyclohexene, 1-methylcyclopentene by half-titanocene catalysts: Effect of ligands

and microstructural analysis of the copolymers. Macromolecules 51: 853-863
78. Nomura K (2019) Solution X-ray absorption spectroscopy (XAS) for analysis of catalytically active species in reactions with ethylene by homogeneous (imido)vanadium(V) complexes – Al cocatalyst systems. Catalysts 9: 1016
79. Yi J, Nakatani N, Nomura K (2020) Solution XANES and EXAFS analysis of active species of titanium, vanadium complex catalysts in ethylene polymerisation/dimerisation and syndiospecific styrene polymerization. Dalton Tran 49: 8008-8028