

Feature Article

**NONBRIDGED HALF-TITANOCENES CONTAINING ANIONIC ANCILLARY
DONOR LIGANDS: PROMISING NEW CATALYSTS FOR PRECISE SYNTHESIS
OF CYCLIC OLEFIN COPOLYMERS (COCs)**

Kotohiro Nomura*

Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST), Japan

Abstract Precise, efficient copolymerizations of ethylene with cyclic olefins [norbornene (NBE), cyclopentene (CPE)] using nonbridged half-titanocenes of type, $\text{Cp}'\text{TiCl}_2(\text{L})$ (Cp' = cyclopentadienyl group, L = aryloxo, ketimide)-MAO catalyst systems have been summarized. $\text{CpTiCl}_2(\text{N}=\text{C}'\text{Bu}_2)$ exhibited both remarkable catalytic activity and efficient NBE incorporation for ethylene/NBE copolymerization: the NBE incorporation by $\text{Cp}'\text{TiCl}_2(\text{X})$ ($\text{X} = \text{N}=\text{C}'\text{Bu}_2$, $\text{O}-2,6\text{-iPr}_2\text{C}_6\text{H}_3$; $\text{Cp}' = \text{Cp}$, C_5Me_5 , indenyl) was related to the calculated coordination energy after ethylene insertion. $(\text{tBuC}_5\text{H}_4)\text{TiCl}_2(\text{N}=\text{C}'\text{Bu})$ exhibited significant catalytic activities with efficient CPE incorporations in ethylene/CPE copolymerization in the presence of MAO. The polymerization proceeded with exclusive 1,2-CPE incorporation, affording high molecular weight (alternating) copolymers with uniform distributions. Therefore, the cyclopentadienyl fragment (Cp') plays an essential role in terms of both the activity and the efficient cyclic olefin incorporation.

Keywords: Titanium; Cyclic olefin copolymers; Copolymerization; Ethylene; Homogeneous catalysts.

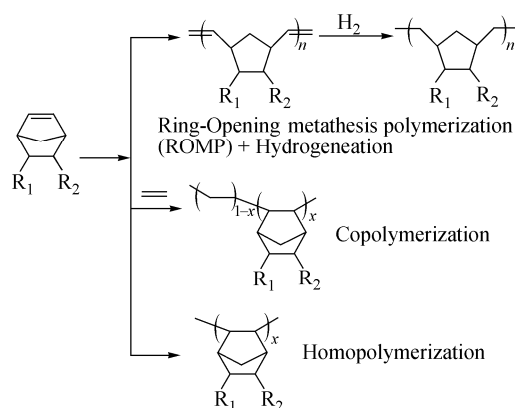
INTRODUCTION

It has been known that certain cyclic olefin copolymers (COCs) are amorphous materials with a promising combination of high transparency in the UV-Vis region along with humidity-, and heat-resistance (high glass transition temperature, T_g)^[1–4]. Three processes shown in Scheme 1, such as (1) ring-opening metathesis polymerization (ROMP) of multi-cyclic olefins and the subsequent hydrogenation, (2) coordination copolymerization of ethylene with cyclic olefins, (3) homopolymerization of cyclic olefins, are generally adopted for the practical production of COCs. In particular, the copolymerization route seems promising, because the desired properties should be tuned by their compositions (cyclic olefin contents *etc.*) as well as their microstructures (including tacticity). Therefore, transition metal catalyzed copolymerization of ethylene with cyclic olefins such as norbornene (NBE) (Scheme 2)^[5–25], cyclopentene (CPE)^[17, 26–36], cyclohexene^[37] attracts considerable attention. It is known that both bridged zirconocenes and linked half-titanocenes showed high catalytic activities for ethylene/NBE copolymerization^[5–15]. However, successful examples for the efficient synthesis of random, high molecular weight copolymers with high NBE contents (> 50 mol%), which possess high T_g (> 150°C), had been limited^[38]. This is not only because both the activity and the molecular weights for the copolymer generally decrease upon increasing the NBE contents, but also because the microstructure in the copolymer possessed few NBE repeat units and contained alternating ethylene-NBE sequences in addition to the isolated NBE units due to the difficulty for repeated insertion of NBE.

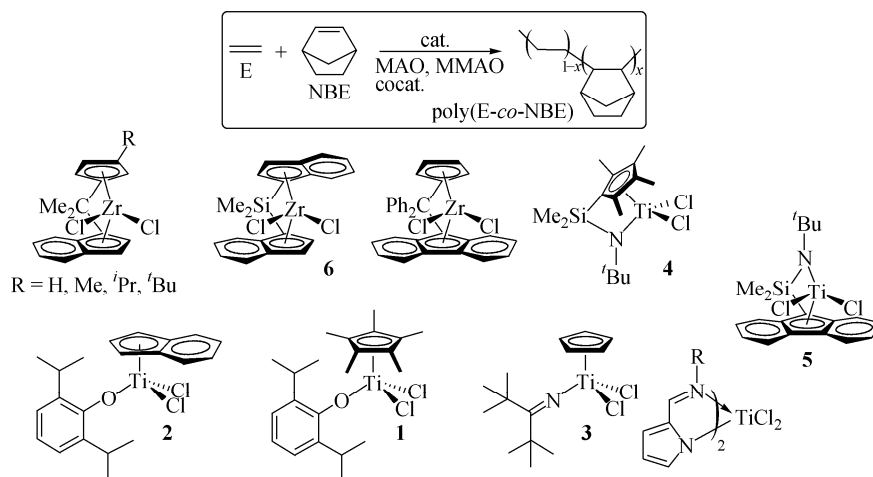
* Corresponding author: Kotohiro Nomura, E-mail: nomurak@ms.naist.jp

Invited lecture presented at the Asian Polyolefin Workshop 2007, 2007, Hangzhou, China

Received February 19, 2008; Revised March 24, 2008; Accepted March 26, 2008



Scheme 1 Process for cyclic olefin copolymers (COCs)



Scheme 2 Ethylene/norbornene (NBE) copolymerization by group 4 transition metal complex catalysts

Although many examples for copolymerization of ethylene with NBE are known, examples for the ethylene/CPE copolymerization have been limited^[17, 26–36]. Moreover, the resultant copolymers prepared by ordinary metallocenes^[26–29] or late metal complexes^[36] possessed a mixture of 1,2- and 1,3-CPE inserted units due to the tendency for favored β -hydrogen elimination-reinsertion after CPE insertion. Recently, the copolymerization with exclusive 1,2-CPE insertion had been achieved by half-titanocenes^[17, 30, 31] and others^[32–34], but the activities were still low^[39] and/or the resultant copolymers possessed low molecular weights.

Design and synthesis of efficient transition metal complex catalysts for precise olefin polymerization attract considerable attention in the fields of catalysis, organometallic chemistry, and polymer chemistry^[40–51]. Nonbridged half-metallocene type group 4 transition metal complexes of the type, $\text{Cp}'\text{M}(\text{L})\text{X}_2$ (Cp' = cyclopentadienyl group; M = Ti, Zr, Hf; L = OAr, NR_2 , NPR_3 , etc.; X = halogen, alkyl), display unique promising characteristics as olefin polymerization catalysts, because these complexes are effective catalyst precursors for production of new polyolefins^[48] that are not prepared by the conventional Ziegler-Natta catalysts, ordinary metallocenes^[40–43] and/or so-called ‘constrained geometry’ (linked Cp-amide) type catalysts^[44, 45]. In particular, nonbridged half-titanocenes (titanium half-sandwich complexes) containing aryloxo or ketimide ligand of the type, $\text{Cp}'\text{Ti}(\text{OAr})\text{X}_2$ (Ar = 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$ etc.) or $\text{Cp}'\text{Ti}(\text{N}=\text{C}'\text{Bu}_2)\text{X}_2$, should be the most promising candidates^[16–19, 35, 37, 48, 52–66], and the efficient catalyst precursors especially for copolymerization of ethylene with α -olefin^[57–60], styrene^[61, 62], norbornene^[16–19], cyclopentene^[35], cyclohexene^[37], 2-methyl-1-pentene^[63, 64],

vinylcyclohexane^[65], allyltrimethylsilane^[66] can be tuned by simple modification of both the cyclopentadienyl fragments (Cp') and the anionic ancillary donor ligands (X)^[48].

We recently succeeded to demonstrate that these complexes are quite effective catalyst precursors for precise, efficient copolymerization of ethylene with cyclic olefins such as NBE^[16–19], CPE^[35], even with cyclohexene^[37], as introduced above. Therefore, we herein summarize our results for copolymerization of ethylene with cyclic olefins catalyzed by half-titanocenes containing aryloxo, ketimide ligands.

RESULTS AND DISCUSSION

Notable Norbornene (NBE) Incorporation in Ethylene/NBE Copolymerization

Selected results for the copolymerization of ethylene with NBE using half-titanocenes containing anionic donor ligands of the type, Cp'TiCl₂(X) [X = O-2,6-*i*Pr₂C₆H₃; Cp' = C₅Me₅ (Cp*, **1**), indenyl (**2**); X = N=C'Bu₂; Cp' = Cp (**3**)], in the presence of methylaluminoxane (MAO) as cocatalyst are summarized in Table 1^[18, 19]. These

Table 1. Copolymerization of ethylene with norbornene (NBE) by Cp'TiCl₂(O-2,6-*i*Pr₂C₆H₃) [Cp' = C₅Me₅ (Cp*, **1**), indenyl (**2**)], CpTiCl₂(N=C'Bu₂) (**3**), [Me₂Si(C₅Me₄)(N^{*i*}Bu)]TiCl₂ (**4**), [Me₂Si(indenyl)₂]ZrCl₂ (**6**)-MAO catalyst systems^{[18] a}

Run	Cat. (μmol)	Time (min)	Temp. (°C)	Ethylene (MPa)	NBE ^b (mmol/mL)	Activity ^c (kg-polymer/ (mol·M·h))	$M_n^d \times 10^{-4}$	M_w/M_n^d	NBE ^e (mol%)
1	1 (0.2)	10	25	0.4	–	8400	65.2	1.90	–
2	1 (0.2)	10	25	0.4	0.2	6540	57.9	1.61	8.2
3	1 (0.2)	10	25	0.4	1.0	2640	29.6	1.46	21.7
4	2 (0.2)	10	25	0.4	–	6960	22.5	1.88	–
5	2 (0.2)	10	25	0.4	0.2	10500	14.6	1.56	14.0
6	2 (0.5)	10	25	0.4	1.0	2300	5.87	1.82	35.2
7	2 (1.0) ^f	10	25	0.2	2.5	678	3.91	1.58	58.8
8	2 (5.0) ^f	10	25	0.2	5.0	126	0.78	2.42	60.1
9	3 (0.1)	10	25	0.4	–	5880	45.2	2.30	–
10	3 (0.02)	10	25	0.4	0.2	21600	70.6	1.85	17.8
11	3 (0.02)	10	25	0.4	1.0	40200	71.9	2.92	40.7
12	3 (0.02)	20	25	0.4	1.0	60150	53.4	2.11	41.5
13	3 (0.02)	30	25	0.4	1.0	59700	61.3	2.18	41.0
14	3 (0.02) ^g	10	25	0.4	1.0	42300	35.5	2.42	41.8
15	3 (0.02) ^h	10	25	0.4	1.0	50400	35.1	2.31	42.9
11	3 (0.02)	10	25	0.4	1.0	40200	71.9	2.92	40.7
16	3 (0.02)	10	40	0.4	1.0	48900	62.0	2.37	45.9
17	3 (0.02)	10	60	0.4	1.0	194000	47.5	2.20	51.2
18	3 (0.02)	20	60	0.4	1.0	173400	45.3	2.24	–
19	3 (0.02)	10	80	0.4	1.0	133000	33.8	2.34	61.7
20	3 (0.01) ^f	10	25	0.2	2.5	90000	32.3	2.09	58.8
21	3 (0.01) ^f	10	25	0.2	5.0	85800	34.0	2.00	65.8
22	3 (0.02) ^f	10	25	0.2	10.0	31500	44.4	2.01	73.5
23	3 (0.1) ^g	10	25	–	0.5	9540	insoluble ⁱ		100
24	6 (0.10)	10	25	0.4	0.2	28860	23.1	2.02	10.8
25	6 (0.10)	10	25	0.4	1.0	4860	22.9	2.37	29.5
26	4 (0.50)	10	25	0.4	0.2	2460	21.1	1.88	9.6
27	4 (0.50)	10	25	0.4	1.0	2000	12.8	2.15	26.5

^a Conditions: toluene + NBE total 50 mL, MAO white solid (prepared by removing AlMe₃, toluene from PMAO) 3.0 mmol;

^b NBE concentration charged (mmol/mL); ^c Activity in kg-polymer/mol·M·h (M = Ti, Zr); ^d GPC data in *o*-dichlorobenzene versus polystyrene standards; ^e NBE content (mol%) estimated by ¹³C-NMR spectra; ^f Conditions: toluene + NBE total 10 mL; ^g MMAO-3A-T (MMAO: modified methylaluminoxane, used as white solids prepared by removing AlMe₃, Al^{*i*}Bu₃ and solvent in *vacuo*), Me^{*i*}Bu = 2.33, 3.0 mmol; ^h MMAO-3A-H, Me^{*i*}Bu = 2.67, 3.0 mmol. ⁱ Insoluble in THF for GPC measurement.

complexes had been chosen, not only because **2** showed efficient NBE incorporation affording random copolymers^[16, 17], but also because both Cp' and the anionic donor ligand affected the comonomer incorporation in the ethylene copolymerizations^[48, 52–66]. [Me₂Si(C₅Me₄)(N^tBu)]TiCl₂ (**4**) and [Me₂Si(indenyl)₂]ZrCl₂ (**6**) were also chosen for comparison.

The indenyl-aryloxo analogue (**2**) showed efficient NBE incorporation with high catalytic activity (run 5)^[16, 17], however, both the activity and the M_n value decreased upon increasing the NBE content (runs 5–8). The same trend was seen in the copolymerization using both bridged metallocene (**6**) and linked half-titanocene (**4**), as reported previously^[5–15], and the NBE incorporations were less efficient compared to **2** (runs 24–27). The Cp*-aryloxo analogue (**1**) showed less efficient NBE incorporation than **2** (runs 2–3)^[16, 17].

Note that CpTiCl₂(N=C^tBu₂) (**3**) exhibited remarkable catalytic activities, and the activity did not decrease at least for 30 min (runs 11–13). The activity increased upon increasing in the initial NBE concentration (runs 9–11), whereas the activities by the other catalysts decreased upon increasing in the NBE concentration. The NBE contents in the copolymers were thus higher than those prepared by other catalysts under the same conditions. It should also be noted that both the activities and the NBE incorporations were not strongly affected by the Al cocatalyst employed (MAO, MMAOs, runs 11, 14–15), and the fact is a unique contrast to that reported in the copolymerization by [Me₂Si(fluorenyl)(N^tBu)]TiMe₂ (**5**) in which both the catalytic activity and NBE incorporation are highly dependent upon the Al cocatalyst employed^[13].

Note that both the activity (by **3**) and the NBE contents in the copolymer increased at higher temperature (runs 16–19, 40–80°C), and the resultant copolymers possessed high molecular weights with unimodal molecular weight distributions ($M_n = 3.38 \times 10^5$ – 6.20×10^5 , $M_w/M_n = 2.20$ – 2.37). The efficient synthesis of high molecular weight copolymers with high NBE contents (58.8 mol%–73.5 mol%) could be thus accomplished upon increasing the NBE concentration at low ethylene pressure (0.2 MPa), and the activities by **3** were much higher than those by **2** under the same conditions (runs 7–8 versus runs 20–21). Moreover, it should also be noted that the activities at higher NBE/ethylene feed ratios were higher than those at lower NBE/ethylene feed ratios (runs 20–21 versus runs 10–11), and the observed facts are significantly unique compared to those in the copolymerization especially using ordinary metallocenes or linked half-titanocenes. This may also be explained by the fact that **3** showed remarkable catalytic activity for NBE homopolymerization (run 23), and the activity was much higher than that reported by [Me₂Si(fluorenyl)(N^tBu)]TiMe₂ (**5**)^[13–15].

¹³C-NMR spectra for poly(ethylene-co-NBE)s showed that the microstructures by **4**, **6** possesses few NBE repeat units and contained both *meso* and *racemo* alternating ethylene-NBE sequences as well as isolated NBE units ($\delta = 33.0$ – 33.5), and the NBE dyads were also observed as a tiny trace. In contrast, resonances ascribed to NBE dyads were observed for the copolymers prepared by **2** and **3**, and the microstructures thus possessed a mixture of NBE repeat units (including dyads, triads, Fig. 1) in addition to the alternating, isolated NBE sequences^[18, 19]. The observed results may be suited as an appropriate explanation for observed difference in the NBE incorporation. Moreover, the amount of alternating sequences by **3** was lower than that by **2**, suggesting that the ratios of isolated/alternative/dyads sequences were highly dependent upon the ligand set employed, as suggested by a series of the Cp'-aryloxo analogues^[17]. The DSC thermograms for resultant copolymers prepared by **3** possessed single T_g and the T_g values increased linearly upon increasing the NBE contents (Fig. 2)^[18], strongly suggesting that the resultant copolymer possessed uniform NBE incorporation.

Cp*TiCl₂(N=C^tBu₂) (**7**) also showed high catalytic activities for the copolymerization, but the activity decreased upon increasing the NBE concentration; the NBE contents for the resultant copolymers prepared by **7** were lower than those by **3** under the same conditions. The copolymerization by CpTiCl₂[N=C(^tBu)Ph], CpTiCl₂(N=CPh₂), Cp*TiCl₂(N=CPh₂)-MAO catalyst systems were also conducted to explore effect of the ketimide substituents toward both the activity and NBE incorporation. However, the observed activities were lower than those by Cp'TiCl₂(N=C^tBu₂) (**3**, **7**)-MAO catalyst systems, and the resultant (co)polymers possessed bimodal molecular weight distributions consisting of low and high molecular weight polymers.

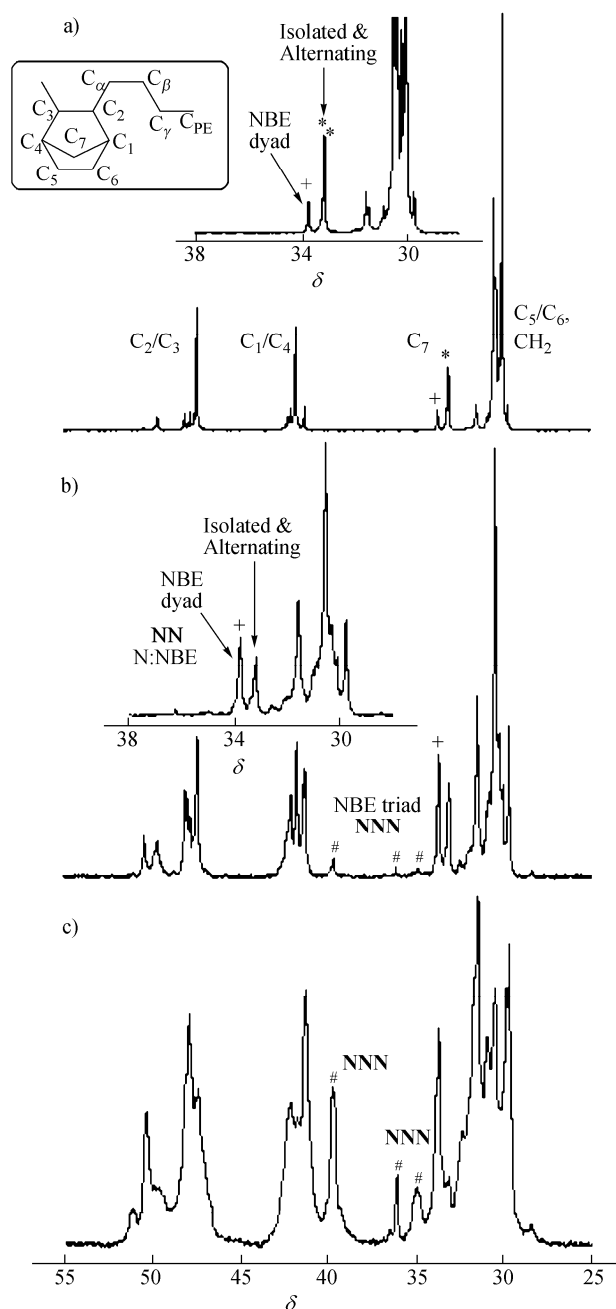


Fig. 1 ^{13}C -NMR spectra for poly(ethylene-co-NBE)s prepared by 3-MAO catalyst system
NBE contents: a) 17.8 (run 10); b) 40.7 (run 11); c) 58.8 mol% (run 20)

We previously reported effect of the ketimide substituent toward the activity for ethylene polymerization using $\text{V}(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Cl}_2[\text{N}=\text{C}(\text{R}^1)\text{tBu}]$ [$\text{R}^1 = \text{tBu}$ (**8a**), CH_2SiMe_3 (**8b**)]-MAO catalyst systems^[67]. The activity by **8b** at 25°C was higher than that by **8a** [activity 985 kg-PE/mol-V·h versus 666 kg-PE/mol-V·h, ethylene 0.8 MPa in toluene], but the activity by **8b** decreased at 50°C whereas increase in the activity was observed in **8a** [543 kg-PE/mol-V·h versus 743 kg-PE/mol-V·h]. We speculated that two *tert*-butyl group in **8a** may be necessary to improve the stability of $\text{V}-\text{N}=\text{C}$ bond under these conditions, especially minimizing the reaction of **8a,b** with MAO (or AlMe_3 contaminated) to give another catalytically-active species. It is also

reported that the imino ($\text{ArN}=\text{CH}-\text{Ar}'$) group in zirconium complexes containing two [*N*-(3-*tert*-butylsalicylidene)anilinato] ligand was reacted with Al^iBu_3 to afford another zirconium complexes containing phenoxy-amide ligands^[68]. Taking into account the above facts, it is thus assumed that the observed difference in the activity might be due to the stability of the imino group, $\text{N}=\text{C}(\text{R}^1)\text{R}^2$, toward the Al cocatalyst in the reaction mixture.

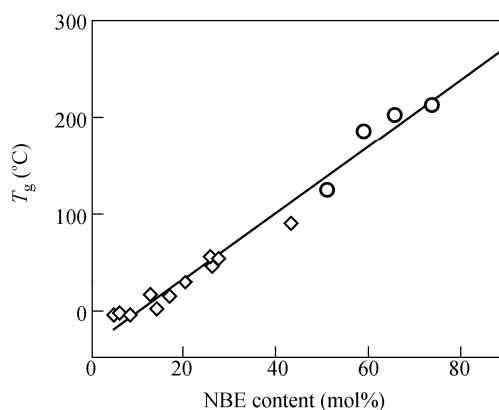


Fig. 2 Plots of T_g versus NBE contents
The details are described in reference [18], ESI.

Optimized structures for proposed catalytically active species (calculated by PM3) after coordination of ethylene or NBE are shown in Fig. 3. Coordination energies (ΔE_{coord}) of ethylene (Et) and NBE to Ti(IV) cationic complexes ($\Delta E_{\text{coord}} = E_{\text{cation}} + E_{\text{monomer}} - E_{\pi\text{-complex}}$), $\text{Cp}^*\text{Ti(X)(Y)}^+$ ($\text{Y} = \text{pentyl or 2-propyl-norbornyl}$), after insertion of previous monomers were calculated by PM3, because recent computational study suggested that the rate-determining step in ethylene polymerization is dependent on the coordination of a monomer to a cationic metal center^[69]. Both $\Delta E_{\text{coord}}^{\text{Et}}$ (coordination energy of ethylene) and $\Delta E_{\text{coord}}^{\text{NBE}}$ values are positive in all case, suggesting that the monomer coordination leads to the stabilization. It should be noted that good linear correlations between $\Delta E_{\text{coord}}^{\text{NBE}}$ and/or $\Delta E_{\text{coord}}^{\text{NBE}} - \Delta E_{\text{coord}}^{\text{Et}}$ after ethylene insertion and the NBE content under

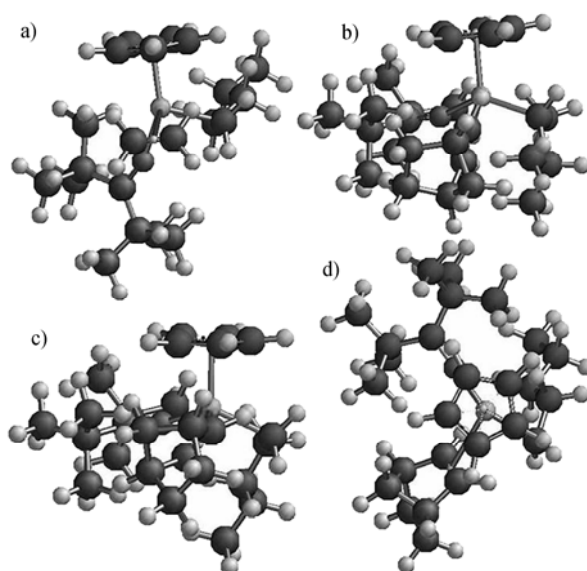


Fig. 3 Optimized structures for (a) $[\text{CpTi}(n\text{-C}_5\text{H}_{11})(\text{L})(\text{ethylene})]^+$ ($\text{L}: \text{N}=\text{C}^i\text{Bu}_2$), (b) $[\text{CpTi}(n\text{-C}_5\text{H}_{11})(\text{L})(\text{NBE})]^+$, and (c), (d) $[\text{CpTi}(n\text{-C}_5\text{H}_{11})(\text{L})(\text{NBE})]^+$ (by semi-empirical PM3, RHF/PM3D Spartan Pro'04 for Windows)^[18]

the same conditions (ethylene 0.4 MPa, NBE 0.20 mmol/mL at 25°C) were observed except the indenyl-aryloxo analogue (**2**)^[18]. These results suggest that the NBE incorporation is affected by the energetic preference of coordination between NBE and ethylene into the alkyl-cationic species. The information seen here should be promising for designing more efficient molecular catalysts.

Efficient Ethylene/Cyclopentene (CPE) Copolymerization with Exclusive 1,2-CPE Insertion

As described above, the resultant copolymers prepared by ordinary metallocenes^[26–29] or late metal complexes^[36] possessed a mixture of 1,2- and 1,3-cyclopentene (CPE) inserted units due to the tendency for favored β -hydrogen elimination-reinsertion after the CPE insertion. Synthesis of the copolymers with the exclusive 1,2-CPE insertion had been achieved by using half-titanocenes^[17, 30, 31] and others^[32–34], however, the activities were low^[39] and/or the resultant copolymers possessed low molecular weights.

Table 2. Copolymerization of ethylene with cyclopentene, norbornene by Cp'TiCl₂(N=C'Bu₂) [Cp': Cp (**3**), Cp* (**7**), indenyl (**9**), ^tBuC₅H₄ (**10**)], Cp'TiCl₂(O-2,6-ⁱPr₂C₆H₃) [Cp' = Cp* (**1**), indenyl (**2**)]-MAO catalyst systems^{[17, 35] a}

Run	Cat. (μ mol)	Cyclic olefin ^b (conc.)	Ethylene (MPa)	Activity ^c (kg-polymer/ (mol-Ti·h))	Cyclic olefin cont. ^d (mol%)	M_n^e $\times 10^{-4}$	M_w/M_n^e
28	3 (0.04)	cyclopentene (1.0)	0.4	14900	18.0	67.3	2.47
29 ^f	3 (1.0)	cyclopentene (2.5)	0.2	1150	41.3	16.9	1.97
30 ^f	3 (1.0)	cyclopentene (5.0)	0.2	906	43.1	17.6	2.01
31	7 (0.05)	–	0.4	10600	–	49.6	2.57
32	7 (0.1)	cyclopentene (1.0)	0.4	8640	1.1	43.1	2.05
33	7 (1.0)	cyclopentene (5.0)	0.4	1580	7.4	16.4	2.19
34 ^f	7 (1.0)	cyclopentene (5.0)	0.2	708	13.3	10.1	2.20
35	9 (0.1)	–	0.4	7320	–	95.6	2.80
36	9 (0.1)	cyclopentene (1.0)	0.4	15800	7.5	29.1	2.48
37	9 (0.1)	cyclopentene (5.0)	0.4	28800	19.4	27.2	2.42
38 ^f	9 (0.1)	cyclopentene (5.0)	0.2	26300	32.9	24.7	2.03
39	10 (0.05)	–	0.4	21800	–	52.2	2.66
40	10 (0.1)	cyclopentene (1.0)	0.4	27300	18.1	31.1	3.59
41	10 (0.1)	cyclopentene (5.0)	0.4	19900	35.1	23.4	3.29
42 ^f	10 (0.1)	cyclopentene (1.0)	0.2	31600	33.5	36.9	3.59
43 ^f	10 (0.1)	cyclopentene (5.0)	0.2	22600	43.6	13.4	1.69
44	1 (0.2)	cyclopentene (0.2)	0.4	7110	3.0	59.3	2.09
45	2 (0.2)	cyclopentene (0.2)	0.4	12900	9.0	0.85	2.08 ^h
46	2 (0.2)	cyclopentene (1.0)	0.4	4980	12.1	0.56	1.88 ^h
11 ^g	3 (0.02)	norbornene (1.0)	0.4	40200	40.7	71.9	2.92
20 ^{f,g}	3 (0.01)	norbornene (2.5)	0.2	90000	58.8	32.3	2.09
21 ^{f,g}	3 (0.01)	norbornene (5.0)	0.2	85800	65.8	34.0	2.00
47	7 (0.05)	norbornene (5.0)	0.4	7560	37.9	17.9	2.32
48 ^f	7 (1.0)	norbornene (5.0)	0.2	3860	41.4	12.7	2.13
49	9 (0.1)	norbornene (5.0)	0.4	9960	45.2	24.5	1.81
50 ^f	9 (0.1)	norbornene (5.0)	0.2	5340	62.1	15.2	2.26
51	10 (0.01)	norbornene (1.0)	0.4	68400	38.2	62.4	2.78
52	10 (0.1)	norbornene (5.0)	0.4	15000	52.7	17.5	2.05
53 ^f	10 (0.1)	norbornene (5.0)	0.2	4980	64.8	14.2	1.94

^aConditions: toluene + norbornene or cyclopentene total 50 mL, d-MAO (prepared by removing AlMe₃ and toluene from PMAO) 3.0 mmol, ethylene 0.2 or 0.4 MPa, 25°C, 10 min; ^bCyclic olefin concentration charged in mmol/mL; ^cActivity in kg-polymer/mol-Ti·h; ^dCyclic olefin (norbornene, cyclopentene) content (mol%) estimated by ¹³C-NMR spectra; ^eGPC data in *o*-dichlorobenzene versus polystyrene standards; ^fConditions: toluene + cyclic olefin total 10 mL (instead of 50 mL);

^gCited from reference [18] (Table 1); ^hHigh molecular weight shoulder was also seen in the GPC trace.

The copolymerizations using a series of half-titanocenes containing ketimide or aryloxo ligands of type, $\text{Cp}'\text{TiCl}_2(\text{N}=\text{C}'\text{Bu}_2)$ [$\text{Cp}' = \text{Cp}$ (**3**), Cp^* (**7**), indenyl (**9**), $^i\text{BuC}_5\text{H}_4$ (**10**)] or $\text{Cp}'\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ [$\text{Cp}' = \text{Cp}^*$ (**1**), indenyl (**2**)] were conducted in toluene in the presence of MAO cocatalyst (Table 2)^[17, 35]. Ethylene/NBE copolymerizations using the same catalyst systems were also explored for comparison.

The Cp-ketimide analogue (**3**) showed both notable catalytic activities and efficient NBE incorporations in ethylene/NBE copolymerization, as reported previously^[18, 19], and the activity did not decrease even under high NBE concentration (NBE/ethylene feed) conditions. In contrast, significant decrease in the activity was observed upon increasing the CPE concentration (initial CPE/ethylene feed molar ratios) in the ethylene/CPE copolymerization by **3**, although **3** exhibited the notable activity with efficient CPE incorporation under certain conditions. The activities by the Cp^* -ketimide analogue (**7**) in the ethylene/CPE copolymerizations were lower than those by the Cp analogue (**3**), and the CPE content in the copolymer was low even under high CPE concentration conditions (13.3 mol%).

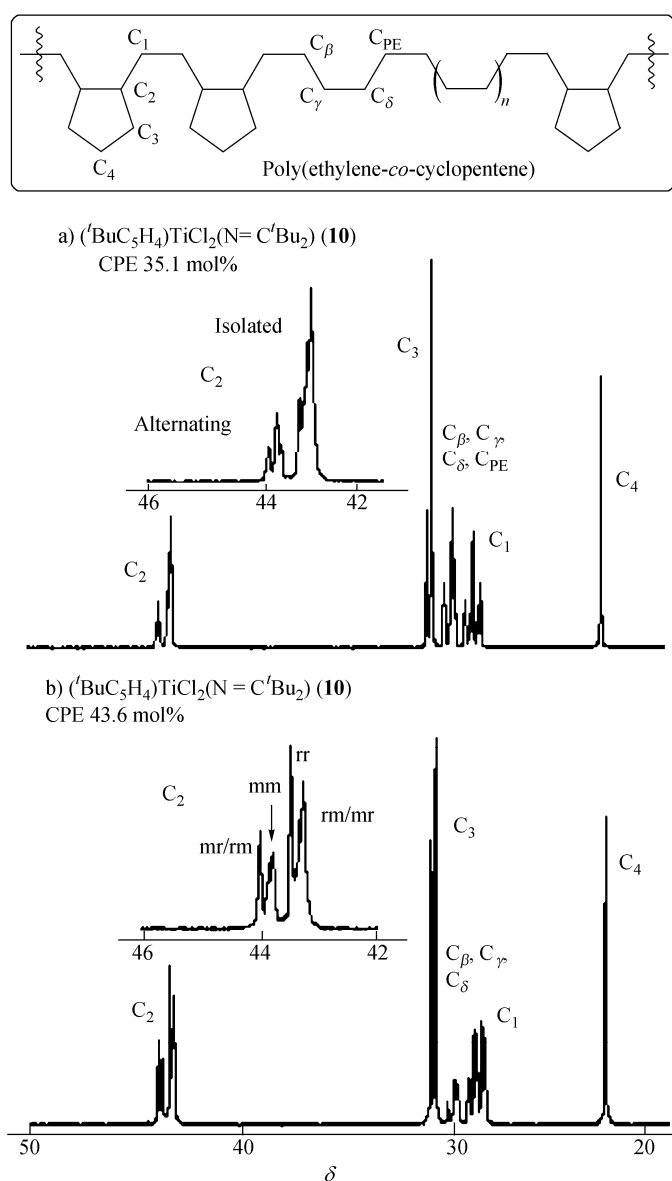


Fig. 4 ¹³C-NMR spectra (in benzene-*d*₆/1,2,4-trichlorobenzene at 110°C) for poly(ethylene-*co*-CPE)s by **10**-MAO catalyst system

Note that both the indenyl-ketimide analogue (**9**) and the ^tBuC₅H₄-ketimide analogue (**10**) showed significant catalytic activities in the ethylene/CPE copolymerization, and significant decreases in the activities by **9**, **10** were not seen even under the high CPE concentration (high initial CPE/ethylene feed molar ratio) conditions. The resultant copolymers possessed high molecular weights with unimodal molecular weight distributions, and the *M_n* values for the copolymers decreased upon increasing the CPE contents. The CPE contents in the copolymers by **10** were higher than those by **9**, and these results thus indicate that the ^tBuC₅H₄ analogue (**10**) should be the most suited catalyst precursor for the ethylene/CPE copolymerization in terms of both the catalytic activity and the CPE incorporation. In contrast, the activity by the indenyl-aryloxo analogue (**2**) significantly decreased upon increasing the CPE concentration and the resultant copolymers possessed low molecular weights with bimodal molecular weight distributions^[17].

In contrast, the activities in the ethylene/NBE copolymerizations by **9**, **10**-MAO catalyst systems decreased upon increasing the NBE concentration (initial NBE/ethylene feed ratio). The observed effect of substituents in the cyclopentadienyl group (Cp') for the copolymerization of between NBE and CPE should be promising, because, as demonstrated previously in the ethylene copolymerizations using the Cp'-aryloxo analogues, the results clearly demonstrate that the efficient catalyst precursors for the desired (co)polymerization can be tuned by modification of the cyclopentadienyl fragment.

Figure 4 shows selected ¹³C-NMR spectra for the resultant poly(ethylene-*co*-CPE)s prepared by **10**-MAO catalyst system. It is clear that CPE was incorporated in a 1,2-insertion manner, and that no or negligible amount of 1,3-inserted units which are observed in the copolymer using ordinary zirconocene catalysts were seen. The fact clearly indicates that the CPE incorporation took place in a regioselective manner as seen in certain titanium complex catalysts^[30–34], and the observed exclusive selectivity would be attributed to the lower tendency to undergo β-hydrogen elimination than those using zirconocene complex catalysts as proposed previously. These microstructures possessed both isolated and alternating CPE sequences, and resonances ascribed to the repeated CPE inserted units were not seen. Although the resultant poly(ethylene-*co*-CPE)s have no stereo regularity (isotactic, syndiotactic *etc.*) in all cases, these results strongly suggest that efficient synthesis of alternating poly(ethylene-*co*-CPE)s are possible in this catalysis.

SUMMARY AND OUTLOOK

As introduced above, nonbridged half-metallocenes containing anionic donor ligand of the type, Cp'(L)MX₂, displayed unique characteristics that are different from those especially by ordinary catalysts. Modifications of both the cyclopentadienyl fragment (Cp') and anionic donor ligands (X, kind of anionic donor ligand, and the substituents) were thus very important for the success. Since several interesting and important findings that should be very important from both academic and industrial viewpoints have been demonstrated, particular attention should be thus paid to explore the possibility for preparing precise polyolefin materials by using precisely controlled polymerization technique.

ACKNOWLEDGMENT The present research is partly supported by Grant-in-Aid for Scientific Research (B) from the Japan Society for the Promotion of Science (JSPS, No. 18350055). K. Nomura expresses his thanks to Tosoh Finechem Co. for donating MAO (PMAO-S).

REFERENCES

- 1 Kaminsky, W., *Angew. Makromol. Chem.*, 1994, 223: 101
- 2 Cherdrón, H., Brekner, M.J. and Osan, F., *Angew. Makromol. Chem.*, 1994, 223: 121
- 3 Kaminsky, W., Beulich, I. and Arndt-Rosenau, M., *Macromol. Symp.*, 2001, 173: 211
- 4 Dragutan, V. and Streck, R., "Catalytic Polymerization of Cycloolefins," *Stud. Surf. Sci. Catal.*, Vol. 131, Elsevier,

- Amsterdam, 2000
- 5 Ruchatz, D. and Fink, G., *Macromolecules*, 1998, 31: 4669; 4674; 4681; 4684
 - 6 Provasoli, A., Ferro, D.R., Tritto, I. and Boggioni, L., *Macromolecules*, 1999, 32: 6697
 - 7 Tritto, I., Marestin, C., Boggioni, L., Zetta, L., Provasoli, A. and Ferro, D.R., *Macromolecules*, 2000, 33: 8931
 - 8 Tritto, I., Marestin, C., Boggioni, L., Sacchi, M.C., Brintzinger, H.H. and Ferro, D.R., *Macromolecules*, 2001, 34: 5770
 - 9 Tritto, I., Boggioni, L., Jansen, J.C., Thorshaug, K., Sacchi, M.C. and Ferro, D.R., *Macromolecules*, 2002, 35: 616
 - 10 Harrington, B.A. and Crowther, D.J., *J. Mol. Catal. A*, 1998, 128: 79
 - 11 McKnight, A.L. and Waymouth, R.M., *Macromolecules*, 1999, 32: 2816
 - 12 Thorshaug, K., Mendichi, R., Boggioni, L., Tritto, I., Trinkle, S., Friedrich, C. and Mülhaupt, R., *Macromolecules*, 2002, 35: 2903
 - 13 Hasan, T., Ikeda, T. and Shiono, T., *Macromolecules*, 2004, 37: 8503
 - 14 Hasan, T., Ikeda, T. and Shiono, T., *Macromolecules*, 2005, 38: 1071
 - 15 Cai, Z., Nakayama, Y. and Shiono, T., *Macromolecules*, 2006, 39: 2031
 - 16 Nomura, K., Tsubota, M. and Fujiki, M., *Macromolecules*, 2003, 36: 3797
 - 17 Wang, W., Tanaka, T., Tsubota, M., Fujiki, M., Yamanaka, S. and Nomura, K., *Adv. Synth. Catal.*, 2005, 347: 433
 - 18 Nomura, K., Wang, W., Fujiki, M. and Liu, J., *Chem. Commun.*, 2006, 2659
 - 19 Nomura, K., Yamada, J., Wang, W. and Liu, J., *J. Organomet. Chem.*, 2007, 692: 4675
 - 20 Altamura, P. and Grassi, A., *Macromolecules*, 2001, 34: 9197
 - 21 Yoshida, Y., Saito, J., Mitani, M., Takagi, Y., Matsui, S., Ishii, S., Nakano, T., Kashiwa, N. and Fujita, T., *Chem. Commun.*, 2002, 1298
 - 22 Yoshida, Y., Mohri, J., Ishii, S., Mitani, M., Saito, J., Matsui, S., Makio, H., Nakano, T., Tanaka, H., Onda, M., Yamamoto, Y., Mizuno, A. and Fujita, T., *J. Am. Chem. Soc.*, 2004, 126: 12023
 - 23 Li, X.F., Dai, K., Ye, W.P., Pan, L. and Li, Y.S., *Organometallics*, 2004, 23: 1223
 - 24 Nomura, K. and Wang, W., *Macromolecules*, 2005, 38: 5905
 - 25 Wang, W. and Nomura, K., *Adv. Synth. Catal.*, 2006, 348: 743
 - 26 Kaminsky, W. and Spiehl, R., *Makromol. Chem., Macromol. Chem. Phys.*, 1989, 19: 515
 - 27 Jerschow, A., Ernst, E., Hermann, W. and Müller, N., *Macromolecules*, 1995, 28: 7095
 - 28 Naga, N. and Imanishi, Y., *Macromol. Chem. Phys.*, 2002, 203: 159
 - 29 Naga, N., *J. Polym. Sci. Part A: Polym. Chem.*, 2005, 43: 1285
 - 30 Lavoie, A.R., Ho, M.H. and Waymouth, R.M., *Chem. Commun.*, 2003, 864
 - 31 Lavoie, A.R. and Waymouth, R.M., *Tetrahedron*, 2004, 60: 7147
 - 32 Fujita, M. and Coates, G.W., *Macromolecules*, 2002, 35: 9640
 - 33 Tang, L.M., Duan, Y.Q., Pan, L. and Li, Y.S., *J. Polym. Sci. Part A: Polym. Chem.*, 2005, 43: 1681
 - 34 Pennington, D.A., Coles, S.J., Hursthouse, M.B., Bochmann, M. and Lancaster, S.J., *Macromol. Rapid Commun.*, 2006, 27: 599
 - 35 Liu, J. and Nomura, K., *Adv. Synth. Catal.*, 2007, 349: 2235
 - 36 McLain, S.J., Feldman, J., McCord, E.F., Gardner, K.H., Teasley, M.F., Coughlin, E.B., Sweetman, B.J., Johnson, L.K. and Brookhart, M., *Macromolecules*, 1998, 31: 6705
 - 37 Wang, W., Fujiki, M. and Nomura, K., *J. Am. Chem. Soc.*, 2005, 127: 4582
 - 38 Some reports were known for synthesis of poly(ethylene-*co*-NBE)s with high NBE contents, in particular, [Me₂Si-(fluorenyl)(N^tBu)]TiMe₂ showed efficient NBE incorporation affording the copolymers with high NBE contents^[13]. However, the catalytic activities were low and both the activities and NBE contents are highly affected by the cocatalyst employed.
 - 39 For reported examples, the catalytic activities by [Me₂Si(C₃Me₄)(N^tBu)]TiCl₂, [Me₂Si(indenyl)(N^tBu)]TiCl₂ or the related complexes (modified by Cp, indenyl fragment)-MMAO catalysts were 10–469 kg/mol-Ti·h (ethylene *ca.* 0.1 MPa, toluene 5 mL, cyclopentene 15 mL)^[30, 31], the activities by bis(phenoxyimine)titanium complex-MAO catalysts were < 49 kg/mol-Ti·h (ex. ethylene < 0.1 MPa, toluene total 10–15 mL, cyclopentene 13.2 mL)^[32]. The activities by [(Ph)NC(R²)CHC(R¹)O]₂TiCl (R¹;R² = CF₃;CH₃, Ph;CF₃, ^tBu;CF₃)-MMAO catalysts were 38–310 kg-polymer/mol-Ti·h

- (ex. ethylene 0.1 MPa, cyclopentene 5.0 mmol/mL in toluene)^[33]. The activities by $\text{Ti}\{3\text{-}i\text{Bu-2-(O)C}_6\text{H}_5\text{CH}=\text{N(C}_6\text{F}_5)\}\{2\text{-(C}_6\text{H}_5\text{NCH)C}_4\text{H}_3\text{N}\Cl}_2\text{-MAO}$ catalyst were 260–1000 kg-polymer/mol-Ti·h (ex. ethylene 0.1 MPa, cyclopentene 0.66–4.9 mmol/mL in toluene)^[34], the activity decreased at higher cyclopentene concentration conditions and the molecular weight distributions for the polymers with high cyclopentene contents were broad ($M_w/M_n = 3.6\text{--}4.5$).
- 40 Brintzinger, H.H., Fischer, D., Mülhaupt, R., Rieger, B. and Waymouth, R.M., *Angew. Chem., Int. Ed. Engl.*, 1995, 34: 1143
- 41 Kaminsky, W., *Macromol. Chem. Phys.*, 1996, 197: 3903
- 42 Kaminsky, W. and Arndt, M., *Adv. Polym. Sci.*, 1997, 127: 143
- 43 Coates, G.W., *Chem. Rev.*, 2000, 100: 1223
- 44 Suhm, J., Heinemann, J., Wörner, C., Müller, P., Stricker, F., Kressler, J., Okuda, J. and Mülhaupt, R., *Macromol. Symp.*, 1998, 129: 1
- 45 McKnight, A.L. and Waymouth, R.M., *Chem. Rev.*, 1998, 98: 2587
- 46 Britovsek, G.J.P., Gibson, V.C. and Wass, D.F., *Angew. Chem., Int. Ed.*, 1999, 38: 429
- 47 Gibson, V.C. and Spitzmesser, S.K., *Chem. Rev.*, 2003, 103: 283
- 48 For recent reviewing article concerning olefin polymerization by nonbridged half-titanocenes, Nomura, K., Liu, J., Padmanabhan, S. and Kitiyanan, B., *J. Mol. Catal. A*, 2007, 267: 1
- 49 “Frontiers in Metal-Catalyzed Polymerization”, ed. by Gladys, J.A., Published as a special issue: *Chem. Rev.*, 2000, 100(4). (a) Ittel, S.D., Johnson, L.K. and Brookhart, M., *Chem. Rev.*, 2000, 100: 1169. (b) Alt, H.G. and Köppl, A., *Chem. Rev.*, 2000, 100: 1205. (c) Chen, E.Y.X. and Marks, T.J., *Chem. Rev.*, 2000, 100: 1391
- 50 “Progress in Olefin Polymerization Catalysts and Polyolefin Materials”, ed. by Shiono, T., Nomura, K. and Terano, M., Published as a special symposium issue on Asian Polyolefin Workshop 2005 (APO2005): *Stud. Surf. Sci. Catal.*, 2006, 161
- 51 Domski, G.J., Rose, J.M., Coates, G.W., Bolig, A.D. and Brookhart, M., *Prog. Polym. Sci.*, 2007, 32: 30
- 52 Nomura, K., Naga, N., Miki, M., Yanagi, K. and Imai, A., *Organometallics*, 1998, 17: 2152
- 53 Nomura, K., Komatsu, T. and Imanishi, Y., *J. Mol. Catal. A*, 2000, 152: 249
- 54 Nomura, K., Tanaka, A. and Katao, S., *J. Mol. Catal. A*, 2006, 254: 197
- 55 Nomura, K., Komatsu, T. and Imanishi, Y., *Macromolecules*, 2000, 33: 8122
- 56 Byun, D.J., Fudo, A., Tanaka, A., Fujiki, M. and Nomura, K., *Macromolecules*, 2004, 37, 5520
- 57 Nomura, K., Naga, N., Miki, M. and Yanagi, K., *Macromolecules*, 1998, 31: 7588
- 58 Nomura, K., Oya, K., Komatsu, T. and Imanishi, Y., *Macromolecules*, 2000, 33: 3187
- 59 Nomura, K., Oya, K. and Imanishi, Y., *J. Mol. Catal. A*, 2001, 174: 127
- 60 Nomura, K., Fujita, K. and Fujiki, M., *J. Mol. Catal. A*, 2004, 220: 133
- 61 Nomura, K., Okumura, H., Komatsu, T. and Naga, N., *Macromolecules*, 2002, 35: 5388
- 62 Zhang, H. and Nomura, K., *J. Am. Chem. Soc.*, 2005, 127: 9364
- 63 Nomura, K., Itagaki, K. and Fujiki, M., *Macromolecules*, 2005, 38: 2053
- 64 Itagaki, K., Fujiki, M. and Nomura, K., *Macromolecules*, 2007, 40: 6489
- 65 Nomura, K. and Itagaki, K., *Macromolecules*, 2005, 38: 8121
- 66 Liu, J. and Nomura, K., *Macromolecules*, 2008, 41: 1070
- 67 Nomura, K., Wang, W. and Yamada, J., *Stud. Surf. Sci. Catal.*, 2006, 161: 123
- 68 Matsui, S., Mitani, M., Saito, J., Tohi, Y., Makio, H., Matsukawa, N., Takagi, Y., Tsuru, K., Nitabaru, M., Nakano, T., Tanaka, H., Kashiwa, N. and Fujita, T., *J. Am. Chem. Soc.*, 2001, 123: 6847
- 69 Xu, Z., Vanka, K. and Ziegler, T., *Organometallics*, 2004, 23: 10