Notable norbornene (NBE) incorporation in ethylene–NBE copolymerization catalysed by nonbridged half-titanocenes: better correlation between NBE incorporation and coordination energy†

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$CpTiCl_2(N{=}C^tBu_2)$ exhibits both remarkable catalytic activity and efficient norbornene (NBE) incorporation for ethylene–NBE copolymerization: the NBE incorporation by $Cp'TiCl_2(X)$ ($X = N{=}C^tBu_2$, O-2,6-$^iPr_2C_6H_3$; $Cp' = Cp$, C_5Me_5, indenyl) was related to the calculated coordination energy after ethylene insertion.

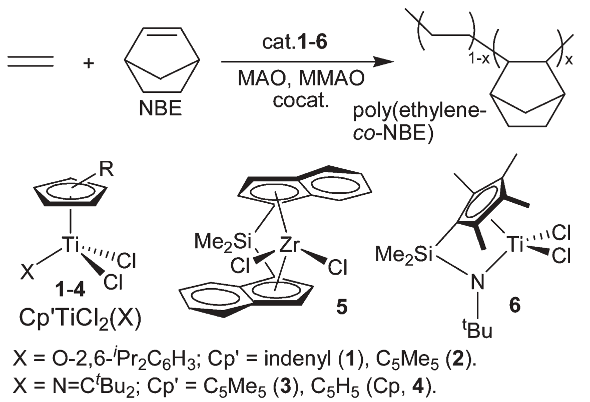
Cyclic olefin copolymers (COC) like poly(ethylene-*co*-norbornene)s attract considerable attention as amorphous materials with a promising combination of high transparency in the UV–Vis region and humidity as well as thermal resistance (high glass transition temperature, T_g).[1] It is known that both bridged zirconocenes and linked half-titanocenes showed high catalytic activities for ethylene–norbornene (NBE) copolymerization.[2–6] 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), have been limited.[7] This is not only because both the activity and molecular weights for the copolymer generally decrease upon increasing the NBE contents (as described below),[7] 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 of achieving repeated insertion of NBE. In this paper, we present that the efficient synthesis of high molecular weight random copolymer with high NBE content has been achieved for the first time by using reported *nonbridged* half-titanocene, $CpTiCl_2(N{=}C^tBu_2)$ (Scheme 1).[8,9]

Various half-titanocenes containing anionic donor ligands of the type, $Cp'TiCl_2(X)$ [$X = O$-2,6-$^iPr_2C_6H_3$; Cp′: indenyl (**1**), C_5Me_5 (Cp*, **2**); $X = N{=}C^tBu_2$; Cp′ = Cp* (**3**), Cp (**4**)], have been chosen, not only because **1** showed efficient NBE incorporation affording random copolymers,[6] but also because both Cp′ and the anionic donor ligand affected the comonomer incorporation, and the activity in the copolymerizations of ethylene with cyclohexene,[10a] 2-methyl-1-pentene (2M1P),[10b] styrene.[9b] $[Me_2Si(indenyl)_2]ZrCl_2$ (**5**) and $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**6**) were also chosen for comparison. The results in the presence of methylaluminoxane (MAO) cocatalyst are summarized in Table 1.[11]

The indenyl-aryloxo analogue (**1**) showed efficient NBE incorporation with high catalytic activity (run 2),[6a] however, both the activity and the M_n value decreased upon increasing the NBE content (run 3). The same trend was seen in the copolymerization using both bridged metallocene (**5**) and linked half-titanocene (**6**), as reported previously,[2–5] and the NBE incorporations were less efficient compared to **1** under the same conditions (runs 17–20).

The Cp*-aryloxo analogue (**2**) showed rather inefficient NBE incorporation compared with **1** (runs 5–6).[6] In contrast, the activity in the copolymerization by the Cp*-ketimide analogue (**3**) was higher than that in the ethylene polymerization (runs 8–9), whereas the NBE contents in the resultant copolymers by **3** were similar to those obtained with **2** under the same conditions (runs 7, 9). The observed results were an interesting contrast to those found in the copolymerization of ethylene with 2M1P,[10b] VCH,[10c] in which **2** showed better comonomer incorporation than **3**.

Note that $CpTiCl_2(N{=}C^tBu_2)$ (**4**) exhibited remarkable catalytic activities, and the activity did not decrease at least for 30 min (runs 12–14). The activity increased upon increasing the initial NBE concentration (runs 11–12), whereas the activities by the other catalysts decreased upon increasing the NBE concentration.[2–6,12] 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 neither the activities nor the NBE incorporations were strongly affected by the Al cocatalyst employed (MAO, MMAOs),[13] in complete contrast to the results reported for the copolymerization by $[Me_2Si(fluorenyl)(N^tBu)]TiMe_2$ in which both the catalytic activity and NBE incorporation were highly dependent upon the Al cocatalyst employed.[4c]



Scheme 1

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† Electronic supplementary information (ESI) available: General experimental procedure, ^{13}C NMR spectra for poly(ethylene-*co*-norbornene)s, DSC thermograms for selected poly(ethylene-*co*-NBE)s and plots of glass transition temperatures (T_g) *vs* NBE contents, results for geometry optimization for proposed catalytically-active species and energy evaluations. See DOI: 10.1039/b605005k

Table 1 Copolymerization of ethylene with norbornene (NBE) by Cp′TiCl$_2$(X) [X = O-2,6-^{i}Pr$_2$C$_6$H$_3$ and Cp′ = indenyl (**1**), Cp* (**2**); X = N=C^{t}Bu$_2$ and Cp′ = Cp* (**3**), Cp (**4**)], [Me$_2$Si(indenyl)$_2$]ZrCl$_2$ (**5**), [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (**6**)–MAO catalyst systems (ethylene 4 atm at 25 °C)[a]

Run	Cat. (μmol)	Time/min	NBE[b]/mmol mL^{-1}	Yield/mg	Activity[c]	M_n[d] × 10^{-4}	M_w/M_n[d]	NBE[e]/mol%
1	**1** (0.2)	10	—	232	6960	22.5	1.88	—
2	**1** (0.2)	10	0.2	350	10500	14.6	1.56	14.0
3	**1** (0.5)	10	1.0	192	2300	5.87	1.82	35.2
4	**2** (0.2)	10	—	280	8400	65.2	1.90	—
5	**2** (0.2)	10	0.2	218	6540	57.9	1.61	8.2
6	**2** (0.2)	10	1.0	88	2640	29.6	1.46	21.7
7	**3** (0.05)	10	—	164	19680	42.2	2.45	—
8	**3** (0.05)	10	0.2	264	31700	52.3	2.47	12.7
9	**3** (0.05)	10	1.0	185	22200	97.0	2.04	20.3
10	**4** (0.1)	10	—	98	5880	45.2	2.30	—
11	**4** (0.02)	10	0.2	72	21600	70.6	1.85	17.8
12	**4** (0.02)	10	1.0	134	40200	71.9	2.92	40.7
13	**4** (0.02)	20	1.0	401	60150	53.4	2.11	41.5
14	**4** (0.02)	30	1.0	597	59700	61.3	2.18	41.0
15	**4** (0.02)[f]	10	1.0	141	42300	35.5	2.42	41.8
16	**4** (0.02)[g]	10	1.0	168	50400	35.1	2.31	42.9
17	**5** (0.10)	10	0.2	481	28860	23.1	2.02	10.8
18	**5** (0.10)	10	1.0	81	4860	22.9	2.37	29.5
19	**6** (0.50)	10	0.2	205	2460	21.1	1.88	9.6
20	**6** (0.50)	10	1.0	167	2000	12.8	2.15	26.5

[a] Conditions: toluene + NBE total 50 mL, MAO white solid (prepared by removing AlMe$_3$, toluene from PMAO, MAO: methylaluminoxane) 3.0 mmol. [b] NBE concentration charged (mmol mL^{-1}). [c] Activity in kg-polymer per mol-Ti h. [d] GPC data in *o*-dichlorobenzene *vs* polystyrene standards. [e] NBE content (mol%) estimated by ^{13}C NMR spectra. [f] MMAO-3A-T (MMAO: modified methylaluminoxane), Me/^{i}Bu = 2.33, 3.0 mmol. [g] MMAO-3A-H, Me/^{i}Bu = 2.67, 3.0 mmol (as white solids prepared by removing AlMe$_3$, Al^{i}Bu$_3$ and solvent *in vacuo*).

Coordination energies (ΔE_{coord}) of ethylene (Et) and NBE to Ti(IV) cationic complexes ($\Delta E_{\text{coord}} = E_{\text{cation}} + E_{\text{monomer}} - E_{\pi\text{-complex}}$), Cp′Ti(X)(Y)$^+$ (Y = pentyl or 2-propyl-norbornyl), after insertion of previous monomers were calculated by PM3,[11] 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.[14] Both $\Delta E_{\text{coord}}{}^{\text{Et}}$ (coordination energy of ethylene) and $\Delta E_{\text{coord}}{}^{\text{NBE}}$ values are positive in all cases,[11] 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 the same conditions (ethylene 4 atm, NBE 0.20 mmol mL^{-1} at 25 °C) were observed (Fig. 1) except the indenyl analogue (**1**). These results suggest that the NBE incorporation is affected by the energetical preference of coordination between NBE and ethylene into the alkyl-cationic species.

Note that both the activity (by **4**) and the NBE contents in the copolymer increased at higher temperature (Table 2, runs 23–26, 40–80 °C),[11] and the resultant copolymers possessed large M_n values with unimodal molecular weight distributions (M_n = 3.38–6.20 × 10^5). The efficient synthesis of high molecular weight copolymer with high NBE contents (58.8–73.5 mol%) could be thus accomplished upon increasing the NBE concentration at low ethylene pressure (2 atm), and the activities by **4** were much higher than those by **1** under the same conditions (runs 19–20 *vs* runs 27–28). 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 27–29 *vs* runs 11–12), and the observed facts are significantly unique compared to those in the copolymerization, especially using ordinary metallocenes or linked half-titanocenes.[15] This may also be explained by the fact that **4** showed remarkable catalytic activity for NBE homopolymerization (run 30), and the activity was much higher than that reported by [Me$_2$Si(fluorenyl)(N^{t}Bu)]TiMe$_2$.[12,16]

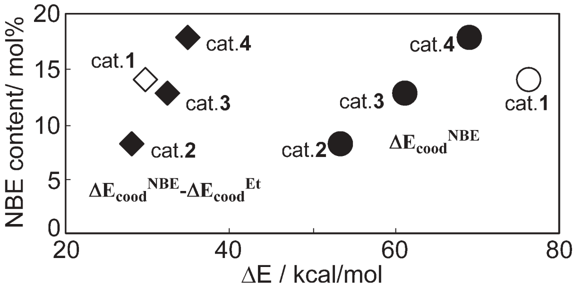

Fig. 1 Relationship between the NBE content *vs* coordination energy after ethylene insertion by PM3 calculation.[11]

Table 2 Ethylene–NBE copolymerization by **1**,**4**–MAO catalyst systems

Run	Cat (μmol)	E[b]/ atm	Temp./ °C	NBE[c]	Activity[d]	M_n[e] × 10^{-4}	M_w/ M_n[e]	NBE[f]/ mol%
3	**1** (0.5)	4	25	1.0	2300	5.87	1.82	35.2
19	**1** (1.0)[g]	2	25	2.5	678	3.91	1.58	58.8
20	**1** (5.0)[g]	2	25	5.0	126	0.78	2.42	60.1
12	**4** (0.02)	4	25	1.0	40200	71.9	2.92	40.7
23	**4** (0.02)	4	40	1.0	48900	62.0	2.37	45.9
24	**4** (0.02)	4	60	1.0	194000	47.5	2.20	51.2
25	**4** (0.02)	4	60	1.0	173400	45.3	2.24	
26	**4** (0.02)	4	80	1.0	133000	33.8	2.34	61.7
27	**4** (0.01)[g]	2	25	2.5	90000	32.3	2.09	58.8
28	**4** (0.01)[g]	2	25	5.0	85800	34.0	2.00	65.8
29	**4** (0.02)[g]	2	25	10.0	31500	44.4	2.01	73.5
30	**4** (0.1)[g]	—	25	0.5	9540	Insoluble[h]		100

[a] Conditions: toluene + NBE total 50 mL, MAO (prepared by removing AlMe$_3$ and toluene from PMAO) 3.0 mmol, 10 min (run 25, 20 min). [b] Ethylene. [c] NBE concentration charged (mol L^{-1}). [d] Activity in kg-polymer per mol-Ti h; [e] GPC data in *o*-dichlorobenzene *vs* polystyrene standards. [f] NBE content (mol%) estimated by ^{13}C NMR spectra. [g] Conditions: toluene + NBE total 10 mL. [h] Insoluble in THF for GPC measurement.

^{13}C NMR spectra for poly(ethylene-*co*-NBE)s showed that the microstructures formed using **5**,**6** possessed few NBE repeat units and contained both *meso* and *racemo* alternating ethylene–NBE sequences as well as isolated NBE units (33.0–33.5 ppm), and a tiny trace of NBE dyads was also observed.[11] In contrast, resonances ascribed to NBE dyads were observed for the copolymers prepared by **1** and **4**, and the microstructures thus possessed a mixture of NBE repeat units (including dyads, triads) in addition to the alternating, isolated NBE sequences.[11] The observed results may be suited as an appropriate explanation for the observed difference in the NBE incorporation. Moreover, the amount of alternating sequences formed using **4** was lower than that using **1**, 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.[6b] The DSC thermograms[11] for resultant copolymers prepared by **4** possessed single T_g and the T_g values increased linearly upon increasing the NBE content,[11,14] strongly suggesting that the resultant copolymer possessed uniform NBE incorporation.

We have shown that efficient synthesis of poly(ethylene-*co*-NBE)s with both high molecular weights and high NBE content has been achieved for the first time by the **4**–MAO catalyst system, and that the catalyst is robust even at higher temperatures. Since **4** showed negligible cyclohexene incorporation in ethylene–cyclohexene copolymerization, there appears no clear reason at this moment why **4** should show efficient NBE incorporation. One possible explanation is that **4** possesses the highest $\Delta E_{\mathrm{coord}}{}^{\mathrm{NBE}}$ value after NBE insertion among **1–4**, which may suggest that repeated NBE coordination (insertion) is preferred.[11] We are now exploring this in more detail, and results will be available in the near future.

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7 Some reports were known for synthesis of poly(ethylene-*co*-NBE)s with high NBE contents,[1,2d,e,3b,d,4c,5c,6a] in particular, [Me_2Si-(fluorenyl)(N^tBu)]$TiMe_2$ showed efficient NBE incorporation affording the copolymers with high NBE contents.[4c] However, the catalytic activities were low and both the activities and NBE contents were highly affected by the cocatalyst employed.

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11 Experimental procedures, ^{13}C NMR spectra for poly(ethylene-*co*-NBE)s, selected DSC thermograms and plots of glass transition temperatures vs NBE contents, results for geometry optimizations and energy evaluations for proposed catalytically-active species in the copolymerization [equilibrium geometry at ground state with semi-empirical PM3, geometry optimization, RHF/PM3D Spartan '04 for Windows (Wavefunction Inc.)], estimation of coordination energies by the PM3 calculation, see the Electronic Supplementary Information†. ^{13}C NMR spectra for poly(ethylene-*co*-NBE) prepared by **5**–MAO catalyst were also shown in the Supporting Information in a previous paper[6a].

12 It is known that the activity by [Me_2Si(fluorenyl)(N^tBu)]$TiMe_2$ in the copolymerization increased at higher NBE/ethylene molar ratios, because this catalyst exhibited catalytic activities for NBE homopolymerization (activity in toluene at 20 °C = 1087 kg-PNBE per mol-Ti h, NBE 1.2 mmol mL^{-1}).[4c] (*a*) T. Hasan, K. Nishii, T. Shiono and T. Ikeda, *Macromolecules*, 2002, **35**, 8933; (*b*) T. Hasan, K. Nishii, T. Shiono and T. Ikeda, *Macromolecules*, 2004, **37**, 7432.

13 MMAO-3A-T ($Me/^iBu = 2.33$), MMAO-3A-H ($Me/^iBu= 2.67$) were used as cocatalysts to compare the effect of cocatalyst, because both the activity and NBE incorporation by [Me_2Si(fluorenyl)(N^tBu)]-$TiMe_2$ were strongly affected by the Al cocatalyst employed[4c].

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15 Glass transition temperatures (T_g) for poly(ethylene-*co*-NBE)s prepared by **4**–MAO catalyst, are 124, 185, 202, 214 °C with the NBE contents of 51.2 (run 24), 58.8 (run 27), 65.8 (run 28), 73.5 mol% (run 29), respectively. A liner relationship between the Tg values and NBE contents in the copolymer was observed, and the results are shown in the Electronic Supplementary Information†.

16 The resultant poly(NBE) was hardly soluble in THF for GPC measurement, but was confirmed as the polymer prepared by vinyl addition polymerization. The reason why the copolymerization showed higher catalytic activities than those in ethylene, NBE homopolymerizations is not clear at this moment.