Electronic Supplementary Information

Notable Norbornene (NBE) Incorporation in Ethylene/NBE Copolymerisation Catalyzed by Nonbrided Half-Titanocenes: Better Correlation between NBE Incorporation and Coordination Energy

Kotohiro Nomura,* Wei Wang, Michiya Fujiki, and Jingyu Liu

Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST), 8916-5 Takayama, Ikoma, Nara 630-0101, Japan

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*Corresponding Author, tel.: +81-743-72-6041, fax: +81-743-72-6049, e-mail: nomurak@ms.naist.jp
1. Experimental

1.1 General Procedure.

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. Anhydrous grade of toluene (Kanto Kagaku Co. Ltd) was transferred into a bottle containing molecular sieves (mixture of 3A and 4A 1/16, and 13X) in the drybox, and was used without further purification. Norbornene (NBE) of reagent grade (Aldrich) was stored in the drybox, and was used without further purification. Syntheses of (indenyl)TiCl2(O-2,6-iPr2C6H3) (1), Cp*TiCl2(O-2,6-iPr2C6H3) (2), Cp*TiCl2(N=CtBu2) (3), and CpTiCl2(N=CtBu2) (4) were according to the previous reports. Toluene and Me3Al in the commercially available methylaluminoxane [PMAO-S, 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.] were taken to dryness under reduced pressure (at ca. 50 ºC for removing toluene, Me3Al, and then heated at >100 ºC for 1 h for completion) in the drybox to give white solids. Other MMAO samples such as MMAO-3A-T (Me/iBu= 2.33), MMAO-3A-H (Me/iBu= 2.67) were supplied from Tosoh Finechem Co., and were used as the white solid after removing solvent and AlMe3, AliBu3 in vacuo according to the analogous procedure as that in PMAO-S except that the resultant solid was re-dissolved in toluene and then removed in vacuo to remove Al'iBu3 completely.

All 1H and 13C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, 1H). All deuterated NMR solvents were stored over molecular sieves under nitrogen atmosphere, and all chemical shifts are given in ppm and are referenced to Me4Si. 13C NMR spectra for polymers were recorded on a JEOL JNM-LA400 spectrometer (100.40 MHz, 13C) with proton decoupling. The pulse interval was 5.2 sec, the acquisition time was 0.8 sec, the pulse angle was 90º, and the number of transients accumulated was ca. 6000-7000. The analysis samples of copolymers were prepared by dissolving polymers in a mixed solution of 1,2,4-trichlorobenzene/ benzene-d6 (90/10 wt) and the spectrum was measured at 110 ºC. The NBE1,4,5 contents in the resultant copolymers were estimated by the 13C NMR spectra of copolymer according to the previous reports.

Molecular weight and molecular weight distribution for polymers were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with polystyrene gel column (TSK gel GMHHR-H HT × 2, 30 cm × 7.8 mmø ID), ranging from <102 to < 2.8×108 MW) at 140 ºC using o-dichlorobenzene containing 0.05 wt/v% 2,6-di-tert-butyl-p-cresol as solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

Geometry optimisations and the energy evaluations for proposed catalytically-active species in the copolymerisation were performed by semi-empirical PM3 [equilibrium geometry at ground state with semi-empirical PM3, geometry optimisation, RHF/PM3D Spartan ‘04 for Windows (Wavefunction Inc.)], and ΔEcoord’s were calculated as the difference in energy between the
optimised $\pi$-complex on one hand and the cationic complex and the monomer on the other hand, namely $\Delta E_{\text{coord}} = E_{\text{cation}} + E_{\text{monomer}} - E_{\pi\text{-complex}}$.

1.2 Ethylene polymerisation, ethylene/norbornene copolymerisation.

Typical reaction procedure for copolymerisation of ethylene with cycloolefin (Table 1, run 12) is as follows. Toluene (49.0 mL), MAO solid 174 mg (3.0 mmol), and norbornene (50 mmol, 4708 mg) were added into the autoclave (100 mL scale, stainless steel) under stirring in the box. The reaction apparatus was then filled with ethylene at 25 ºC. A toluene solution (1.0 mL) containing 4 (0.02 $\mu$mol) was then added into the autoclave, and the reaction apparatus was then immediately pressurized to 3 atm (total 4 atm). The mixture was magnetically stirred for 10 min, the ethylene remaining was purged after reaction, and the mixture was then poured into MeOH (50 mL) containing HCl (5 mL). The resultant polymer was collected on a filter paper by filtration, and was adequately washed with MeOH, and was then dried in vacuo for several hours. Ethylene polymerisation was performed similarly in the absence of norbornene.

References

2. $^{13}$C NMR spectra for poly(ethylene-<i>co</i>-norbornene)s.

Run 2, by (Ind)TiCl$_2$(O-2,6-$^6$Pr$_3$C$_6$H$_3$) (1), NBE14.0 mol%.

Run 3, by (Ind)TiCl$_2$(O-2,6-$^6$Pr$_3$C$_6$H$_3$) (1), NBE 35.2 mol%.
Run 19,
by (Ind)TiCl$_2$(O-2,6-$^t$Pr$_2$C$_6$H$_3$) (I),
NBE 58.8 mol%.

Run 20,
by (Ind)TiCl$_2$(O-2,6-$^t$Pr$_2$C$_6$H$_3$) (I),
NBE 60.1 mol%. 
Run 5, by Cp*TiCl₂(O-2,6-iPr₂C₆H₃) (2), NBE 8.2 mol%.

Run 6, by Cp*TiCl₂(O-2,6-iPr₂C₆H₃) (2), NBE 21.7 mol%.
Run 8, by $\text{Cp}^*\text{TiCl}_2(\text{N}=\text{C}^\text{Bu}_2)$ (3), NBE 12.7 mol%.

Run 11, by $\text{CpTiCl}_2(\text{N}=\text{C}^\text{Bu}_2)$ (4), NBE 17.8 mol%.

Run 12, by $\text{CpTiCl}_2(\text{N}=\text{C}^\text{Bu}_2)$ (4), NBE 40.7 mol%.
Run 23, by CpTiCl$_2$(N=C'Bu$_2$) (4), NBE 45.9 mol%.

Run 24, by CpTiCl$_2$(N=C'Bu$_2$) (4), NBE 51.2 mol%.

Run 26, by CpTiCl$_2$(N=C'Bu$_2$) (4), NBE 61.7 mol%.
Run 27,
by CpTiCl$_2$(N=C′Bu$_2$) (4),
NBE 58.8 mol%.

Run 28,
by CpTiCl$_2$(N=C′Bu$_2$) (4),
NBE 65.8 mol%.

Run 29,
by CpTiCl$_2$(N=C′Bu$_2$) (4),
NBE 73.5 mol%.
\(^{13}\)C NMR spectra for poly(ethylene-co-NBE)s prepared by 1,4-6 MAO catalysts. NBE contents: a) 35.2 mol\% (by 1, run 3), b) 40.7 mol\% (by 4, run 12), c) 29.5 mol\% (by 5, run 18), d) 26.5 mol\% (by 6, run 20). Conditions: ethylene 4 atm, NBE 1.0 mmol/mL in toluene, at 25 °C (Table 1).
3. DSC thermograms for poly(ethylene-co-NBE)s prepared by CpTiCl$_2$(N=C'Bu$_2$) (4) - MAO catalyst, and plots of glass transition temperature ($T_g$) vs NBE contents.
Plots of $T_g$ vs NBE contents. ♦: plots of glass transition temperatures vs NBE contents for poly(ethylene-co-NBE)s prepared by (aryloxo)(cyclopentadienyl)titanium complexes - MAO catalysts (cited from K. Nomura et al. *Macromolecules* 2003, 36, 3797-3799.). ○: plots of glass transition temperatures vs NBE contents for poly(ethylene-co-NBE)s prepared by CpTiCl$_2$(N=C$^\prime$Bu$_2$) - NBE catalysts.
4. Optimised geometries for proposed catalytically-active species in the copolymerisation. Optimized structures by semi-empirical PM3 [(RHF/PM3D Spartan Pro '04 for Windows (Wavefunction Inc.))]

**Optimized geometry for Cp**\(^\star\)**Ti(C\(_5\))(OAr)(NBE2)**
\[\Delta E_{\text{coord}}^E = 52.964 \text{ kcal/mol}\]
\[\Delta E_{\text{NBE}}-\Delta E_{\text{Et}} = 27.526 \text{ kcal/mol}\]

**Optimized geometry for Cp**\(^\star\)**Ti(C\(_5\))(OAr)(E)**
\[\Delta E_{\text{coord}}^E = 25.438 \text{ kcal/mol}\]

**Optimized geometry for (Ind)**\(^\star\)**Ti(C\(_5\))(OAr)(NBE1)**
\[\Delta E_{\text{coord}}^E = 73.184 \text{ kcal/mol}\]
\[\Delta E_{\text{NBE}}-\Delta E_{\text{Et}} = 28.536 \text{ kcal/mol}\]

**Optimized geometry for (Ind)**\(^\star\)**Ti(C\(_5\))(OAr)(NBE2)**
\[\Delta E_{\text{coord}}^E = 76.362 \text{ kcal/mol}\]
\[\Delta E_{\text{NBE}}-\Delta E_{\text{Et}} = 29.764 \text{ kcal/mol}\]

\(E = \text{ethylene, NBE = norbornene, } C_5 = \text{penty1, OAr = O-2,6-Pr}_2-C_6H_3, \text{Cp}^\star = C_5Me_5\)

\(\text{Ind = Indenyl}\)
Optimized geometry for 
\(\text{Cp}^*\text{Ti(C}_5\text{)(Ket)(NBE2)}\)

\[\Delta E_{\text{coord}}^E = 60.780 \text{ kcal/mol}\]

\[\Delta E_{\text{NBE}} - \Delta E_{\text{Et}} = 31.908 \text{ kcal/mol}\]

\(E = \text{ethylene},\)
\(\text{NBE} = \text{norbornene}\)
\(C_5 = \text{pentyl},\)
\(\text{Ket} = \text{N=C\text{t}Bu}_2\)
\(\text{Cp}^* = \text{C}_5\text{Me}_5\)

Optimized geometry for 
\(\text{Cp}^*\text{Ti(C}_5\text{)(Ket)(NBE1)}\)

\[\Delta E_{\text{coord}}^E = 61.187 \text{ kcal/mol}\]

\[\Delta E_{\text{NBE}} - \Delta E_{\text{Et}} = 32.315 \text{ kcal/mol}\]

Optimized geometry for 
\(\text{CpTi(C}_5\text{)(Ket)(E)}\)

\[\Delta E_{\text{coord}}^E = 28.872 \text{ kcal/mol}\]

Optimized geometry for 
\(\text{CpTi(C}_5\text{)(Ket)(NBE2)}\)

\[\Delta E_{\text{coord}}^E = 69.062 \text{ kcal/mol}\]

\[\Delta E_{\text{NBE}} - \Delta E_{\text{Et}} = 34.897 \text{ kcal/mol}\]

Optimized geometry for 
\(\text{CpTi(C}_5\text{)(Ket)(NBE1)}\)

\[\Delta E_{\text{coord}}^E = 68.588 \text{ kcal/mol}\]

\[\Delta E_{\text{NBE}} - \Delta E_{\text{Et}} = 34.423 \text{ kcal/mol}\]

Optimized geometry for 
\(\text{CpTi(C}_5\text{)(Ket)(E)}\)

\[\Delta E_{\text{coord}}^E = 34.165 \text{ kcal/mol}\]

E = ethylene, 
NBE = norbornene 
C\(_5\) = pentyl, 
Ket = N=C\text{t}Bu\(_2\)

Optimized geometry for 
\(\text{Cp}^*\text{Ti(C}_5\text{)(Ket)(NBE2)}\)

\[\Delta E_{\text{coord}}^E = 69.062 \text{ kcal/mol}\]

\[\Delta E_{\text{NBE}} - \Delta E_{\text{Et}} = 34.897 \text{ kcal/mol}\]
Summary for coordination energies for optimised structures by semi-empirical PM3
[(RHF/PM3D Spartan Pro ’04 for Windows (Wavefunction Inc.))]

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<th>$\Delta E_{\text{coord}}^{\text{Et}}$</th>
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<td><strong>after NBE insertion</strong></td>
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