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Living ethylene/norbornene copolymerisation catalyzed by titanium complexes having two pyrrolide-imine chelate ligands†

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Ethylene/norbornene copolymerisation behaviour of titanium complexes with two pyrrolide-imine chelate ligands is described.

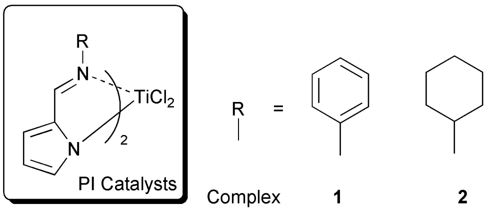
The increased interest in the development of new polymers using well-defined transition metal complexes has resulted in the introduction of a variety of high performance polymers such as syndiotactic polystyrene (sPS), ethylene/styrene interpolymers (ESI), elastomeric polypropylene, and cyclic olefin copolymers (COC).[1–3]‡ Among these polymers, COC is one of the most important engineering plastics which possess high thermal stability and excellent optical properties (*e.g.*, high transparency and high refractive indices), and is thus used in heat-resistant and optical applications. COC can be produced by the copolymerization of cyclic olefins such as norbornene (NB) with ethylene or α-olefins using various transition-metal based catalysts (*e.g.*, vanadium catalysts and group 4 metallocene catalysts). Until now, a number of high performance catalysts for the production of COC have been developed.[4,5] There are, however, only a few examples of catalysts (Tritto and coworkers[6] and Cherdron *et al.*[4b]) that form COC in a living fashion.

Previously, we have described a strategy to develop new olefin polymerisation catalysts on the basis of non-symmetric bidentate ligands having moderate electron donating properties combined with transition metals.[7] This approach has led to the discovery of high performance olefin polymerisation catalysts based on phenoxy-imine,[8,9] indolide-imine,[10] phenoxy-pyridine,[11] or pyrrolide-imine[12,13] ligands combined with group 4 transition metal centres. In this paper, we describe the unique catalytic properties of titanium complexes bearing two pyrrolide-imine chelate ligands, denoted PI Catalysts. These catalysts promote living copolymerisation of ethylene with NB to produce high molecular weight copolymers (COC) with extremely narrow molecular weight distributions.

The titanium complexes (Scheme 1) employed in this study are $[2\text{-}(PhNCH)C_4H_3N]_2TiCl_2$ (complex **1**) and $[2\text{-}(CyNCH)C_4H_3N]_2TiCl_2$ (complex **2**), which were synthesised according to the procedure reported in our previous paper.[12]

Ethylene/NB copolymerisations were carried out with complexes **1** and **2** using methylalumoxane (MAO) as a cocatalyst at 25 °C under atmospheric pressure. The polymerisation results are summarised in Table 1. Complexes **1** and **2** displayed very high activities (complex **1**; 576 kg polymer mol complex^{-1} h^{-1}, complex **2**; 2730 kg polymer mol complex^{-1} h^{-1}) and produced amorphous polymers (Tg: entry 1; 130 °C, entry 2; 120 °C).§ Microstructural analyses using ^{13}C NMR spectroscopy[4j] suggest that the polymers are ethylene/NB copolymers produced *via* vinyl-type polymerisation, with NB contents of 48.6 mol% (complex **1**) and 44.5 mol% (complex **2**), respectively. The distributions of the NB incorporated in the copolymers reveal that the catalyst systems show a very high propensity to yield alternating copolymers [complex **1**; alternating part (–NB–ethylene–*NB*–ethylene–NB–): 91%, isolated part (–ethylene–*NB*–(ethylene)$_n$–; $n \geqslant 2$): 9%, complex **2**; alternating part: 91%, isolated part: 9%] (Fig. 1).¶ These practically alternating copolymers contain similar amounts of *meso* and *racemic –NB–*ethylene–*NB*– sequences (Table 1, entry 1; *meso/racemic* = 54.9/45.1, entry 2; *meso/racemic* = 53.8/46.2), indicating that the alternating part in the copolymers are practically atactic though the catalyst precursor possesses C_2 symmetry. Thus, the microstructures of the copolymers arising from complexes **1** and **2** resemble that formed with the C_s constrained geometry catalyst, $Me_2Si(Me_4Cp)(NBu^t)TiCl_2$,[4i] which provides stereoirregular alternating copolymers.

GPC analyses reveal that the copolymers possess very high molecular weights (M_n) of 127000 (complex **1**) and 521000 (complex **2**), respectively. However, more significantly, the copolymers have extremely narrow molecular weight distribu-



Scheme 1

Table 1 Ethylene/NB copolymerisation results with complexes **1** and **2**

Entry	Complex	Gas: C_2H_4/N_2/L h^{-1}	Time/min	Charged NB/g	Yield/mg	Activity[a]	M_n[b]	M_w/M_n[b]	NB content[c]/mol%	T_g[d]/°C
1	**1**	50/0	10	10	96	576	127000	1.10	48.6	130
2	**2**	50/0	10	10	455	2730	521000	1.16	44.5	120
3	**1**	0/50	20	10	0	0	—	—	—	—
4	**2**	0/50	20	10	0	0	—	—	—	—
5	**1**	100/0	5	0	500	6000	30000	2.21	0	—
6	**2**	2/100	10	0	18	106	50000	2.90	0	—

Conditions: 25 °C, atmospheric pressure, complex: 1 μmol, cocatalyst; MAO (purchased from Albemarle) 1.25 mmol as Al, toluene 250 mL.[a] kg polymer (mol-complex)$^{-1}$ h^{-1}. [b] M_n and M_w/M_n values were determined by GPC, equipped with refractive index (RI) detector, by using polystyrene calibration (entries 1 and 2) or polyethylene calibration (entries 5 and 6). [c] NB contents were determined by ^{13}C NMR. [d] T_g measured by DSC.

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† Electronic supplementary information (ESI) available: general procedures and materials, ligand and complex syntheses and analyses, polymerisation procedure, polymer analyses, ^{13}C NMR spectra for polymers (entries 1 and 2). See http://www.rsc.org/suppdata/cc/b2/b202391a/

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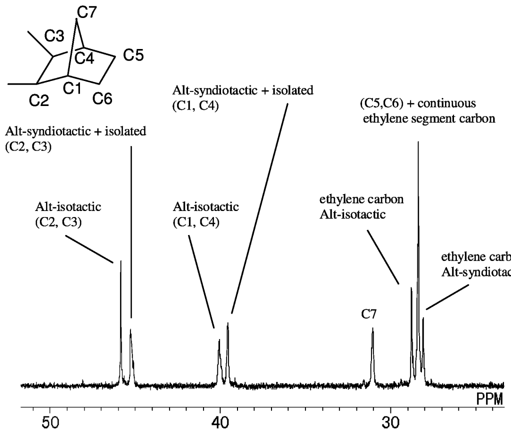

Fig. 1 ^{13}C NMR spectrum for the ethylene/NB copolymer prepared by complex **2**/MAO (entry 2).

tions (M_w/M_n; 1.10, 1.16). The M_w/M_n values suggest that complexes **1** and **2**/MAO catalyst systems may have the characteristics of a living ethylene/NB copolymerisation under the conditions employed.

The plots of M_n and M_w/M_n as a function of polymerisation time are shown in Fig. 2. The M_n increased proportionally with the polymerisation time while the narrow M_w/M_n (complex **1**; M_w/M_n 1.07–1.15, complex **2**; M_w/M_n 1.07–1.25) was retained for each case, which indicates that the copolymerisations are living. To our knowledge, these are the first examples of non-metallocene catalysts which initiate living ethylene/NB copolymerisations to furnish monodisperse COC with very high molecular weights (Max. M_n 800000). Considering that the MAO used as the cocatalyst is a potential chain transfer agent, the room-temperature living copolymerisations exhibited by complexes **1** and **2** are highly significant. The M_n value, 800000, represents one of the highest molecular weights among COCs ever known. It is obvious that the presence of NB in the reaction medium and/or in the polymer chain is a requirement for living copolymerisation since complexes **1** and **2** promote neither ethylene nor NB polymerisation in a living fashion (entries 3–6). Preliminary DFT calculations suggest that the steric obstacle derived from an inserted NB near the metal centre suppresses chain termination or transfer steps (*e.g.*, β-H elimination and chain transfer to a cocatalyst) regarding the complexes employed.‖

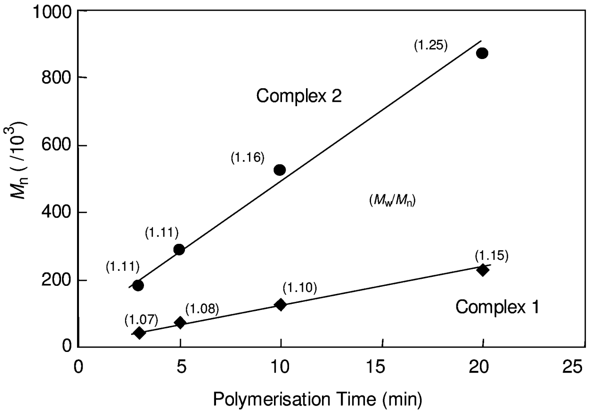

Fig. 2 Plot of M_n as a function of polymerisation time for the copolymerisation of ethylene/NB with complexes **1** and **2**/MAO at 25 °C.

Detailed mechanistic studies together with the synthesis of COC with novel architectures are underway.

In summary, ethylene/NB copolymerisation behaviour of titanium complexes with two pyrrolide-imine chelate ligands, denoted PI Catalysts, has been introduced. These complexes combined with MAO are capable of promoting room-temperature living copoplymerisation of ethylene with NB to form very high molecular weight copolymers having extremely narrow molecular weight distributions with high activities. The results described herein along with our previous reports[12] indicate that PI Catalysts have high potential for the production of polymers which are difficult or impossible to prepare using conventional Ziegler–Natta catalysts.

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Notes and references

‡ COC is commercially available from Mitsui Chemicals (APEL™) and Ticona (TOPAS™).

§ Under the same conditions, Cp_2ZrCl_2 did not produce any polymers, indicating that complexes **1** and **2** possess high potential for the copolymerisation of ethylene with NB.

¶ The –NB–NB– sequences are not detected in the NMR for copolymers produced by complexes **1** and **2**.

‖ The possibility cannot be ruled out that the active species are different between ethylene homopolymerisation (non-living type active species) and ethylene/NB copolymerisation (living type active species). Several stereoisomers of the complexes can exist as a consequence of different binding geometries of the two non-symmetric ligands.

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