Synthesis of aryloxide-containing half-titanocene catalysts grafted to soluble polynorbornene chains and their application in ethylene polymerization: Integration of multiple active centres in a random coil

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A series of monodisperse polynorbornene (PNB) chains bearing different contents of aryloxide ligands at their side chain were synthesized by Grubbs ring-opening metathesis copolymerization between norbornene and 2-aryloxonorbornene. These PNB chains were employed as a soluble support for grafting half-titanocene complexes to afford structurally well-defined supported catalysts, where a pre-defined number of Ti centres was confined in a nano-sized random coil of PNB chains. Extensive investigation in ethylene polymerization revealed unique catalytic features of these soluble polymer-supported catalysts, represented by a synergistic activity enhancement among multiple active centres confined in a random coil. The well-defined nature of these novel polymer-supported catalysts is powerful in studying interactions between active centres and supports as well as among active centres themselves in catalysis.

1. Introduction

Catalysts, which are the integral component of most of the modern chemical processes, can be categorized into two primary classes: Molecular catalysts and solid catalysts. The former class corresponds to small molecules, including transition metal complexes. They are soluble and featured with the advantage of tailor-made performance by a variety of metal-ligand combinations [1–2]. Moreover, integrated knowledge of organic and organometallic chemistry enables the precise bottom-up design of active site structures for a superior activity and selectivity. This is exemplified by the success story of C—C cross coupling reactions, olefin metathesis/polymerization reactions, asymmetric synthesis and so on [3–9]. To the other extreme, solid catalysts utilize coordinative unsaturation created on solid surfaces [10]. In general, they are cheap, separable, reusable and thermally robust, which make them suitable for industrial applications. The most notable applications include oil refineries, production of fine chemicals, automotive catalytic converters, industrial polyolefin productions, conversion of biomass into fuels and chemicals, green and sustainable chemical transformations and so on [11–17]. Solid catalysts offer the advantage of the integration of multi-components over multi-length scales for the accumulation of multiple functions

[18]. Whereas, their inherent chemical and structural complexities lead to ill-defined characteristics, which are hardly controlled based on conventional top-down design, resulting in inferior catalytic selectivity. Thus, the contrast of the characteristics encourages the catalyst community to focus on new concepts so as to bridge the gap between molecular and solid catalysts. An illustration is the "International Symposium on Relations between Homogeneous and Heterogeneous Catalysis", which already has accomplished seventeen successful meetings [19].

In the field of olefin polymerization, the above-mentioned bridging concept has been long regarded as an important subject in both academy and industry, as accounted by the industrial relevance of both the classical solid catalysts and the tailored molecular catalysts in the production of distinct grades of polyolefins [20–23]. In this regard, different approaches have been developed for the establishment of a "bridging" catalyst. One of these approaches is from the side of solid catalysts, especially based on surface organometallic chemistry [24,25]. A uniform active site structure is constructed on solid surfaces through precise control of each reaction occurring between an organometallic complex and support (*e.g.* silica) surfaces. Characterization of the supported complex gives molecular insight of the identity and behaviour of model catalytic species, thus being powerful to study structure-performance relationships of solid catalysts. Another approach is based on supported molecular catalysts [26–28], which aims to transfer the distinguished features of the molecular catalysts to

existing plants. For this purpose, a molecular catalyst is grafted to a solid support such as silica or cross-linked polystyrene by replacing one of its ligands with a similar ligand that is covalently bonded to the support *via* a linker. Here, the solid support mitigates reactor fouling during polymerization and the use of a linker helps to retain the single-site nature of the molecular catalyst on solid surfaces. Further successes have been brought by immobilizing two types of molecular catalysts (tandem catalysis) on a single support. Representatively, a macromonomer forming site and a stereoselective polymerization site are co-supported on a solid surface for the *in-situ* production of long-chain branched polypropylene, which had been hardly achieved by conventional catalysts [29]. Function integrations have also been achieved in a class of binuclear molecular catalysts by the cooperation between two proximate metal centres present in a binuclear complex [30]. In the pioneering research of Marks et al., a series of constrained geometry based homo and hetero binuclear molecular catalysts were synthesized, and their synergistic combination with a binuclear cocatalyst was explored [30–32]. In these binuclear catalysts, cooperation between two metal centres *via* secondary agostic interaction significantly influenced the monomer enchainment and the chain transfer kinetics, which in turn led to unique catalytic consequences such as higher activity, enhanced branching, higher α-olefin incorporation, and molecular weight increment as compared to their mononuclear analogues. Most notably, the binuclear catalysts have embodied catalytic multifunctionality at a molecular precision, even though the synthetic limitation restricts the number of nuclei, *i.e.* the number of functions, integrable in a single molecule. The integration on solid surfaces would not have such limitation, but combination over two molecular catalysts have not been realized to the best of our knowledge. Thus, a concept to embody catalytic multifunctionality on the basis of well-defined structural features is an important direction to design a bridging catalyst in the field of olefin polymerization.

Based on the above discussions, here we provide another option of bridging catalysts for olefin polymerization: Polynorbornene (PNB) with uniform chain length and bearing ancillary donor ligands at side chain was synthesized by Grubbs ring-opening metathesis polymerization (ROMP) [33,34], and used as a soluble support for a molecular catalyst. Such a supported catalyst equips well-defined characteristics in terms of active site design analogous to the molecular catalyst as well as controlled active site density in a random coil of a single polymer chain, whose size is defined by the Flory radius. Moreover, potential synergy among neighboring active sites confined in a random coil would help to accumulate functionality in an unrestricted way.

There have been a few examples in literature, in which chain-end or side-chain functionalized linear/star shaped PNB was used as a support for molecular catalysts and employed in organic transformations, where performance similar to the molecular catalyst was obtained [35–39]. In addition, the solubility of PNB can be exploited to perform catalysis under homogeneous conditions in a good solvent and recycle the catalyst by recovering it through reprecipitaion in a poor solvent. Nomura and co-workers immobilized half-titanocene complexes at the chain end of PNB through aryloxide ligands and employed the resultant catalysts in ethylene (co)polymerization [40]. These catalysts showed similar performance to the molecular analogues in terms of the molecular weight, molecular weight distribution and comonomer incorporation. These previous studies established PNB as a promising support for molecular catalysts, but exploration of support-mediated catalytic multifunctionality by confining multiple active centres in the random coil of soluble and well-defined PNB has been scarcely studied, especially in olefin polymerization.

In the present contribution, we have synthesized a norbornene derivative containing an aryloxo pendant group by a Pd-catalysed reductive Heck-coupling reaction, followed by its copolymerization with norbornene. A series of well-defined PNB supports were synthesized with different comonomer contents and utilized to graft half-titanocene complexes [41]. The synthetic methodologies and the potential synergy among multiple active centres confined in a random coil were discussed.

2. Experimental

2.1. Materials

All commercially available reagents were of a research grade and used without further purification unless specified. Bicyclo[2.2.1]hepta-2,5-diene (norbornadiene), 4-bromo-2,6-dimethyphenol, bis(triphenylphosphine)palladium(II) dichloride (Pd(PPh$_3$)$_2$Cl$_2$), bicyclo[2.2.1]hept-2-ene (norbornene), 2,6-dimethylphenol, pentamethylcyclopentadienyltitanium (IV) trichloride (Cp*TiCl$_3$), and trityl tetrakis(pentafluorophenyl)borate (Ph$_3$CB(C$_6$F$_5$)$_4$) were purchased from Tokyo Chemical Industry. Ammonium formate (NH$_4$HCO$_2$), the Grubbs 1 st generation catalyst, and ethyl vinyl ether were purchased from Sigma-Aldrich. Triethylamine (Kanto Chemical) was purified by distillation under reduced pressure. *N,N*-dimethylformamide (DMF, Wako Pure Chemical Industries) was dried over molecular sieves 4A and N$_2$ bubbling. Trimethyl pentamethylcyclopentadienyltitanium (IV) (Cp*TiMe$_3$) was purchased from Strem Chemicals. Modified methylaluminoxane (MMAO) and tri-*iso*-butylaluminum (TIBA) were donated by Tosoh Finechem. Ethylene of a research grade was donated by Sumitomo Chemical and used as delivered. Dichloromethane (CH$_2$Cl$_2$) and toluene of an anhydrous grade (Sigma-Aldrich and Wako Pure Chemical Industries) were used for the synthesis of PNB supports and catalysts. They were further dehydrated over molecular sieves 3A and 4A, respectively, in Teflon sealed flasks and bubbled with N$_2$ prior to use. Diethyl ether of an anhydrous grade was purchased from Tokyo Chemical Industry and degassed before use. Toluene (Kanto Chemical) for polymerization was stored in a pressurized tank after being passed through a column of molecular sieves 4A and bubbled with N$_2$. Deuterated chloroform (CDCl$_3$, Kanto Chemical) was stored over molecular sieves 3A in a Teflon sealed schlenk tube and degassed before use.

2.2. Measurements

All ^{1}H and ^{13}C {^{1}H} NMR spectra were recorded on a 400 MHz Bruker Advance spectrometer in CDCl$_3$ at 25 °C and all chemical shifts were given in ppm. The residual peak of CHCl$_3$ at 7.26 ppm and the peak of CDCl$_3$ at 77.16 ppm were used as reference in the ^{1}H and ^{13}C NMR, respectively. The number-average molecular weight (M_n), weight-average molecular weight (M_w) and the polydispersity index (M_w/M_n) of PNB supports were determined by gel permeation chromatography (GPC, Shimadzu SCL-10A) equipped with a RID-10A detector and calibrated with polystyrene standards. Tetrahydrofuran (THF) of a GPC grade (Wako Pure Chemical Industries, stabilizer-free) was used as the eluent with an isocratic flow rate of 1.0 mL/min at 35 °C. The size of a PNB chain, defined as a hydrodynamic diameter, was determined by dynamic light scattering (DLS, Zetasizer 3000) at a scattering angle of 173° in toluene (1.0 mg/mL). The molecular weight distribution of polyethylene (PE) was determined by high-temperature GPC (Waters 150C) equipped with polystyrene gel columns (Showa Denko AD806M/S) and an IR detector (MIRAN 1A) at 140 °C using 1,2,4-trichlorobenzene as the eluent and calibrated with polystyrene standards. The melting temperature (T_m) and crystallinity (X_c) of PE were acquired on a differential scanning calorimeter (DSC,