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Title	ポリマー分子鎖への活性点集積と協奏的触媒作用の設計
Author(s)	Thakur, Ashutosh
Citation	
Issue Date	2018-03
Type	Thesis or Dissertation
Text version	ETD
URL	http://hdl.handle.net/10119/15338
Rights	
Description	Supervisor:谷池　俊明，マテリアルサイエンス研究科，博士

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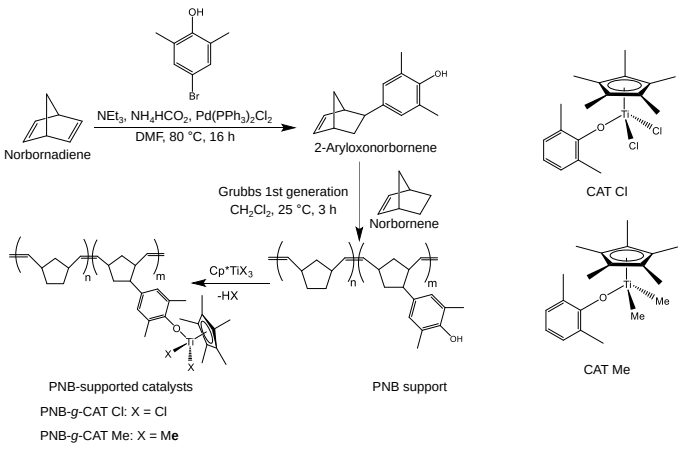
Cooperative Catalysis Among Active Sites Integrated in Polymer Random coil

Ashutosh Thakur

s1440154

Transition metal-based olefin polymerization catalysts have tremendous industrial applications for the production of polyolefins which occupy half of the plastic industry. They are represented by two extreme classes: Molecular catalysts (metallocene and post-metallocene) and classical solid catalysts (Ziegler-Natta and Phillips). The former class exploits the advantage of precise design of active site structures by a variety of metal-ligand combinations for a superior activity and selectivity. In contrast, the latter class is advantageous for the accumulation of multiple functions over multi-length scales, while their inherent chemical and structural complexities lead to ill-defined characteristics and lower catalytic selectivity. Thus, the contrast of the characteristics has encouraged the development of a new class of catalysts, which would enable multifunctionality and high selectivity with well-defined features in a way to bridge the gap between molecular and solid catalysts. In this research, I attempt to develop a new catalyst system, with the aim to conceptually bridge the two extreme classes of catalysts. This involves, a bottom-up strategy based on the synthesis of well-defined polynorbornene (PNB) supports bearing different contents of aryloxide ligands at their side chain, and subsequent grafting of a half-titanocene precursor to confine a predefined number of metal centres in a nano-sized random coil of polymer chains (**Scheme 1**). A potential synergy or cooperation among multiple active sites integrated in a random coil is explored to accumulate functionality in a well-defined way.

The PNB supports were synthesized by Grubbs catalysed copolymerization between norbornene and 2-aryloxonorbornene, at a fixed norbornene/catalyst ratio of 200 mol/mol. Approximately 90% of the yield and nearly quantitative comonomer incorporation were observed over a wide range of feed composition. The PNB supports exhibited M_w/M_n values close to one. These facts assured the well-defined nature of the synthesized PNB supports. Dynamic light scattering (DLS) measurements revealed a random coil conformation of the chains of the PNB supports in a dilute toluene solution.



Scheme 1. Synthesis of PNB-supported catalysts.

The PNB supports with different comonomer contents were used to graft two half-titanocene precursors Cp^*TiCl_3 and Cp^*TiMe_3. Successful synthesis was confirmed by comparing the ^1H, ^{13}C NMR and UV-Vis spectra of the PNB-supported catalysts with their molecular analogues (CAT Cl and CAT Me). The PNB-supported catalysts were employed in ethylene polymerization using modified methylaluminoxane (MMAO) or TIBA/$Ph_3CB(C_6F_5)_4$ as an activator. Ethylene polymerization was also conducted using the corresponding molecular analogues for comparison. It was found that the activation of the supported catalysts using MMAO was sterically hindered especially in terms of alkylation, which was circumvented by the utilization of a less bulky TIBA/$Ph_3CB(C_6F_5)_4$ activator system. When TIBA/$Ph_3CB(C_6F_5)_4$ activator system was used, the activity of the supported catalysts was found to be greater than the corresponding molecular analogues. Furthermore, the activity improved by the increase of Ti centres per PNB chain, plausibly due to a synergy or cooperation among multiple active centres confined in a nano-sized random coil of PNB chains. Secondly, it was found that at a higher temperature, the highest activity in ethylene polymerization was achieved by employing a PNB-supported catalyst with the lowest active site density. In the absence of synergistic or cooperative effect, the enhanced activity of the PNB-supported catalyst with the lowest active site density indicated the stabilization of the active sites by site isolation. Also, the supported catalysts were superior to the molecular analogues in producing polyethylene with a higher molecular weight and narrower polydispersity when activated by TIBA/$Ph_3CB(C_6F_5)_4$ activator system.

Keywords: Bridging catalyst; soluble polymer support; half-titanocene catalyst; ethylene polymerization; active site density.