New Tactics for Stereospecificity in Metallocene-based Olefin Polymerization

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Introduction

The relationship between the nature of catalyst systems and the resulting polymer has been well established in single-site olefin polymerization systems, providing now various opportunities to tailor the polymer properties.[1-3] In particular, the stereochemical control in polypropylenes and styrene-ethylene copolymers based on homogeneous single-site polymerization catalysts has received great attention. For polypropylenes, the chiral *ansa*-metallocene catalysts that conform to enantiomorphic site-control mechanism have been intensively investigated for the stereochemical control via the variation of the ligand structure but the unbridged metallocene-based systems have received a little attention. For styrene-ethylene copolymers, extensive efforts to produce copolymers with syndiotactic styrene-styrene sequence by employing the group 4 metallocene systems were not successful although scandium half-metallocene is known to incorporate such a sequence in copolymers.[4] We have developed new tactics for isospecificity in propylene polymerization with the unbridged metallocene-based systems and syndiospecific styrene-styrene sequence in styrene-ethylene copolymerization with the group 4 metallocene system. In this long abstract, brief details of the first subject [5] will only be given although the second subject will be also touched during the session lecture.

Experimental

Strategy. Considering the synthetic easiness of *unbridged* metallocenes compared to *ansa*-metallocenes, we have been pursuing to develop isospecific *unbridged* metallocene catalytic systems that can be *in-situ* generated during the activation step. For this end, we designed 'class I' *unbridged* metallocenes, a new class analogous to the known aspecific *unbridged* metallocenes 'class II'. Lewis base sites E in 'class I' may interact with bulky MAO or [Me-MAO] and thus generate rigid *rac*-like cationic active species, endowing aspecific *unbridged* metallocene precatalysts with isospecificity.

E = NR$_2$, OR, SR, etc.   R = H, CH$_3$, C$_6$H$_5$

class I   class II

Synthesis.

X = Cl (**2**), Me (**3**)
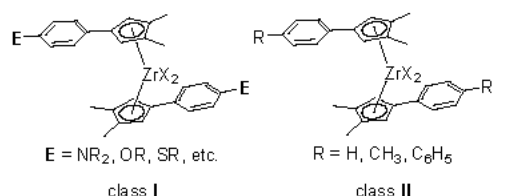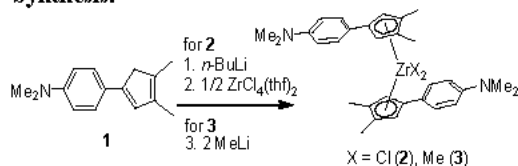
Results and discussion

Polymerization. The polymerization of propylene with [1-(p-Me$_2$NC$_6$H$_4$)-3,4-Me$_2$C$_5$H$_2$]$_2$ZrCl$_2$(**2** or (**AP**)$_2$ZrCl$_2$)/MAO ([Al]/[Zr] = 1000) was achieved at various polymerization temperatures of T_p = 0, 25, 50, and 70 °C. When being compared with the well known isospecific catalyst, *rac*-Et(Ind)$_2$ZrCl$_2$/MAO under the identical reaction conditions, the **2**/MAO system shows lower catalytic activity but produces higher molecular weight polypropylenes. DSC and GPC diagrams indicate that all the crude polypropylenes from the **2**/MAO

system show multi melting transitions (T_m) and broad molecular weight distribution of M_w/M_n = 4.5 − 10, respectively.

The crude polypropylenes were fractionated by stepwise solvent extraction method into three portions for further analysis: diethyl ether-soluble, diethyl ether-insoluble and *n*-heptane-soluble, and diethyl ether-insoluble and *n*-heptane-insoluble portions. The [*mmmm*] methyl pentad values suggest that the foregoing portions correspond to atactic-like, moderately isotactic, and highly isotactic polypropylenes, respectively. The amount of *n*-heptane-insoluble portion decreases as the polymerization temperature increases while that of diethyl ether-soluble portion increases. The *n*-heptane-insoluble portions have remarkably high [*mmmm*] values of ca. 86% and T_m = 151 °C. But, 'class II' [1-(*p*-C$_6$H$_5$C$_6$H$_4$)-3,4-Me$_2$C$_5$H$_2$]$_2$ZrCl$_2$ gives atactic polypropylene even at 0 °C. These results clearly demonstrate not only that the *unbridged* zirconocene **2**/MAO system is capable of producing highly isotactic polypropylene but also that the simple functionalization of 'class II' to 'class I' metallocenes would be an effective route to endowing aspecific *unbridged* metallocene precatalysts with isospecificity.

Nature of Active Species. When [1-(*p*-Me$_2$NC$_6$H$_4$)-3,4-Me$_2$C$_5$H$_2$]$_2$ZrMe$_2$ **3** was activated with [Ph$_3$C][B(C$_6$F$_5$)$_4$] in the presence of TIBA or TOA ([Al]/[Zr] = 200), the resulting catalytic systems gave completely diethyl ether-soluble, atactic polypropylenes while **3**/MAO afforded polypropylene whose tacticity distribution is similar to that from **2**/MAO. Furthermore, when the activation of **3** was effected by the initial treatment with MAO followed by the additional treatment with [Ph$_3$C][B(C$_6$F$_5$)$_4$] or initially with [Ph$_3$C][B(C$_6$F$_5$)$_4$] then by with MAO, the resulting catalytic species gave completely atactic diethyl ether-soluble polypropylene. The ^{1}H-NMR experiments reveal that the addition of [Ph$_3$C][B(C$_6$F$_5$)$_4$] to **3**/MAO causes the formation of Ph$_3$C*Me* as judged by the appearance of the signal at 1.96 ppm, while the treatment of neutral MAO with [Ph$_3$C][B(C$_6$F$_5$)$_4$] at room temperature does not produce Ph$_3$CMe. Since [Me-MAO] is the generally assumed counter anion formed in metallocene/MAO system, the formation of Ph$_3$CMe can be understood in terms of Me abstraction by [Ph$_3$C]$^+$ from [Me-MAO].

The foregoing observations and the additional VT ^{1}H-NMR spectral studies on **3**, **3**/MAO (Al/Zr = 200), **3**/TMA and **3**/TOA solutions are in support of the formation of *rac*-like ion pair of type [(**AP**)$_2$ZrP]$^+$[Me-MAO] (**IS**) as isospecific catalytic species. The concurrent presence of the cation-anion pairing and the interactions of Lewis acid sites in the [Me-MAO] with nitrogen atoms of amine-functionalized unbridged zirconocene cation in **IS** leads to effective prevention of the ligands from the rapid rotation, leading to the prevailing racemic C$_2$-symmetric like active species that is in thermal equilibrium with the related species shown below.
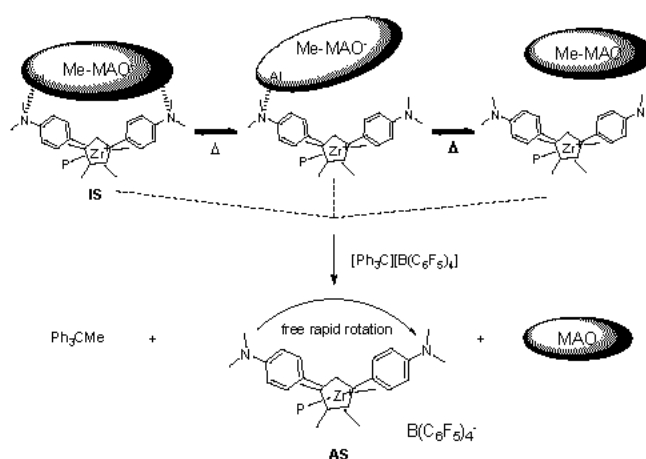
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