New Tactics for Stereospecificity in Metalloocene-based Olefin Polymerization

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Introduction

The relationship between the nature of catalyst systems and the resulting polymers has been well established in single-site olefin polymerization systems, providing new opportunities to tailor the polymer properties[1-3]. In particular, the stereoechemical control in polypropylenes and styrene-ethylene copolymers based on homogeneous single-site polymerization catalysts has received great attention. For polyproplylenes, the chain-end metallocene catalysts that conform to metallocene-like ate-control mechanism have been extensively investigated for the stereoselective control of the tacticity of the resulting homopolymer or the stereoselective control of the tacticity of the resulting copolymer[4]. For styrene-ethylene copolymers, extensive efforts to produce copolymers with syndiotactic styrene-ethylene sequence by employing the group 4 metallocone systems were not successful since both syndiotactic monomer isomer is known to incorporate such a sequence in copolymers[4]. We have developed new tactics for isopropylidene propylene polymerization with the unconstrained metallocone-based systems and syndiotactic styrene-ethylene sequence in styrene-ethylene copolymerization with the group 4 metallocone 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 review lecture.

Experimental

Strategy. Considering the synthetic easiness of unbridged metallocones compared to aza-metallocones, we have been pursuing to develop isospecific unbridged metallocone catalytic systems that can be easily generated during the activation step. For this end, we designed class I unbridged metallocone, a new class analogues to the known specific unbridged metallocone 'class II Lewis base site E in class I may interact with bulky MAO or [Me3Al] and thus generate rigid 1,3-diketonic active species, endowing specific unbridged metallocone precatalysts with isospecificity.

E = NR2, OR, SR, etc
R = H, CH3, C6H5

class I

e

class II

Synthesis

\[
\begin{align*}
\text{Mo=Cl}(2) \text{Me}=\text{X} \quad \text{Me}=\text{Cl} (2) \\
\end{align*}
\]

Results and discussion

Polymerization. The polymerization of propylene with [1-(η5-C5H4MMe2)][M1]-[M2]MAO (113) [12] - (1000) was achieved at various polymerization temperatures of 70, 25, 50, and 70 °C. When being compared with the well known isospecific catalyst, rac-Et[MoCl3(η5-C5H4)]MAO under the identical reaction conditions, the 2MMAO system shows lower catalytic activity but produces higher molecular weight polypropylene. GPC diagrams indicate that all the crude polypropylenes from the 2MMAO system show multi-melting transitions (Tm) and broad molecular weight distribution of Mw/Mn = 4.5 – 10.

The crude polypropylenes were fractioned by stepwise solvent extraction method into three portions for further analysis: dialkyl ether-soluble, dialkyl ether-insoluble and styrene-soluble, and dialkyl ether insoluble and n-heptane insoluble portions. The [meso]metal 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 dialkyl ether insoluble portion increases. The n-heptane insoluble portions have remarkably high [meso] values of ca. 80% and Tm = 151 °C. But, class II [1-(η5-C5H4C6H5)-3-Me2C5H4C]Cl2 gives atactic polypropylene even at 0 °C. These results clearly demonstrate not only that the unbridged metallocene 2MMAO system is capable of producing highly isotactic polypropylene but also that the single functionalization of 'class II' to 'class I metallocone would be an effective route to endeavor specific unbridged metallocene precatalysts with isospecificity.

Nature of Active Species. When [1-(η5-Me2C5H4)][M1]-[M2]MAO (3) was activated with [Ph3C][B(C6F5)4], in the presence of TIBA or TiOPh(Al)(2) = 200), the resulting catalytic systems gave completely dialkyl ether-soluble, atactic polypropylenes while 3MAO afforded polypropylene whose tacticity distribution is similar to that from 2MAO. Furthermore, when the activation of 3 was effected by the initial treatment with MAO followed by the additional treatment with [Ph3C][B(C6F5)4] or initially with [Ph3C][B(C6F5)4] then by with MAO, the resulting catalytic species gave completely atactic dialkyl ether-soluble polypropylene. The H NMR experiments reveal that the addition of [Ph3C][B(C6F5)4] to 3MAO causes the formation of Ph3CMMA as judged by the appearance of the signal of at 1.96 ppm, while the treatment of neutral MAO with [Ph3C][B(C6F5)4] at room temperature does not produce Ph3CMMA. Since [Me3Al] is the generally assumed counter anion formed in metallocone MAO system, the formation of Ph3CMMA can be understood in terms of Me3Al abstraction by [Ph3C] from [Me3Al].

The foregoing observations and the additional VT H NMR spectroscopic studies on 3, 2MAO (Al/3 = 200), 3MAO and NTOA solutions are in support of the formation of rac-1,3-diketone ion pair of type [APh3C][BF4][Me2AlO] (IS) as isospecific catalytic species. The concurrent presence of the cation-anion pairing and the interactions of Lewis acid sites in the [Me3AlO] with nitrogen atoms of amine-functionalized unbridged metallocene cation in IS leads to effective prevention of the ligands from the rapid rotation, leading to the prevailing racemic 1,3-symmetric like active species that is in thermal equilibrium with the related species shown below.