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Polynuclear Catalysis: Enhancement of Enchainment Cooperativity between Different Single-Site Olefin Polymerization Catalysts by Ion Pairing with a Binuclear Cocatalyst

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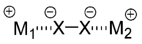
An important material resulting from the intense research in homogeneous single-site olefin polymerization catalysis[1−4] is linear low-density polyethylene (LLDPE).[5] The branched-chain structure decreases crystallinity, which facilitates processing and imparts favorable product properties for myriad applications.[6] Typically, LLDPE branching is achieved via copolymerization of ethylene with an α-olefin comonomer; however an alternative approach that has recently received attention is homogeneous "tandem catalysis".[7] Here one catalyst produces α-olefin oligomers which are incorporated into high-molecular weight polyethylene by a second catalyst in the reaction mixture, utilizing the *same* ethylene feed. Since this type of polymerization requires intermolecular processes at low catalyst concentrations (**I**), the question arises as to whether two catalyst centers constrained to close spatial proximity (**II**) might perform such functions more efficiently. The ability of the binuclear activator $[Ph_3C^+]_2[1,4\text{-}(C_6F_5)_3BC_6F_4B(C_6F_5)_3{}^{-2}]$[8] (**B$_2$**) to spatially confine two cations via tight ion pairing[4] allows us to address this question.

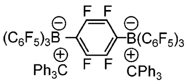

$\overset{\oplus}{M_1}\cdots\overset{\ominus}{X} \quad \overset{\oplus}{M_2}\cdots\overset{\ominus}{X}$

I

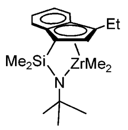

$\overset{\oplus}{M_1}\cdots\overset{\ominus}{X}-\overset{\ominus}{X}\cdots\overset{\oplus}{M_2}$

II

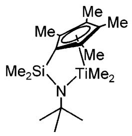
In the experiments described, $Me_2Si(^tBuN)(\eta^5\text{-3-ethylindenyl})ZrMe_2$[8] (**Zr**) is the source of vinyl-terminated polyethylene oligomers, and $Me_2Si(^tBuN)(\eta^5\text{-}C_5Me_4)TiMe_2$[9] (**Ti**) is the source of high-molecular weight polymer, due to its ability to efficiently co-enchain α-olefins.[9,10] Mononuclear $[Ph_3C^+]\,[B(C_6F_5)_4{}^-]$[11] (**B$_1$**) was used for control experiments. We report that use of **B$_2$** in ethylene polymerizations with stoichiometrically appropriate quantities of **Zr** and **Ti** produces a *significantly* more homogeneous polyethylene than that produced by polymerizations under identical conditions with **B$_1$** as cocatalyst. The bulk and spectroscopic properties of the **B$_2$**-derived polymer are consistent with highly branched polyethylene.[12]



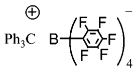
B$_2$



Zr



Ti



B$_1$

The ethylene polymerization properties of the individual group 4 catalysts with **B$_1$** and **B$_2$** (Table 1, entries 1−4) were first examined using previously described methodology[4a,c] to provide a baseline for assessing cooperativity effects. Polymerizations of **Zr** + **B$_1$** or **B$_2$** yield low-molecular weight polymers (by ^{1}H NMR) having predominantly ethyl branches (by ^{13}C NMR[13]) and low melting points. Polymerizations with **Ti** + **B$_1$** or **B$_2$** are ~50× more active than those with **Zr** and produce high-molecular weight polyethylenes (by GPC) with melting points consistent with unbranched structures.[12] Next, a series of polymerizations with **B$_2$** as cocatalyst was carried out to probe the effect of relative catalyst concentrations on product properties, along with parallel experiments using mononuclear **B$_1$** (Table 1, entries 5−12). At a 1:1 **Zr**:**Ti** stoichiometric ratio (Table 1, entries 5, 6) use of a mononuclear or binuclear cocatalyst has little discernible effect on the resultant polymer. Importantly, from the activities in entries 1−4, >95% of the product is produced by **Ti** in both cases, as is reinforced by the similarity of the polymeric product properties. Similarly, at 20:1 **Zr**:**Ti** with **B$_2$**, ~85% of the product should be produced by **Ti** and 95% of **Ti** should be paired with **Zr**.[14]

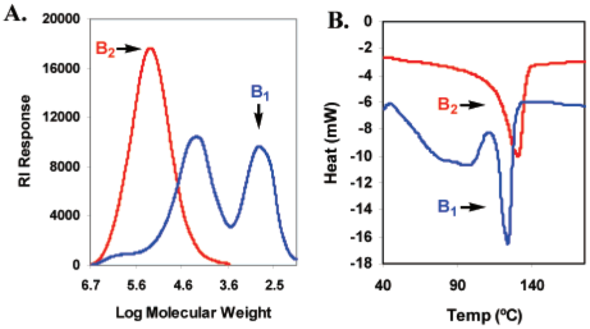
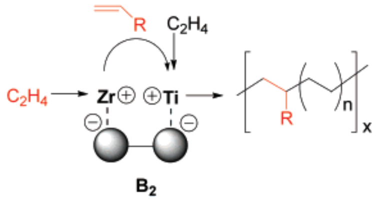


Figure 1. GPC (A) and DSC (B) data for ethylene polymerization with a 20:1 **Zr**:**Ti** catalyst ratio at 95 °C with activators **B$_1$** and **B$_2$**.

Scheme 1



For the polymers synthesized with **Zr**:**Ti** ≥ 20:1 (Table 1, entries 7−14), ^{13}C NMR[13] confirms the presence of branches (≥C_6 in length) along the chain backbone for polymers produced using **B$_1$** and **B$_2$** as the cocatalysts. There are, however, significant differences in polydispersities and thermal properties between the polyethylenes produced with binuclear and mononuclear cocatalysts. For polymerizations cocatalyzed by **B$_1$**, as **Zr**:**Ti** increases, the GPC traces become *bimodal or polymodal*. DSC analysis of the **B$_1$**-derived polyethylene reveals low melting points and in some cases multiple endothermic transitions. In marked contrast, GPC traces of the

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Table 1. Catalytic Olefin Polymerization Data[a]

entry	**Zr** (μmol)	**Ti** (μmol)	$\mathbf{B_2}$ (μmol)	$\mathbf{B_1}$ (μmol)	time (min)	temp (°C)	activity[b]	M_n[c]	PD[c]	T_m (°C)
1	10	0	0	10	45	23	1.3×10^5	610[d]		59.6
2	10	0	5.0	0	70	23	9.3×10^4	630[d]		54.2
3	0	4.0	0	4	1	29.5	8.5×10^6	408 000	2.8	139.2
4	0	7.0	3.4	0	1.7	31.5	4.9×10^6	109 000	2.24	139.8
5	5.0	5.0	5.0	0	4	28	9.3×10^5	274 000	3.88	137.5
6	5.0	5.0	0	10	3	31.5	3.5×10^6	226 000	2.24	140.4
7	9.9	0.5	5.0	0	15	26.5	1.8×10^5	780 000	2.34	118.6
8	9.9	0.5	0	10	12	26	6.1×10^5	451 000	2.56	72
9	9.9	0.28	5.0	0	12	25	1.5×10^5	347 000	3.46	128.4
10	9.9	0.28	0	10	14	30	1.2×10^5	181 000; 320	1.80; 1.21	75.1
11	9.9	0.2	5.0	0	21	25	1.7×10^5	455 000	2.69	122.4
12	9.9	0.2	0	10	17	25	4.8×10^5	396 000; 7600; 360	2.31;1.88; 1.28	122.1
13	9.9	0.5	5.0	0	12	95	1.0×10^6	66 700	2.89	130.6
14	9.9	0.5	0	10	10	96	1.2×10^6	14 900; 540	6.16; 1.69	~85, 123.6

[a] Conditions: 100 mL toluene solvent, 1.0 atm ethylene. [b] Activity in units of g (mol metal)$^{-1}$ (atm ethylene)$^{-1}$ h^{-1}. [c] By GPC with universal calibration using polystyrene standards. [d] By ^{1}H NMR.

polyethylenes from analogous $\mathbf{B_2}$-cocatalyzed polymerizations are *monomodal*, indicating a more homogeneous polymer, and polydispersities are essentially constant with rising **Zr**:**Ti** ratio (Table 1). DSC-measured melting points of the $\mathbf{B_2}$-derived polymers are consistent with LLDPE.[12] At elevated temperatures, polymerizations with 20:1 **Zr**:**Ti** (Table 1, entries 13, 14) not surprisingly show increased activity. Again, polymer produced with $\mathbf{B_1}$ exhibits a bimodal GPC trace, and the DSC exhibits two endothermic transitions, a broad one centered at ~85 °C and a sharp one at 123.6 °C (Figure 1). High-temperature polymerization with $\mathbf{B_2}$ produces a more homogeneous polymer with a monomodal GPC trace and a single endothermic DSC transition.

These results show that binuclear activator $\mathbf{B_2}$ dramatically increases the efficiency of homogeneous heterobimetallic olefin enchainment processes for LLDPE synthesis and are consistent with a pathway in which the binuclear center preferentially binds/detains α-olefin fragments for subsequent enchainment (Scheme 1).[15] This unprecedented enhancement of cooperativity between two single-site centers via electrostatic spatial confinement is a step towards rational design of tailored multisite polymerization catalysts, and the generality of this effect is under continuing investigation.

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Supporting Information Available: Details of polymer synthesis and characterization (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Calculations make the reasonable assumption that individual activities do not change greatly in binary catalyst mixtures and that all ion pairs have essentially the same free energy, yielding statistical distributions of species. Results of similar calculations for all pairs are contained in Supporting Information.

(15) That this pathway is predominantly intramolecular is supported by: (1) time-dependent experiments show that $\mathbf{B_2}$-derived products are homogeneous at reaction times as short as 1 min, whereas $\mathbf{B_1}$-derived product are not; (2) ethylene + 1-octene copolymerization studies show comonomer incorporation is enhanced by only ~2× for 2**Ti** + $\mathbf{B_2}$ vs 2**Ti** + 2$\mathbf{B_1}$.

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