

THE CURIOUS CASE OF THE MOLECULAR CATALYSTS THAT BEHAVED LIKE A DUAL-SITE CATALYST

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Semi-batch, solution copolymerizations of ethylene and 1-hexene were performed using both dichloride (Hf-Cl_2) and dimethyl (Hf-Me_2) analogues of the bis(*n*-propylcyclopentadienyl) hafnium precatalyst. Either tetrakis(pentafluorophenyl) borate dimethylanilinium salt ($[\text{B}(\text{C}_6\text{F}_5)_4][\text{Me}_2\text{NHPPh}]^+$) (B) or methyl aluminoxane (MAO) was employed as the activator, and tri-*n*-octylaluminum (TOA) was used as the scavenger for the borate-activated experiments. For the copolymerization study using $\text{Hf-Cl}_2/\text{B}/\text{TOA}$, 1-hexene, borate and TOA concentrations were varied systematically. Crystallization analysis fractionation (CRYSTAF) or crystallization elution fractionation (CEF) profiles were used interchangeably to compare the chemical composition distributions (CCD) of the copolymers. Above a minimum threshold 1-hexene level, the CCD profiles of all the copolymers were bimodal and the areas under the peaks depended on the B/ Hf-Cl_2 and B/Al ratios. Decreasing the TOA concentration reduced the weight fraction of the higher crystallinity polymer component.

Copolymerization using MAO as activator also produced copolymers with bimodal CRYSTAF profiles. For the copolymerization using the $\text{Hf-Me}_2/\text{B}/\text{TOA}$ activator system, eliminating TOA from the polymerization recipe removed the higher crystallinity component from the composition distribution (CCD), yielding a copolymer with a unimodal CCD. These results suggest that TOA reacts with either the catalyst or the activator generating a new active site with a lower propensity for incorporating comonomer than the original catalyst system. These results are unexpected and show that much more complex behavior can be expected from certain molecular coordination catalysts than usually admitted in the open literature.