

Stereospecific Living Ziegler–Natta Polymerization via Rapid and Reversible Chloride Degenerative Transfer between Active and Dormant Sites

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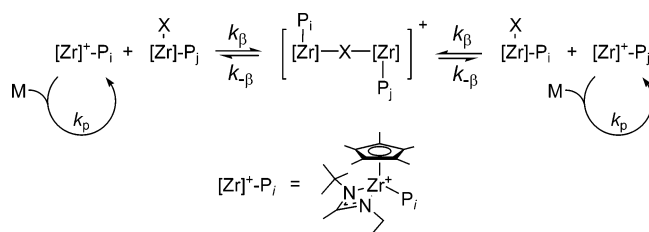
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The development of highly active transition metal catalysts for the homogeneous Ziegler–Natta polymerization of ethylene, propylene, and higher α -olefins is a remarkable success story whose origins are principally rooted in the discovery of methods by which neutral transition metal “precatalysts” containing either a M–Cl or M–R (R = alkyl) bond can be “activated” by a stoichiometric or greater amount of an organometallic main group “cocatalyst” to produce catalytically active cationic transition metal species.¹ The development of new catalysts and polymerization processes that can either eliminate or greatly reduce cocatalyst dependency, however, remain sought-after goals.² Recently, we reported a new living Ziegler–Natta polymerization process based on activation of the precatalyst, Cp*ZrMe₂[N(^tBu)C(Me)N(Et)] (Cp* = η^5 -C₅-Me₅) (**1**),³ with *substoichiometric* amounts of the borate, [PhNMe₂H]-[B(C₆F₅)₄] (**2**), that proceeds through fast and reversible degenerative transfer of a methyl group between active and dormant propagating centers according to Scheme 1, where X = Me and P_i and P_j represent polymer chains of *i* and *j* length, respectively.⁴ Importantly, due to k_{β} and $k_{-\beta}$ being much larger than k_p , this living methyl degenerative transfer (MeDET) process produces polyolefins of narrow polydispersity [M_w/M_n (D) \leq 1.05] for which the number average degree of polymerization, X_n , is simply defined by the ratio of the initial concentrations of monomer and the precatalyst **1**, i.e., $X_n = [M]_0/[I]_0$, and not by the amount of cocatalyst **2** employed.⁵ However, due to a dormant state that is configurationally unstable toward metal-centered epimerization, with k_{epi} , k_{β} , and $k_{-\beta} \gg k_p$, a loss of stereocontrol occurs during propagation as documented by the nearly atactic character of the obtained polymer microstructure, which is strictly isotactic in the absence of MeDET.^{3,4} Thus, by turning MeDET “on” and “off” between successive monomer additions, a new route to well-defined isotactic–atactic stereoblock polyolefins has been demonstrated.⁴

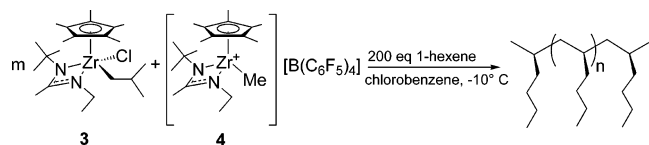
The stereochemical characteristics of MeDET immediately raised the question of whether a *stereospecific* living degenerative transfer Ziegler–Natta process that proceeds with substoichiometric activation of a precatalyst could be developed based upon a situation in which all the species involved are configurationally stable. Herein, we now document the successful realization of this goal for a chloride degenerative transfer (ChloDET) process (i.e., X = Cl in Scheme 1) that provides isotactic polyolefins of narrow polydispersity ($D \leq 1.05$).

In contrast to **1**, the chloro, isobutyl compound **3**, shown in Scheme 2, has been determined to be, along with a large number of other chloro, alkyl derivatives, configurationally stable toward metal-centered racemization even at elevated temperatures.⁶ Accordingly, given that the cationic initiator **4** (generated in situ from equimolar amounts of **1** and **2**) and diastereomerically pure cationic living polymers derived from it are both known to be configurationally stable,^{3b,4} it was reasoned that the combination of **3** and **4** might be capable of producing an isospecific living ChloDET process, if chloride transfer between the two species is fast and reversible.

Scheme 1



Scheme 2



Given the known propensity of halide ligands to form strong bridging interactions within bimetallic complexes, however, this requirement appeared a priori to represent an enormous obstacle. Fortunately, as Figure 1 shows, this fear proved groundless when polymerizations of 1-hexene were conducted according to Scheme 2.⁷ More specifically, in the absence of **3**, polymerization of 200 equiv of 1-hexene using **4** provided isotactic poly(1-hexene) with M_n and D values of 23 800 and 1.03, respectively (relative to polystyrene standards). By now keeping [4]₀ constant, preformed mixtures of **3** and **4** were found to polymerize the same amount of 1-hexene to produce isotactic poly(1-hexene) possessing M_n values that were linearly proportional to the ratio of the initial monomer concentration to the total concentration of **3** and **4** (i.e., $[M]_0/[3 + 4]_0$ or $[M]_0/[Zr]_{\text{total}}$), as expected for living polymerizations proceeding via chloride degenerative transfer according to Scheme 1 where X = Cl.⁴ Furthermore, observation that each polymer had an associated D value of ≤ 1.05 establishes that both active and dormant chain ends formally propagate at the same rate, which once again establishes that k_{β} and $k_{-\beta} \gg k_p$.^{8,9} Most importantly, ¹³C-¹H NMR spectra confirmed that each poly(1-hexene) sample possesses a strictly isotactic polymer microstructure, thereby confirming that all species involved in this ChloDET process are configurationally stable, at least on the time scale of the polymerizations.⁷

Successful demonstration of a stereospecific living Ziegler–Natta polymerization that proceeds via rapid and reversible chloride group transfer between neutral and cationic transition metal centers is quite surprising given the aforementioned known strength of halide bridging interactions between metal centers. Accordingly, it was of interest to further investigate the lifetime of the presumed μ -Cl dizirconium intermediate that must be involved in the reversible chloride transfer step (see Scheme 1). To begin, upon mixing equimolar amounts of **3** and **5**, which are models for dormant and active polymeryl states, respectively,⁴ variable-temperature NMR studies performed in chlorobenzene-*d*₅ revealed only a single set

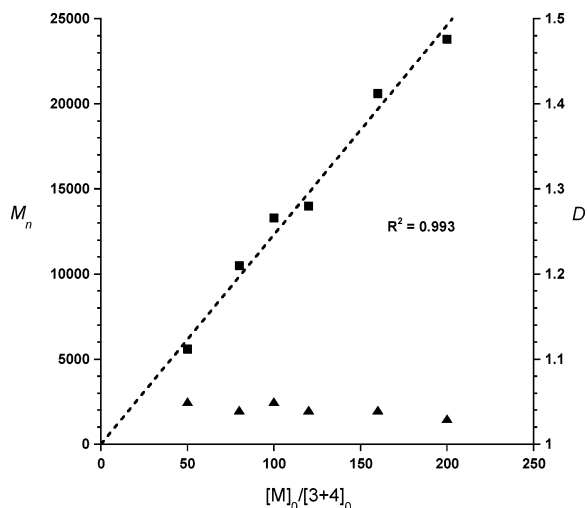
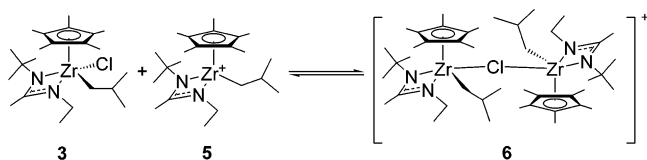


Figure 1. Dependence of poly(1-hexene) M_n (■) and D (▲) values on $[M]_0/[3+4]_0$ at constant $[M]_0 = 0.50$ M and $[4]_0 = 2.5$ mM. M_n and D values were obtained by GPC and are reported relative to polystyrene standards.

Scheme 3



$[B(C_6F_5)_4]$ is the counterion for **5** and **6**

of sharp resonances down to the temperature limit of the solvent (ca. -35 °C).⁷ These observations are consistent with the equilibrium involving **3**, **5**, and **6** shown in Scheme 3 being within the fast exchange limit¹⁰ at all temperatures investigated, and they support the expected large magnitudes for both k_β and $k_{-\beta}$ shown in Scheme 1.⁷ Additional information regarding the relative magnitudes of k_β and $k_{-\beta}$, which define the equilibrium constant for the bimolecular association of active and dormant centers during polymerization as defined by $K_{\text{assoc}} = k_\beta/k_{-\beta}$, was obtained by evaluating the kinetics of polymerization with increasing initial concentrations of **3** relative to **4** (e.g. $[3]_0 = 0-7.12$ mM and $[4]_0 = 1.56$ mM).⁷ Gratifyingly, for each initial value of $[4]_0/[3+4]_0$, kinetic analysis revealed strictly first-order consumption of monomer over several half-lives as expected for a living system.^{7,11} However, these studies also revealed that the apparent rate constant for polymerization, k_{app} , decreases with increasing $[3]_0$ as shown by Figure 2. Retardation of polymerization rates with an increase in dormant state concentration have been observed for other degenerative transfer polymerization processes, such as RAFT,⁹ and it is consistent with k_β being larger than $k_{-\beta}$ ($K_{\text{assoc}} > 1$). More detailed quantitative kinetic investigations of both MeDET and ChloDET are currently in progress.

As a final note, in the above experiments, the methyl cation **4** was used to initiate ChloDET living polymerization, but it too is consumed in the process by engaging in polymer chain growth. Thus, with an eye toward eventually being able to use ChloDET for a range of different precatalyst types based on the general structure of **1**, including polynuclear initiators, it was desirable to

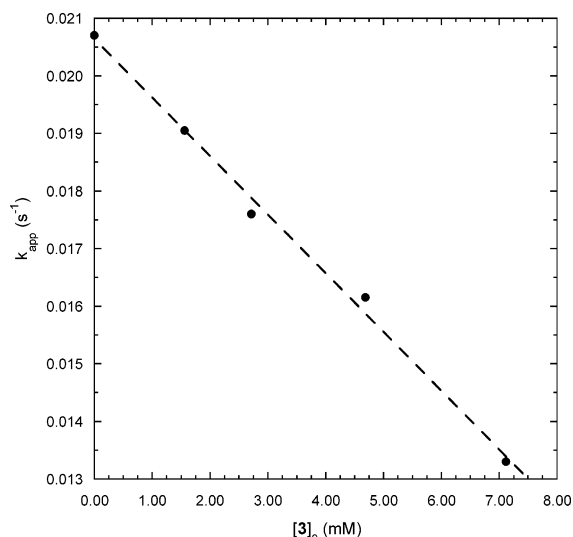


Figure 2. Dependency of k_{app} vs $[3]_0$ with $[4]_0$ held constant at 1.56 mM. The dashed line is for a guide to the eye only.

determine whether the same type of process could be initiated by direct halide abstraction from **3**. Consideration of the exceptionally strong Si–Cl bond¹² led to a selection of the silylium perfluorophenyl borate, $[Et_3Si][B(C_6F_5)_4]$ (**7**),¹³ as a potential cocatalyst for this purpose, and in practice, by using 200 equiv of 1-hexene, it was determined that ChloDET could indeed be performed using a 2:1 ratio of **3** to **7** to provide isotactic poly(1-hexene) with M_n and D values of 24 100 and 1.02, respectively, which are close to the expected values.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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