

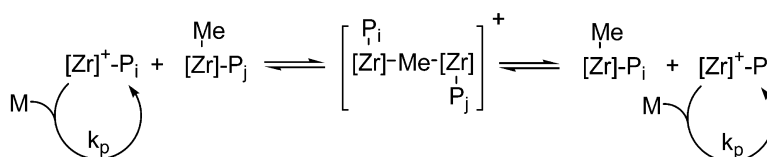
Article

# Degenerative Transfer Living Ziegler–Natta Polymerization: Application to the Synthesis of Monomodal Stereoblock Polyolefins of Narrow Polydispersity and Tunable Block Length

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## Degenerative Transfer Living Ziegler–Natta Polymerization: Application to the Synthesis of Monomodal Stereoblock Polyolefins of Narrow Polydispersity and Tunable Block Length

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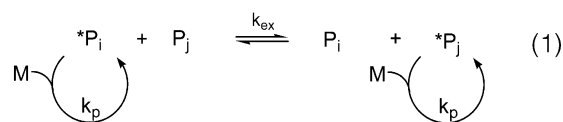
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**Abstract:** The neutral dimethyl pentamethylcyclopentadienylzirconium acetamidinate,  $(\eta^5\text{-C}_5\text{Me}_5)\text{ZrMe}_2\text{-[N}(t\text{-Bu)C(Me)N(Et)]}$ , can serve as a highly active initiator for the living Ziegler–Natta polymerization of  $\alpha$ -olefins to produce polyolefins of narrow polydispersity ( $D \leq 1.05$ ) when “activated” through mono demethylation by a substoichiometric amount of the borate,  $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ . The mechanism by which this living polymerization proceeds is through a process of degenerative transfer involving rapid and reversible methyl group exchange between cationic (active) zirconium propagating centers and neutral (dormant) methyl, polymeryl zirconium end groups. Facile metal-centered epimerization of the dormant species is responsible for a loss of stereocontrol during propagation that produces iso-rich material in contrast to the pure isotactic polymer microstructure obtained when degenerative transfer is not present. By turning degenerative transfer “on” and “off” between successive monomer polymerizations, a successful strategy for the production of monomodal stereoblock polyolefins of narrow polydispersity and tunable block length has been demonstrated.

### Introduction

Living polymerizations that occur with reversible deactivation of the propagating centers during propagation, that is, the reversible formation of inactive or “dormant” species, have now been documented for anionic, cationic, group transfer, and controlled/living free radical polymerizations.<sup>1–4</sup> Slow exchange between active and dormant species, relative to propagation, can lead to a broadening of molecular weight distributions over those for living polymerizations in which such exchange processes are absent [cf., polydispersity index,  $D$ ,  $> 1.1$  vs  $< 1.1$ , respectively].<sup>1,2</sup> On the other hand, when the equilibrium between active and dormant species lies far to the dormant side, undesired bimolecular reactions involving active species are minimized, thereby providing more controlled polymerization reactions. Indeed, the enormous success and popularity of controlled/living free radical polymerization for making well-defined block copolymers and other polymer architectures rest on this fact.<sup>1,3,4</sup> Further, Gibson and co-workers<sup>5</sup> recently documented the use of a fast and reversible chain transfer

between iron (active) and zinc (inactive) centers ( $\text{Zn:Fe} = 500:1$ ) for the production of low molecular weight polyethylene of narrow polydispersity in a Ziegler–Natta polymerization of ethylene that is uncontrolled in the absence of the zinc species. Regarding living Ziegler–Natta polymerization, in recent years, a small number of homogeneous transition metal complexes have been reported that can serve as initiators for the polymerization of  $\alpha$ -olefins in a living fashion, and, in a few cases, a high degree of stereocontrol during propagation can be achieved, providing either isotactic or syndiotactic polyolefin microstructures.<sup>6</sup> To date, however, reversible deactivation during propagation, and its potential consequences, has not been documented for living Ziegler–Natta polymerization. Herein, we now report a system that undergoes rapid and reversible degenerative transfer between active and dormant species according to the schematic shown by eq 1 where  $^*\text{P}_i$  and  $\text{P}_j$  represent active and dormant chain ends of  $i$  and  $j$  chain length, respectively.<sup>2</sup> Importantly, by switching degenerative transfer “on” or “off” through manipulation of the dormant state (i.e.,



either present or absent), a successful strategy for the synthesis of monomodal stereoblock polyolefins of narrow polydispersity

- (1) (a) Greszata, D.; Mardare, D.; Matyjaszewski, K. *Macromolecules* **1994**, *27*, 638–644. (b) Matyjaszewski, K. *Macromol. Symp.* **2001**, *174*, 51–67 and references therein.  
 (2) (a) Müller, A. H. E.; Zhuang, R.; Yan, D.; Litvinenko, G. *Macromolecules* **1995**, *28*, 4326–4333 and references therein. (b) Müller, A. H. E.; Yan, D.; Litvinenko, G.; Zhuang, R.; Dong, H. *Macromolecules* **1995**, *28*, 7335–7338.  
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 (4) (a) Chong, Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 2071–2074. (b) Goto, A.; Sato, K.; Tsujii, Y.; Fukuda, T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2001**, *34*, 402–408.  
 (5) Britovsek, G. J. P.; Cohen, S. A.; Gibson, V. C.; Maddox, P. J.; van Meurs, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 489–491.

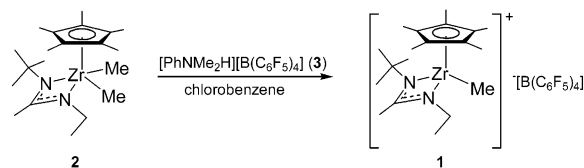
- (6) For a recent review, see: Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236–2257.

( $D \leq 1.05$ ) and tunable block lengths has been developed. As stereoblock polyolefins, which have not yet to date been prepared in such a controlled fashion, are materials of significant technological interest,<sup>7</sup> the present findings may serve to open a new chapter for polyolefin materials engineering.

## Results and Discussion

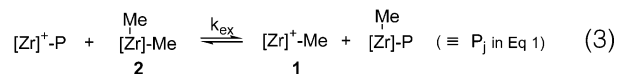
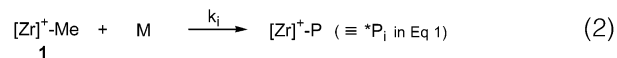
We have previously shown that the cationic zirconium acetamidinate,  $[\text{Cp}^*\text{ZrMe}\{\text{N}(t\text{-Bu})\text{C}(\text{Me})\text{N}(\text{Et})\}][\text{B}(\text{C}_6\text{F}_5)_4]$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) (**1**), prepared through demethylation of neutral  $\text{Cp}^*\text{ZrMe}_2[\text{N}(t\text{-Bu})\text{C}(\text{Me})\text{N}(\text{Et})]$  (**2**) with  $[\text{PhNMMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$  (**3**) according to Scheme 1, can serve as a highly active initiator for the isospecific living polymerization of  $\alpha$ -olefins.<sup>8</sup> It has

Scheme 1

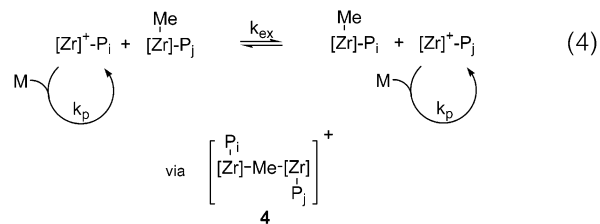


also been shown that **1** exists in the solid state as a dimeric dication with bridging methyl groups<sup>8c</sup> and that, in solution, rapid methyl, polymeryl group exchange can occur between a living polymer derived from **1** (LP-**1**) and either **1** itself, or structurally related cationic initiators.<sup>8e</sup> The latter observation that alkyl group exchange between two cationic zirconium centers could be so facile led us to consider the proposal for reversible deactivation by degenerative transfer that is based on methyl group exchange between an active cationic propagating chain and a dormant neutral chain according to eqs 2–4. More specifically, eqs 2 and 3 represent initiation steps when substoichiometric amounts of the borate **3** are initially used to demethylate **2** to generate cationic **1**. To explain further, consider the case where  $[\text{3}]/[\text{2}] = 0.5$ , which would result in a 1:1 initial mixture of **1** and **2** existing in solution. Now, upon addition of monomer (M), **1** can undergo olefin insertion, with associated rate constant,  $k_i$ , to produce an active cationic propagating center,  $[\text{Zr}]^+\text{-P}$ , that can then either undergo further insertions (i.e., propagate with associated rate constant,  $k_p$ ) or engage in rapid methyl group exchange with **2**, which is governed by rate constant  $k_{ex}$ , to generate additional **1** at the expense of producing a dormant neutral chain,  $\text{Me}-[\text{Zr}]-\text{P}$  (see eq 3). Because this freshly generated **1** is now free to further react with monomer, in the case where  $k_i, k_{ex} \gg k_p$ , near instantaneous consumption of **1** and **2** will occur to produce a 1:1 mixture of  $[\text{Zr}]^+\text{-P}_i$  (active) and  $\text{Me}-[\text{Zr}]-\text{P}_j$  (inactive) species, both of which can subsequently engage in chain growth via degenerative transfer according to eq 4, and presumably through intermediacy of the monocationic methyl-bridged dinuclear species **4** for which

Initiation



Propagation



precedence of such structures exists.<sup>9</sup> Müller and co-workers<sup>2a</sup> have presented a detailed theoretical treatment of a similar kinetic scheme for degenerative transfer polymerization with respect to the evolution of the number average and weight average degree of polymerization,  $\bar{X}_n$  and  $\bar{X}_w$ , respectively, and the polydispersity index,  $D = \bar{X}_w/\bar{X}_n$ , as a function of different relative rate constants and concentrations of species that are present. These authors found that when  $\beta = k_{ex}/k_p \gg 1$ , and  $[\text{M}]_0/[\text{I}]_0 \geq 25$ , the initiator is rapidly consumed within a small time interval, and at full monomer conversion,  $\bar{X}_n$  and  $D$  are given by eqs 5 and 6, respectively. In the case where  $\beta \gg \alpha$ , where  $\alpha$  is the fraction of initiator that is converted to active end groups, eq 6 simplifies further to eq 7. To apply these results to our system, we must first define **2** as being the initiator with initial concentration,  $[\text{I}]_0 = [\text{2}]_0$ , and the amount of **3** employed then sets the fraction of **2** that is converted to active groups as defined by  $\alpha = [\text{3}]_0/[\text{2}]_0$ , and, in the present study,  $\alpha$  will be in the range of 0.25–1.0.

$$\bar{X}_n \approx \frac{[\text{M}]_0}{[\text{I}]_0} \quad (5)$$

$$D \approx \frac{\beta + 1}{\beta + \alpha} \quad (6)$$

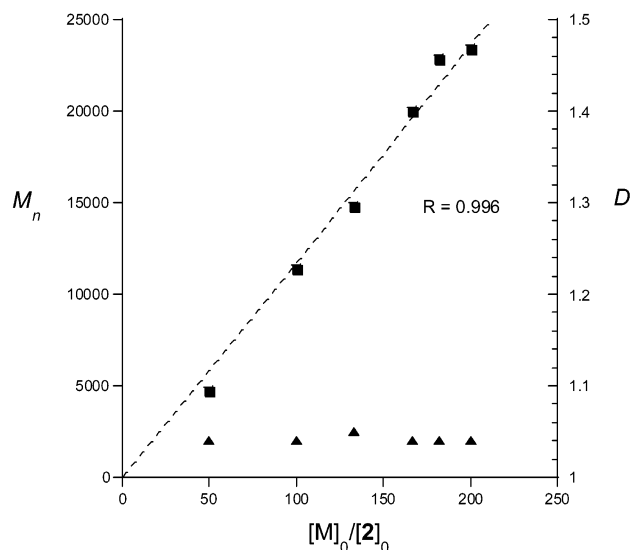
$$D \approx 1 + \frac{1}{\beta} = 1 + \frac{k_p}{k_{ex}} \quad (7)$$

Although conceptually simple, it is far from given that the scheme presented by eqs 2–4 will either provide an active living polymerization system or that narrow polydispersities will be obtained (i.e.,  $\beta \gg 1$ ). Schrock and co-workers<sup>9d</sup> previously found for their homogeneous Ziegler–Natta system that an excess of the neutral dimethyl zirconium precursor relative to the cationic zirconium initiator produced a dead system, presumably due to an equilibrium that lies far to the right of formation of a cationic methyl-bridged dinuclear complex, which is similar in structure to that of **4**, that is then inactive for polymerization. Marks and co-workers<sup>9b</sup> further found that, while producing an active, nonliving polymerization system,

(7) See, for instance: (a) Mallin, D. T.; Rausch, M. D.; Lin, Y. G.; Dong, S.; Chien, J. C. W. *J. Am. Chem. Soc.* **1990**, *112*, 2030–2031. (b) Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217–219. (c) Volkis, V.; Nelkenbaum, E.; Lisovskii, A.; Hasson, G.; Semiat, R.; Kapon, M.; Botoshansky, M.; Eishen, Y.; Eisen, M. S. *J. Am. Chem. Soc.* **2002**, *125*, 2179–2194.

(8) (a) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 958–959. (b) Jayaratne, K. C.; Keaton, R. J.; Henningsen, D. A.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 10490–10491. (c) Keaton, R. J.; Jayaratne, K. C.; Fettinger, J. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 12909–12910. (d) Keaton, R. J.; Jayaratne, K. C.; Henningsen, D. A.; Koterwas, L. A.; Sita, L. R. *J. Am. Chem. Soc.* **2001**, *123*, 6197–6198. (e) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2001**, *123*, 10754–10755.

(9) (a) Bochmann, M.; Lancaster, S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634–1637. (b) Chen, Y. X.; Stern, C. L.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 12451–12452. (c) Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842–857. (d) Mehrkhodavandi, P.; Bonitatebus, P. J.; Schrock, R. R. *J. Am. Chem. Soc.* **2000**, *122*, 7841–7842. (e) Vollmerhaus, R.; Rahim, M.; Tomaszewski, R.; Xin, S.; Taylor, N. J.; Collins, S. *Organometallics* **2000**, *19*, 2161–2169.



**Figure 1.** Dependence of poly(1-hexene)  $M_n$  (■) and  $D$  ( $M_w/M_n$ ) (▲) values on  $[M]_o/[2]_o$  at constant  $[M]_o = 0.50$  M and  $[3]_o = 2.5$  mM and at full monomer conversion.  $M_n$  and  $D$  ( $M_w/M_n$ ) values were obtained by GPC and are reported relative to polystyrene standards.

their cationic methyl-bridged dinuclear complex provided broader polydispersities relative to mononuclear cationic initiators, possibly due to slow dissociation and initiation. Fortunately, as the experimental data presented in Figure 1 attest, with **1–4**, all of the critical rate and equilibrium constants appear to be of the proper magnitude for degenerative transfer living Ziegler–Natta polymerization to occur as envisioned.<sup>10</sup> Specifically, as shown in this figure, not only was the number average molecular weight value,  $M_n$  ( $=\bar{X}_n \cdot$  formula weight of monomer), of poly(1-hexene), at full monomer conversion, found to be inversely proportional in a linear fashion to  $[2]_o$  as expected from eq 5 (keeping both  $[M]_o$  and  $[3]_o$  constant), but for each  $[M]_o/[2]_o$  ratio, a  $D$  value of  $\leq 1.05$  (as determined from  $M_w/M_n$ ) was obtained, indicating that both conditions,  $\beta \gg 1$  and  $\beta \gg \alpha$ , are being met. Indeed, from the data in Figure 1 and eq 7, the value of  $\beta$  would appear to be in the range of 25–30, assuming no chain termination.

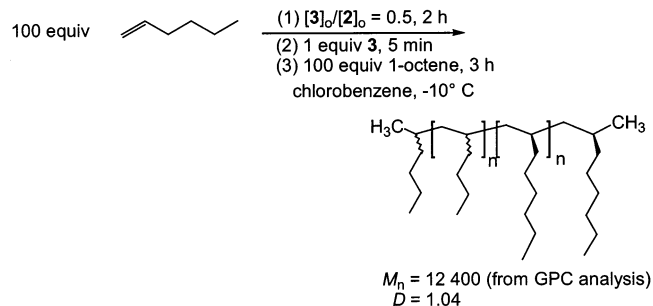
Demonstration of degenerative transfer living Ziegler–Natta polymerization using substoichiometric amounts of the borate **3** relative to the neutral dimethyl complex **2** becomes of potential technological value upon examination of the polymer microstructures that are obtained from the process. As stated, polymerization of 1-hexene using pure **1** is isospecific,<sup>8</sup> whereas with ratios of  $[3]_o/[2]_o < 1$ , loss of stereocontrol is now observed as exemplified by the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra for poly(1-hexene) that are presented in Figure 2, where the material produced under degenerative transfer conditions,  $[3]_o/[2]_o = 0.5$ , is now only iso-rich at best with a % mm triad content of about 45–50% (cf., % mm = 25% for a pure atactic microstructure).<sup>11</sup> Indeed, the influence on stereocontrol of a small amount of **2** being present during propagation cannot be overstated. For example,

(10) Full experimental details are provided in the Supporting Information.

(11) The microstructure of this material is most likely that of an isotactic stereoblock with fairly short block lengths. Unfortunately, the small  $^{13}\text{C}$  NMR chemical shift dispersion of the pentad stereocenters for the C3 resonance of poly(1-hexene) does not allow us to make a quantitative microstructural analysis, see: Asakura, T.; Demura, M.; Nishiyama, Y. *Macromolecules* **1991**, *24*, 2334–2340. Full microstructural analyses of other polyolefins prepared under degenerative transfer conditions are currently in progress.

even with  $[3]_o/[2]_o = 0.91$ , a ratio that might commonly be employed to ensure complete consumption of the borate in a standard homogeneous Ziegler–Natta polymerization, one still observes a significant degradation of the perfect isotactic microstructure obtained in the absence of degenerative transfer. Where the utility of this observation comes into play then is in the development of a strategy for the production of stereoblock polymers and copolymers of narrow polydispersity and tunable stereoblock length that involves simply turning “on” and “off” degenerative transfer after each successive monomer addition (i.e.,  $[3]_o/[2]_o < 1$  and  $[3]_o/[2]_o \geq 1$ , respectively). As a proof-of-concept that is shown in Scheme 2, 100 equiv of 1-hexene was first polymerized at  $-10$  °C in chlorobenzene under standard conditions using  $[3]_o/[2]_o = 0.5$  (on-state) to produce a living poly(1-hexene) block with a calculated  $\bar{X}_n$  ( $=[\text{1-hexene}]_o/[2]_o$ ) value of 50 that hereafter will be referred to as being “atactic” for convenience sake. Addition of 1 equiv of **3**, relative to the first amount of **3** employed, then served to selectively demethylate the remaining methyl groups of the dormant chains [i.e.,  $[3]_o/[2]_o$  now equal to 1 (off-state)],<sup>12</sup> after which time, 100 equiv of 1-octene was added to produce an isotactic poly(1-octene) block which is once again calculated to have a  $\bar{X}_n$  value of 50. After standard acidic quenching and isolation of the atactic-poly(1-hexene)-*b*-isotactic-poly(1-octene) stereoblock copolymer, GPC analysis shown in Figure 3 revealed a monomodal molecular weight distribution with  $M_n = 12\,400$  (cf.,  $M_n(\text{calc}) = 9\,800$ ) and  $D = 1.04$ . Further, the inverse-gated  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum shown in Figure 4 not only confirmed the expected stereochemical microstructures, but it provided a near 1:1 integrated ratio of the two polyolefin blocks, confirming that the blocks were essentially identical in length as designed. In the present case, two different  $\alpha$ -olefins

#### Scheme 2

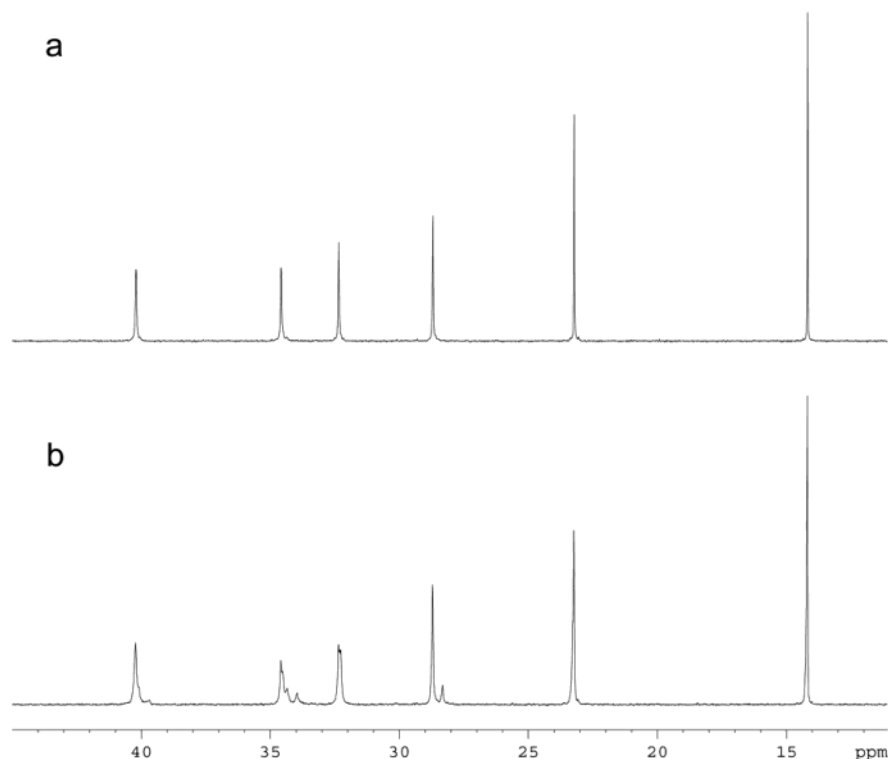


were used to aid in structure verification of this proof-of-concept; however, extension of this strategy for the controlled synthesis of homopolymer stereoblock materials that are expected to possess properties of technological interest (e.g., as thermoplastic elastomers perhaps<sup>7</sup>) is straightforward.

Mechanistic details of the degenerative transfer process and the origin of associated loss of stereocontrol during propagation are of interest, and, therefore, to aid in these studies, the isobutyl derivative,  $\text{Cp}^*\text{Zr}(\text{Me})(i\text{-Bu})[\text{N}(t\text{-Bu})\text{C}(\text{Me})\text{N}(\text{Et})]$  (**5**), which is stable toward  $\beta$ -hydride elimination of the isobutyl group,<sup>13</sup> was prepared as a neutral model for a dormant polymer chain end,

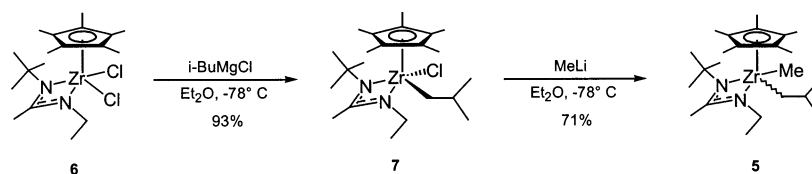
(12) Chemoselective demethylation using borate **3** has been observed for a series of  $\text{Cp}^*\text{ZrMe}[\text{N}(t\text{-Bu})\text{C}(\text{Me})\text{N}(\text{Et})]$  derivatives, an example of which is also detailed in the present study (Keaton, R. J.; Harney, M. B.; Sita, L. R., manuscript in preparation).

(13) Keaton, R. J.; Koterwas, L. A.; Fetters, J. C.; Sita, L. R. *J. Am. Chem. Soc.* **2002**, *124*, 5932–5933.

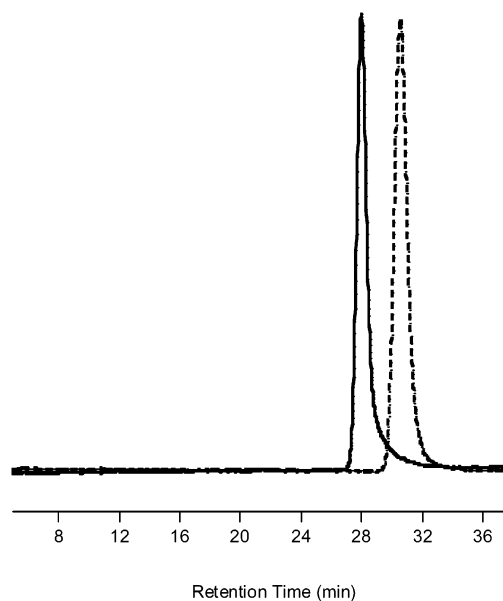


**Figure 2.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, chloroform- $d_1$ , 25 °C) spectra of poly(1-hexene) prepared using (a)  $[3]_o/[2]_o = 1$  and (b)  $[3]_o/[2]_o = 0.5$ .

### Scheme 3



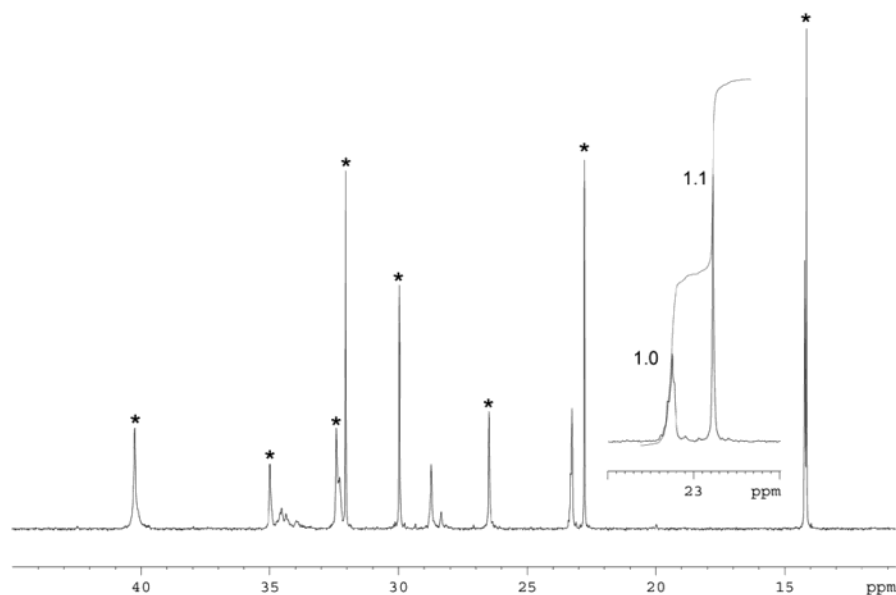
and as a precursor to a cationic model for an active propagating species. As shown in Scheme 3, compound **5** was conveniently prepared from the dichloro starting material **6** through a stepwise procedure that proceeds through the isobutyl, chloride derivative **7** as an intermediate. Interestingly, **7** was shown by  $^1\text{H}$  NMR spectroscopy to be configurationally stable with respect to amidinate “ring-flipping”<sup>14</sup> on the NMR time scale above room temperature, and X-ray crystallography served to establish the configuration of the zirconium center as that depicted in Scheme 3 (i.e., with the chloro group positioned on the same side as the *N*-*tert*-butyl acetamidinate substituent).<sup>12</sup> In contrast, although a crystal structure obtained for **5** previously revealed the same configurational arrangement as **7**, an apparent static  $^1\text{H}$  NMR spectrum of this complex taken at room temperature indicated that two diastereomers of **5** exist in solution in a 4:1 ratio (see Supporting Information from ref 13). To determine whether these diastereomers are actually interconverting on the NMR time scale through amidinate ring-flipping according to Scheme 4, the zirconium-bonded methyl group in **5** was isotopically enriched with  $^{13}\text{C}$  (99%), hereafter referred to as  $^{13}\text{CH}_3$ -labeled **5**, and the two well-resolved  $^{13}\text{C}$  NMR resonances for the diastereomeric zirconium-bonded methyl groups,  $\text{Me}_a$  and  $\text{Me}_b$ , were subjected to a 2D  $^{13}\text{C}\{^1\text{H}\}$  EXSY NMR



**Figure 3.** GPC analysis of *atactic*-poly(1-hexene)-*b*-*isotactic*-poly(1-octene) (solid trace) and an aliquot of the *atactic* poly(1-hexene) block formed before addition of the 1-octene monomer (dashed trace).  $D = 1.04$  for both polymers.

experiment.<sup>15</sup> Surprisingly, it was found that, even at  $-10$  °C, the interconversion of **5a** and **5b** through amidinate ring-flipping is a facile process as indicated by the magnitude of the cross-

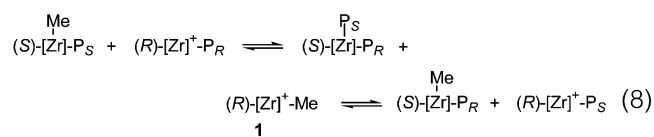
(14) (a) Sita, L. R.; Babcock, J. R. *Organometallics* **1998**, *17*, 5228–5230. (b) Koterwas, L. A.; Fettingner, J. C.; Sita, L. R. *Organometallics* **1999**, *18*, 4183–4190.



**Figure 4.** Inverse-gated  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, chloroform- $d_1$ , 25 °C) spectrum of *atactic*-poly(1-hexene)-*b*-*isotactic*-poly(1-octene).  $^{13}\text{C}$  NMR resonances for the isotactic poly(1-octene) block are marked with an asterisk (\*).

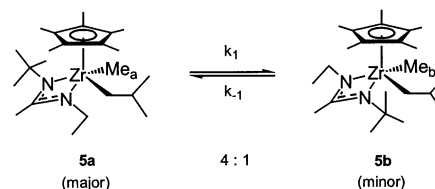
peaks observed in the 2D  $^{13}\text{C}\{^1\text{H}\}$  EXSY NMR spectrum that is reproduced in Figure 5. Furthermore, from an analysis of the magnitude of these cross-peaks as a function of mixing time,<sup>15</sup> values for  $k_1$  and  $k_{-1}$  of 0.6 and 2.5  $\text{s}^{-1}$ , respectively, which are the associated rate constants of this zirconium-centered epimerization process, could be obtained. In comparing the values of  $k_1$  and  $k_{-1}$  to the previously determined rate constant for propagation for 1-hexene polymerization initiated by **1** that was obtained under pseudo first-order conditions<sup>8d</sup>, that is,  $k_{\text{obs}}/[\mathbf{1}]_0 = 0.354 \text{ M}^{-1} \text{ s}^{-1}$ , it is obvious that the rate of epimerization of **5** is faster than the rate of propagation even in the presence of a large concentration of monomer. It should also be noted that from the estimated value of  $\beta$  obtained for Figure 1 using eq 7, the rate of epimerization of **5** will still be far greater than the rate of methyl group exchange that occurs between dormant and active end groups during degenerative transfer. Thus, it would appear that if a similarly fast rate of epimerization for dormant methyl, polymeryl zirconium complexes, that is,  $\text{Me}-[\text{Zr}]-\text{P}_j$ , can be established, then a claim can be made that the origin of the loss of stereocontrol that occurs during degenerative transfer polymerization has been found.

Before the configurational stability of the dormant polymer end groups was addressed, a study was undertaken to determine whether stereochemical integrity could be lost during degenerative transfer polymerization through possible rapid methyl, polymeryl exchange between enantiomeric dormant and active centers according to eq 8. As shown, if this process were to



occur, the additional equivalent of **1** produced would reasonably be able to initiate the growth of a new polymer chain. To rule out this mechanism, it was first determined that **3** can selectively demethylate **5** according to Scheme 5 to produce the stable

**Scheme 4**

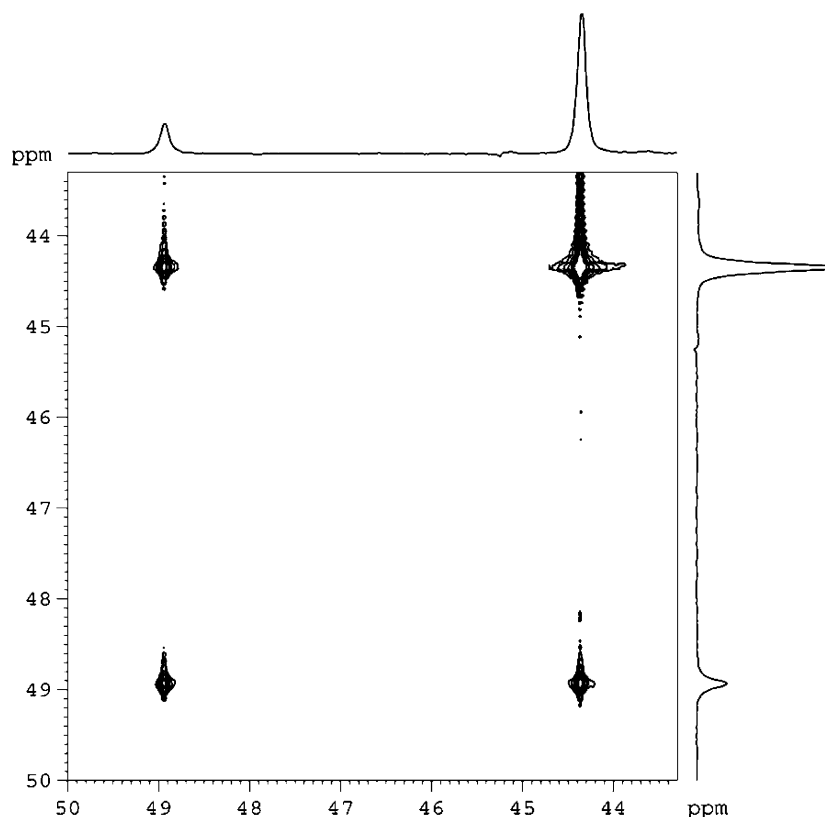


isobutyl cationic complex **8** in high yield as the single product as determined by  $^1\text{H}$  NMR spectroscopy. The NMR data also revealed that, although a **5a/5b** mixture exists in solution, a single diastereomer of **8** is produced which is engaged in a strong  $\beta$ -hydrogen agostic interaction with the zirconium center as evidenced by both the upfield chemical shift and the reduced  $^1J(^{13}\text{C}-^1\text{H})$  coupling constant for the  $\beta$ -hydrogen of the isobutyl group (cf.,  $-0.27 \text{ ppm}$  and  $92 \text{ Hz}$ , respectively).<sup>16</sup> In keeping with prior observations of both **1** and living polymers derived from **1**,<sup>8e</sup> cationic **8** was shown to be configurationally stable on the NMR time scale at both  $-10$  and  $25$  °C as determined by the absence of cross-peaks between the separate resonances for the two diastereotopic methyl groups of the isobutyl substituent in 2D  $^1\text{H}$  EXSY NMR spectra recorded at these two temperatures with a range of mixing times. Finally, a crystal structure obtained for **8** confirmed its structure as being that presented in Scheme 5.<sup>12</sup>

With **5** and **8** in hand, a series of polymerization studies were conducted. To begin, it was first proven that **8** can function in the same capacity as **1** in being a highly active initiator for the isospecific living polymerization of 200 equiv of 1-hexene (cf.,  $M_n = 21\,400$ ,  $D = 1.03$ ). Next, it was demonstrated that polymerization of 80 equiv of 1-hexene conducted with a 1:1 mixture of **5** and **8** (i.e.,  $[\mathbf{3}]_0/[\mathbf{5}]_0 = 0.5$ ) proceeded with degenerative transfer to provide atactic poly(1-hexene) of narrow polydispersity ( $D = 1.04$ ) possessing a  $\bar{X}_n$  value similar to that expected had a 1:1 ratio of **1** and **2** been used for initiation [i.e.,  $\bar{X}_{n(\text{calc})} = 40$ ]. In other words, replacement of the methyl

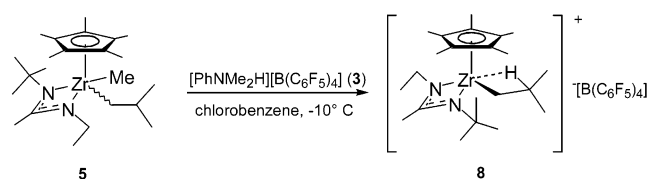
(15) Perrin, C. L.; Dwyer, T. J. *Chem. Rev.* **1990**, *90*, 935–967.

(16) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1–124.



**Figure 5.** 2D  $^{13}\text{C}\{^1\text{H}\}$ EXSY NMR (100 MHz, chlorobenzene- $d_5$ ,  $-10^\circ\text{C}$ ) spectrum of the diastereotopic methyl resonances for the  $^{13}\text{CH}_3$ -labeled **5a/5b** mixture obtained with a mixing time of 0.4 s.

#### Scheme 5

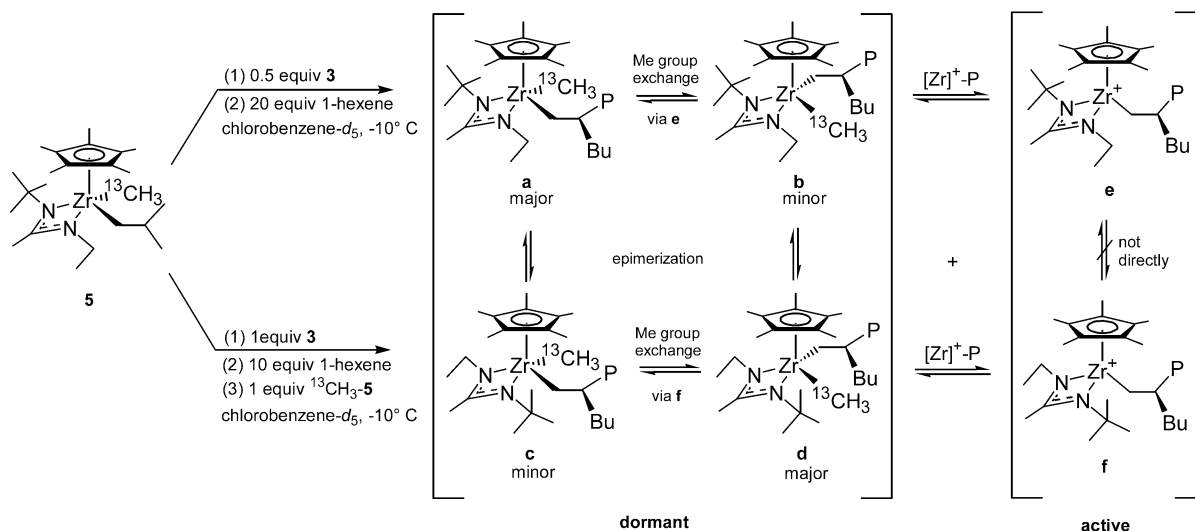


group in **1** and **2** by the isobutyl group in **5** and **8** had no apparent effect on the overall degenerative transfer process in terms of initiation, exchange, and propagation according to eqs 2–4. Importantly, carrying out this same polymerization now using  $^{13}\text{CH}_3$ -labeled **5** produced the same expected atactic poly(1-hexene) material for which a side-to-side comparison of  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra obtained for this material, and that prepared using unlabeled **5**, revealed that no  $^{13}\text{CH}_3$ -label had been incorporated into poly(1-hexene) methyl end groups. Thus, this last experiment would appear to eliminate from further mechanistic consideration any polymeryl group exchange process that would generate **1** during the course of polymerization, such as that depicted in eq 8.

To provide evidence that methyl group exchange is occurring during degenerative transfer polymerization according to eq 4, additional NMR studies were conducted with  $^{13}\text{CH}_3$ -labeled **5** and **8**. First, it should be noted that while  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of a 1:1 mixture of **5** and **8** both provided evidence for a dynamic exchange process involving these two species as revealed by the appearance of exchange-broadened resonances, no evidence for a discrete methyl-bridged structure, such as **4**, could be obtained even down to the temperature limit of the chlorobenzene- $d_5$  solvent which is ca.  $-40^\circ\text{C}$ . Further, attempts to grow crystals of a methyl-bridged dinuclear species from a

1:1 solution of **5** and **8** provided only crystalline **8**.<sup>12</sup> Together, these results suggest that the methyl-bridged dinuclear species proposed as an intermediate in degenerative transfer (i.e., **4**) does not represent the thermodynamically favored resting state of the system. The next two NMR experiments involving **5** and **8** are schematically outlined in Scheme 6, and they provide further support for this conclusion. As shown, the first of these involved the addition of 20 equiv of 1-hexene to a 1:1 mixture of  $^{13}\text{CH}_3$ -labeled **5** and **8** [ $\bar{X}_n(\text{calc}) = 10$ ] at  $-10^\circ\text{C}$  to produce a mixture of cationic (active) atactic-polymeryl zirconium and neutral (dormant) methyl, atactic-polymeryl zirconium species, the latter of which gives rise to four  $^{13}\text{C}$ -labeled methyl resonances, two major and two minor, in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum between 44 and 50 ppm as shown in Figure 6a. As presented in Figure 6b, these same four methyl resonances were produced in about the same ratios by first polymerizing 10 equiv of 1-hexene in an isotactic fashion using only **8** as the initiator, followed by the addition of 1 equiv of  $^{13}\text{CH}_3$ -labeled **5** at  $-10^\circ\text{C}$  and recording the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum within minutes thereafter. As depicted in Scheme 6, we assign these four methyl resonances to the four possible diastereomers, **a–d**, expected for the dormant methyl, polymeryl zirconium complexes with the fine structure now appearing for the narrower resonances in Figure 6b most likely originating with chain length effects due to the small  $\bar{X}_n$  value used in the experiment. Significantly, this assignment supports the two conclusions that: (1) diastereomeric dormant end groups are produced and exist during degenerative transfer polymerization and (2) formation of a neutral methyl, polymeryl zirconium end group results in rapid metal-centered epimerization. Indeed, to verify that the four proposed methyl, polymeryl zirconium species **a–d** are all

Scheme 6

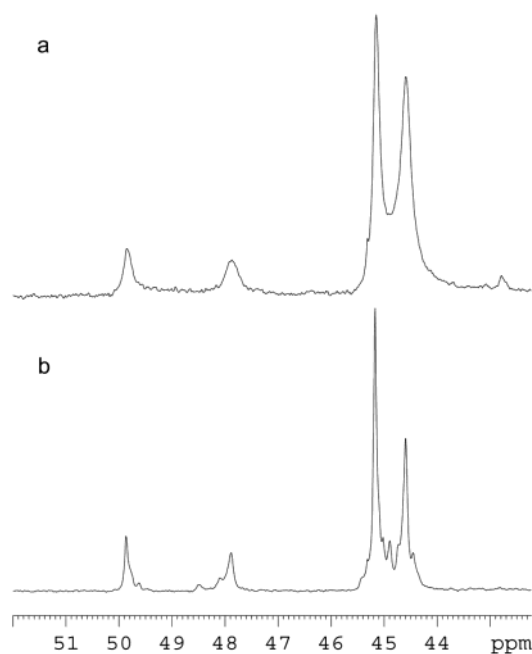


involved in dynamic exchange with one another at  $-10^\circ\text{C}$ , a 2D  $^{13}\text{C}\{^1\text{H}\}$  EXSY NMR experiment was conducted which revealed the presence of cross-peaks between all of the resonances as presented in Figure 7. In this regard, it is important to point out that both methyl group exchange and metal-centered epimerization are required for all four species to be in equilibrium with one another; methyl group exchange alone would result in two sets of equilibrated diastereomers (i.e., **a** and **b**; **c** and **d**) that do not interconvert between the sets (see Scheme 6). Another way to look at this is to consider that, if metal-centered epimerization of the methyl, polymeryl zirconium end groups were not occurring along with methyl group exchange that is mediated by  $[\text{Zr}]^+\text{-P}$ , the lower reaction process of Scheme 6 would only produce one set of dormant methyl, polymeryl diastereomers and one active cationic species (i.e., **a**, **b**, and **e** or **c**, **d**, and **f**) rather than the complete set that is

observed. As a final proof then that the presence of methyl group exchange also provides an indirect pathway for metal-centered epimerization of the active cationic polymeryl zirconium species, which have previously been found to be configurationally stable at  $-10^\circ\text{C}$  in the absence of methyl group exchange for extended periods of time,<sup>8e</sup> 10 equiv of 1- $^{13}\text{C}$ -1-dodecene was first polymerized with **1** to produce a cationic living isotactic polymer (LP-**1**) that displays a single  $^{13}\text{C}$  NMR resonance for the zirconium-bound  $\alpha$ -carbon of the polymeryl group as shown in Figure 8a and as observed previously.<sup>8e</sup> In relation to Scheme 6, this single resonance then represents that for a single active cationic species (i.e., either **e** or **f**). Upon the addition of 1 equiv of **5** to LP-**1** at  $-10^\circ\text{C}$ , followed by chemoselective demethylation using 1 equiv of **3**, a  $^{13}\text{C}$  NMR spectrum recorded within minutes thereafter revealed that metal-centered epimerization had occurred to produce, as shown in Figure 8b, a near 1:1 ratio of two resonances for two diastereomers of cationic LP-**1** (i.e., **e** and **f** of Scheme 6) that presumably arise as the result of methyl group transfer, epimerization of the methyl, polymeryl species, and then methyl group back transfer to regenerate the cationic species. Once again, it must be pointed out that methyl group exchange alone between neutral and cationic species is not sufficient for the appearance of the two diastereomers, **e** and **f**, of LP-**1**.

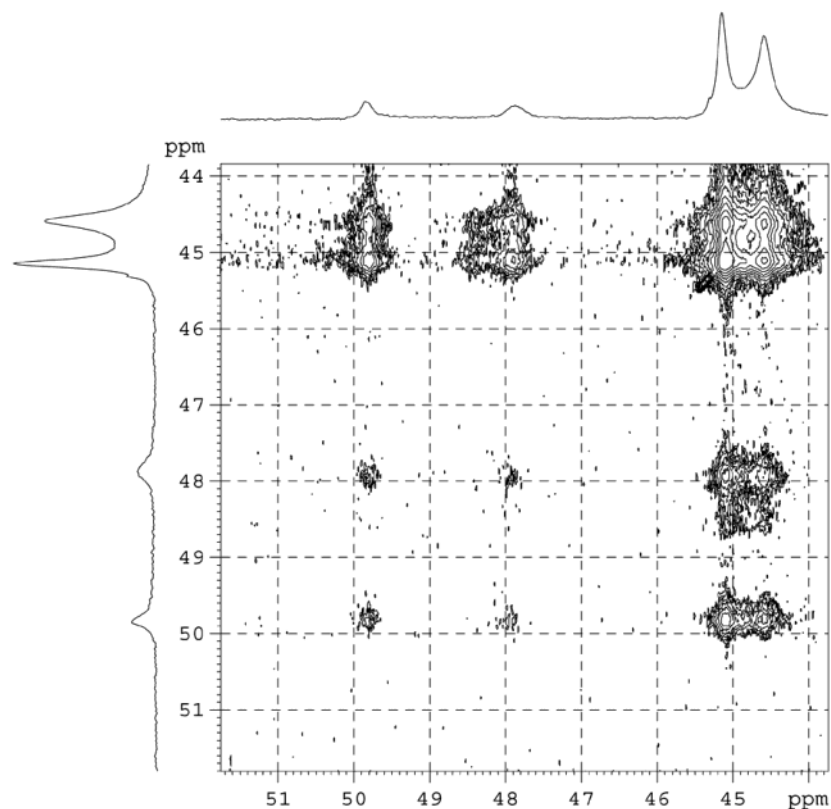
## Conclusions

The present studies document a degenerative transfer living Ziegler–Natta polymerization process that involves rapid and reversible methyl group exchange between cationic (active) and neutral (dormant) end groups that can produce polyolefin materials of narrow polydispersity. A potential practical benefit of this degenerative transfer living process is that, in principle, only a small amount of the borate **3** (often referred to as the “cocatalyst” in conventional homogeneous Ziegler–Natta polymerizations which utilize a 1:1 B:Zr ratio) is required to initiate near simultaneous chain growth of all of the neutral zirconium centers of a specified amount of **2**. Further, because a wide range of pentamethylcyclopentadienylzirconium acetamidates bearing alkyl groups possessing  $\beta$ -hydrogens have now been found to be stable toward  $\beta$ -hydride elimination/abstraction,<sup>12,13</sup> the long-term storage of isolated methyl, poly-

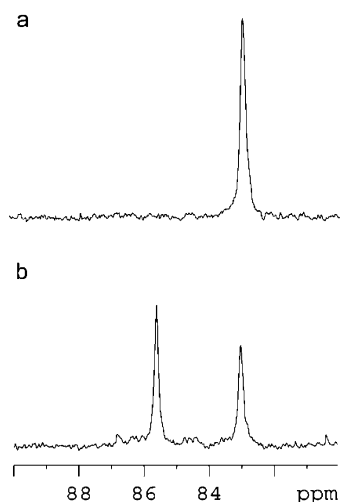


**Figure 6.** Partial  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, chlorobenzene- $d_5$ ,  $-10^\circ\text{C}$ ) spectrum of methyl, polymeryl dormant species **a–d** prepared according to (a) upper reaction sequence of Scheme 6 and (b) lower reaction sequence of Scheme 6.





**Figure 7.** 2D  $^{13}\text{C}\{^1\text{H}\}$ EXSY NMR (125 MHz, chlorobenzene- $d_5$ ,  $-10\text{ }^\circ\text{C}$ ) spectrum of methyl, polymeryl dormant species **a–d** of Figure 6a recorded with a mixing time of 0.1 s.



**Figure 8.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, chlorobenzene- $d_5$ ,  $-10\text{ }^\circ\text{C}$ ) spectrum of (a) LP-**1** and (b) same as (a) but after addition of 1 equiv of **5** followed by addition of 1 equiv of **3**.

meryl zirconium complexes that can reengage in active Ziegler–Natta polymerization once an amount of **3** has been added should be possible. In this sense, an “immortal” Ziegler–Natta polymerization process can be envisioned in the manner described by Inoue and co-workers.<sup>17</sup> Finally, though, documentation that these methyl, polymeryl zirconium complexes

undergo epimerization at rates that are far greater than propagation to give rise to a loss of stereocontrol provides the basis for a unique strategy by which well-defined monomodal stereoblock polyolefins of narrow polydispersity and tunable block length can be produced. Access to a range of these stereoblock polyolefins whose specific microstructures are known with respect to their relative stereoblock lengths should help to build structure/property relationships that are fruitful for the design of new generations of polyolefin materials with technologically important properties. Present studies are now directed toward extending the concept of switching degenerative transfer “on” and “off” to produce well-defined tri- and multiblock stereoblock microstructures, and the results of these efforts will be reported in due course.

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**Supporting Information Available:** Full experimental details of polymerization studies, polymer synthesis, and NMR studies (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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