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Direct Methyl Group Exchange between Cationic Zirconium Ziegler−Natta Initiators and Their Living Polymers: Ramifications for the Production of Stereoblock Polyolefins[†]

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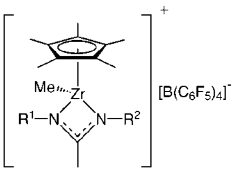
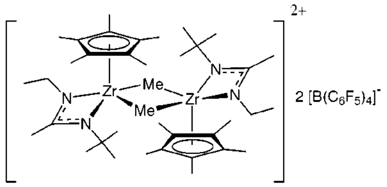
Given their technological potential, stereoblock polyolefins, i.e., those with adjoining blocks of differing polymer microstructure, have been the subjects of current interest.[1,2] One strategy employed to obtain such materials relies upon the use of mixtures of zirconocene catalysts that express different stereoselectivities during propagation (e.g., isotactic and atactic) so that a stereoblock microstructure will result if polymeryl transfer from one propagating species to another occurs.[2] In systems studied to date, a trialkylaluminum cocatalyst is added to act as the mediator for polymeryl transfer through zirconium−aluminum alkyl group exchange. Chien and co-workers,[2a] however, originally hypothesized that direct polymeryl transfer between two zirconocenium ions might also occur through an alkyl-bridged dimeric dication, but experimental evidence for such an intermediate was lacking at the time.[3] Brintzinger and co-workers,[2d] on the other hand, cited the lack of ^{13}C-labeled methyl group exchange between the corresponding neutral dimethyl zirconocene precatalysts as evidence against direct polymeryl transfer. Finally, while Collins and co-workers[4] have presented evidence in support of methyl group exchange between cationic zirconium initiators and their neutral dimethyl precursors, Marks and co-workers[5] have speculated that the mechanism for a similar exchange process in their system is possibly mediated by the counterion used.[6] Herein, we now present unequivocal evidence for direct methyl group exchange within a class of cationic zirconium Ziegler−Natta initiators represented by **1** and **2**.[7] We also document that methyl−polymeryl transfer is possible between these initiators and their corresponding living polymers. With documentation of these results, the foundations for a new strategy for the controlled production of well-defined stereoblock polyolefins are now established.



1: R^1 = Et, R^2 = ^{t}Bu
2: R^1 = R^2 = ^{i}Pr



(*R, S*) - **3**

The recent isolation and solid-state structural characterization of single crystals of the dication **3**,[7c] which represents the formal dimerization of **1** via the formation of two bridging methyl group interactions, prompted us to look for the possibility of methyl group exchange occurring in solution within this class of initiators. For this study, compounds **1** and **2** were selected since the steric environment around each of the zirconium metal centers is expected to be similar. Further, to greatly reduce the chance that any exchange is being mediated by a small, undetected amount of the neutral dimethyl precatalysts, **1** and **2** were generated each time by using a 10 mol % excess of the borate cocatalyst, $[Ph_3C][B(C_6F_5)_4]$. Finally, to report that exchange between these initiators had occurred, the precatalyst for ^{13}C-labeled **1** was prepared in high yield through carbodiimide insertion into (η^5-C_5Me_5)Zr($^{13}CH_3$)$_3$.[7]

Variable-temperature ^{1}H NMR (500 MHz, chlorobenzene-d_5) spectra taken of **1** and **2** revealed the following for both: (1) quantitative formation of the cationic initiator had occurred, (2) if a monomer−dimer equilibrium is present, it is very rapid on the NMR time scale down to the temperature limit of the solvent ($\sim$233 K), (3) ion-pair reorganization (i.e., site-isomerization[8]) is also a very facile process over the same temperature regime as evidenced by the lack of resonances for discrete diastereomeric ion-pairs, (4) racemization/epimerization of the metal center via amidinate-ring flipping,[9] on the other hand, is a *very slow process* on the NMR time scale, especially at 263 K, which is the temperature at which polymerizations employing **1** and **2** are performed, and finally, (5) both cationic complexes are stable in solution for extended periods of time, even at 298 K.[10] Importantly, as Figure 1a reveals, mixing of near equimolar amounts of ^{13}C-labeled **1** and **2** at 263 K resulted in rapid scrambling of the ^{13}C-labeled methyl groups between the two complexes. Given this apparent ease with which methyl group exchange occurs, we were immediately interested in determining whether a similar process was available to effect exchange between these initiators and their respective living polymers. As the ^{1}H NMR spectrum of Figure 1b shows, this indeed proved to be the case. More specifically, a living polymer derived from **2** (LP-**2**) was first prepared at 263 K by quantitatively polymerizing 15 equiv of 1-decene with **2**. Upon addition, at this temperature, of a solution containing 2 equiv of ^{13}C-labeled **1**, rapid methyl−polymeryl exchange occurred as supported by the appearance of a resonance for ^{13}C-labeled **2**. It is important to note that, in Figure 1b, the lack of a resonance for the ^{12}C-isotopomer of **2** is clear evidence that the original generation of **2** from the neutral dimethyl precatalyst and consumption of **2** in the formation of LP-**2** are both quantitative processes.

[†] Presented in part at the 221st ACS National Meeting, San Diego, March 2001.

(1) For stereoblock polymer formation via "oscillating" catalysts, see, for example: (a) Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217−219. (b) Lin, S.; Tagge, C. D.; Waymouth, R. M.; Nele, M.; Collins, S.; Pinto, J. C. *J. Am. Chem. Soc.* **2000**, *122*, 11275−11285.

(2) For stereoblock polymers derived from mixtures of two catalysts, see: (a) Chien, J. C. W.; Iwamoto, Y.; Rausch, M. D.; Wedler, W.; Winter, H. H. *Macromolecules* **1997**, *30*, 3447−3458. (b) Chien, J. C. W.; Iwamoto, Y.; Rausch, M. D. *J. Polym. Sci., Part A* **1999**, *37*, 2439−2445. (c) Przybyla, C.; Fink, G. *Acta Polym.* **1999**, *50*, 77−83. (d) Lieber, S.; Brintzinger, H. H. *Macromolecules* **2000**, *33*, 9192−9199.

(3) Chien and co-workers have also suggested that direct polymeryl exchange between enantiomeric pairs of propagating species can be a source of stereoerrors, see: Song, W.; Zhengtian, Y.; Chien, J. C. W. *J. Organomet. Chem.* **1996**, *512*, 131−140.

(4) (a) Li, Y.; Ward, D. G.; Reddy, S. S.; Collins, S. *Macromolecules* **1997**, *30*, 1875−1883. (b) Vollmerhaus, R.; Rahim, M.; Tomaszewski, R.; Xin, S.; Taylor, N. J.; Collins, S. *Organometallics* **2000**, *19*, 2161−2169.

(5) Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842−857.

(6) Cationic zirconium initiators and their neutral dimethyl precursors are known to form cationic methyl-bridged dinuclear species in which methyl groups can be reasonably expected to scramble, see ref 5 and the following: (a) Bochmann, M.; Lancaster, S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634−1637. (b) Mehrkhodavandi, P.; Bonitatebus, P. J.; Schrock, R. R. *J. Am. Chem. Soc.* **2000**, *122*, 7841−7842.

(7) (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.

(8) Ewen, J. A. *J. Mol. Catal. A: Chemistry* **1998**, *128*, 103−109 and references therein. (b) Giardello, M. A.; Eisen, M. S.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 12114−12129.

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

(10) Representative spectra are presented in the Supporting Information.

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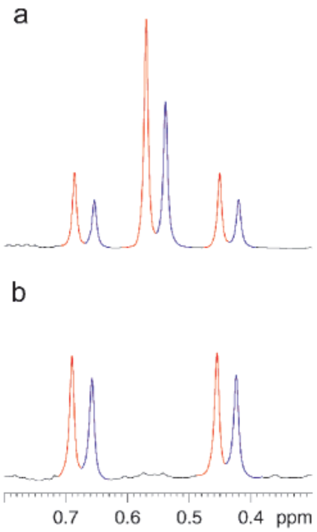


Figure 1. ^1H NMR (500 MHz, chlorobenzene-d_5, 263 K) spectra for the Zr-CH_3 region of (a) a near equimolar mixture of ^{13}C-labeled **1** (blue trace, δ 0.54 ppm, $^1J(^{13}C-^1H = 117$ Hz) and **2** (red trace, δ 0.57 ppm, $^1J(^{13}C-^1H = 118$ Hz) and (b) a mixture of LP-**2** and 2 equiv of ^{13}C-labeled **1**. Spectra were recorded within 30 min after mixing at 263 K.

Additional support and information regarding methyl−polymeryl group exchange within this class of initiators was obtained by performing a series of ^{13}C NMR experiments, the results of which are summarized in Figure 2. To begin, by utilizing 1-^{13}C-1-decene (15 equiv), LP-**1** and LP-**2** were first prepared and found to be stable at 263 K for at least 18 h. Importantly, as Figures 2a and 2b reveal, the formation of LP-**2** is nonstereospecific with respect to the microstructure of the polymer chain, while for LP-**1**, it is isospecific as expected on the basis of previously reported results.[7] It was also satisfying to observe that LP-**1**, prepared through direct polymerization of monomer, consists of a single set of enantiomeric propagating species as evidenced by the single resonance appearing at δ 82.3 ppm in Figure 2b. It is important to note, however, that in the absence of monomer, initially formed LP-**1** does eventually racemize at 263 K ($t_{1/2} \sim 8$ h) to produce a resonance at 85.0 ppm for the new diastereromeric pair. Figure 2c next shows that, upon addition of a solution containing 1 equiv of **2** to LP-**1**, *rapid transfer of a highly stereoregular polymer chain to a nonstereospecific propagating center has occurred*. In this spectrum, the resonance at δ 85.0 ppm for the diastereomeric living polymer of LP-**1** has once more appeared, and its formation may be due either to nonstereospecific back exchange between stereoregular LP-**2** and **1** to regenerate LP-**1** or to a racemization of LP-**1** that is catalyzed by generated **1** according to Scheme 1. Additional support for this latter mechanism was provided by the experiment of Figure 2d in which LP-**1** was now found to completely racemize within 30 min in the presence of **1**, presumably now via exchange rather than through amidinate ring-flipping.

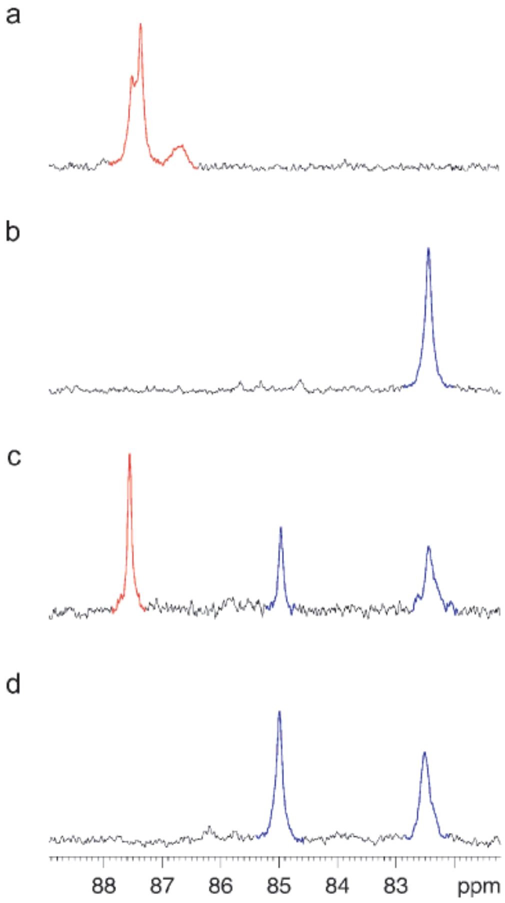
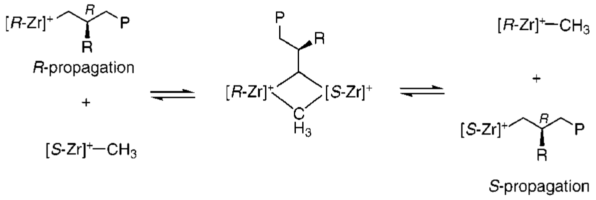


Figure 2. ^{13}C NMR (125 MHz, chlorobenzene-d_5, 263 K) spectra for the Zr-CH_2 region of (a) LP-**2**, (b) LP-**1**, (c) a mixture of LP-**1** and 1 equiv of **2**, and (d) a mixture of LP-**1** and 1 equiv of **1**. Spectra c and d were recorded 30 min after mixing.

Scheme 1



The experiments presented in Figure 2 provide the basis for a new strategy by which well-defined stereoblock polyolefins can possibly be produced. Namely, after equilibration between a living polymer and an added amount of initiator has occurred, the introduction of more monomer should now lead to production of, for example, an isotactic−atactic or pure isotactic stereoblock microstructure in cases exemplified by Figures 2c and 2d, respectively. Although these simple examples would produce mixtures of stereoblock and stereoregular polymers,[11] the possibility exists that, either through the design of ligand steric effects, which might be used to drive the exchange equilibrium exclusively to one side, or through the engineering of relative rates of propagation of the different species involved, pure stereoblock polymers of narrow PDI might be obtained. Such studies are currently under investigation.

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Supporting Information Available: ^1H NMR spectra of **1** and **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] Preliminary results show that multimodal materials resulting from competing living propagating species derived through exchange are indeed produced upon addition of more monomer. Efforts to isolate pure stereoblock polymers from these mixtures through preparative GPC are now in progress.