Dramatic Enhancement of Activities for Living Ziegler−Natta Polymerizations Mediated by “Exposed” Zirconium Acetamidinate Initiators: The Isospecific Living Polymerization of Vinylcyclohexane

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In addition to high activities and stereoselectivities, it is desirable to have homogeneous Ziegler−Natta catalysts that can extend the range of polyolefin materials that are obtainable from readily available monomers. Commercially, it is of further interest if these catalysts can be procured in as few steps as possible, and from “nonexotic” starting materials. Recently, we reported that initiators derived from mono-demethylation of the half-sandwich zirconium acetamidinate precatalysts, $(\eta^5\text{-}C_5R_5)ZrMe_2[N(R^1)C(Me)N(R^2)]$ (R = Me) (**1**), can mediate the stereospecific living polymerization of linear α-olefins and the living cyclopolymerization of nonconjugated dienes at −10 °C in chlorobenzene.[1] Herein, we now report extension of these results with the family of cyclopentadienyl derivatives **2** (R = H in **1**) which can be used to carry out the living polymerization of “difficult” monomers, such as vinylcyclohexane (VCH), including the synthesis of well-defined block copolymers containing high T_g poly(vinylcyclohexane) (PVCH) segments.[2,3] We further show that these precatalysts can be prepared in one step from inexpensive, commercially available precursors. As homopolymers and block copolymers that are derived, or formally derived, from the Ziegler−Natta polymerization of vinylcycloalkanes may prove of technological value,[4,5] the present results serve to open the door to an important new area for polymer engineering.

The synthesis of **2** by carbodiimide insertion[1a] into a $Zr-C_{Me}$ bond of $CpZrMe_3$ ($Cp = \eta^5\text{-}C_5H_5$) is complicated by the chemical and thermal sensitivity of this compound which appears to have never been isolated in pure form. Indeed, in our hands, methylation of $CpZrCl_3$ with a slight excess of methyllithium[6] invariably leads to decomposition of the initially formed methylated product. Fortunately, a critical solution to this problem was found by coupling strict control of the amount of MeLi employed with an excess of trimethylsilyl chloride that serves to “quench” the methylation reaction prior to the addition of a carbodiimide in a one-pot procedure conducted according to Scheme 1.[7] Importantly, this route to **2** occurs in high yield to provide a crude material that contains few byproducts that must be separated. Compounds **2a**−**c** were found to be indefinitely stable at room temperature, and of low configurational stability in solution in the case of chiral C_1-symmetric **2c**.[8] Finally, the solid-state structures of **2a** and **2c**, as obtained by X-ray crystallography, revealed no surprises in terms of any unusual geometrical parameters being observed.[7]

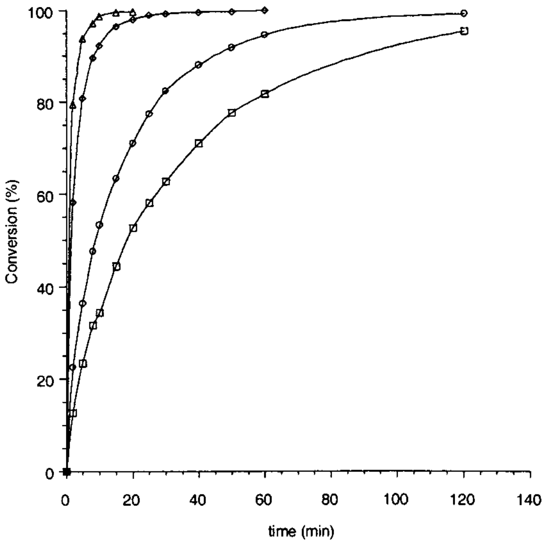
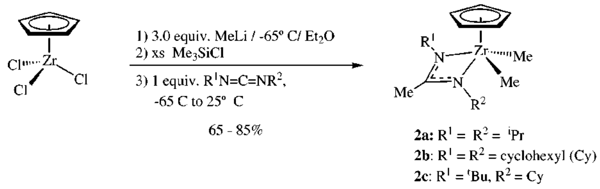


Figure 1. Monomer conversion as a function of time for 1-hexene using (△) **2a**, (◇) **2b** and (○) **2c** and for (□) VCH using **2b**. Solid lines are guides for the eye.

Scheme 1



As can be seen by Figure 1, catalysts derived from **2a**−**c** and the borate cocatalyst, $[PhNMe_2H][B(C_6F_5)_4]$, were found to be extremely active for the polymerization of 1-hexene at −10 °C. Further, in each case, polymerizations were found to go to completion, and M_n and M_w/M_n values similar to those obtained for the living system derived from **1a** (R^1 = Et, R^2 = ^{t}Bu)[1a] were observed (see Table 1). Regarding kinetic data, due to the very rapid consumption of monomer observed for **2a** and **2b**, reliable numbers could not be obtained for polymerizations employing these precatalysts (i.e., 79% monomer conversion within 2 min in the case of **2a**). However, for the **2c** system, the rate of propagation was now amenable for kinetic analysis and a plot of $\ln([M_0]/[M_t])$ versus time (not shown) was found to be linear (R = 0.993), which is consistent with a living system in which the concentration of propagating species remains constant.[9] Quantitatively, from these data, a value of 0.051 min^{-1} could be extracted for the apparent rate constant for propagation, k_{obs}, and this is similar in magnitude to the k_{obs} of 0.057 min^{-1} recorded for the

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[1] (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*, 10490−10491.

[2] To the best of our knowledge, only one report of the homopolymerization of VCH using a homogeneous catalyst has appeared (activity = 0.017 $kg\cdot mol_{cat}^{-1}\cdot h^{-1}$), see: Longo, P.; Grassi, A.; Grisi, F.; Milione, S. *Macromol. Rapid Commun.* **1998**, *19*, 229−233 (footnote a).

[3] For the properties of homopolymers and block copolymers of PVCH as derived from the hydrogenation of polystryene precursor polymers, see: (a) Gehlsen, M. D.; Bates, F. S. *Macromolecules* **1993**, *26*, 4122−4127. (b) Gehlsen, M. D.; Bates, F. S. *Macromolecules* **1994**, *37*, 3611−3618. (c) Hamley, I. W.; Fairclough, J. P. A.; Bates, F. S.; Ryan, A. J. *Polymer* **1998**, *39*, 1429−1437.

[4] For potential technological applications of PVCH, see: (a) Nishikawa, Y.; Murakami, S.; Kohjiya, S.; Kawaguchi, A. *Macromolecules* **1996**, *29*, 5558−5566. (b) Tullo, A. *Chem. Eng. News* **1999**, *77(51)*, 14−15.

[5] For the structures and properties of crystalline isotactic poly(vinylcycloalkanes) prepared via heterogeneous Ziegler−Natta polymerization, see: (a) Natta, G.; Corradini, P.; Bassi, I. W. *Makromol. Chem.* **1959**, 247−248. (b) Noether, H. D. *J. Polym. Sci., Part C: Polym. Lett.* **1967**, *16*, 725−753. (c) Ammendola, P.; Tancredi, T.; Zambelli, A. *Macromolecules* **1986**, *19*, 307−310. (d) Endo, K.; Otsu, T. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 679−683.

[6] Giannini, U.; Cesca, S. *Tetrahedron Lett.* **1960**, *14*, 19−20.

[7] Details are provided in the Supporting Information.

[8] For $R^1 \neq R^2$, racemization in these complexes proceeds via a facile amidinate “ring-flipping” process, see: Koterwas, L. A.; Fettinger, J. C.; Sita, L. R. *Organometallics* **1999**, *18*, 4183−4190.

[9] Matyjaszewski, K. *J. Phys. Org. Chem.* **1995**, *8*, 197−207.

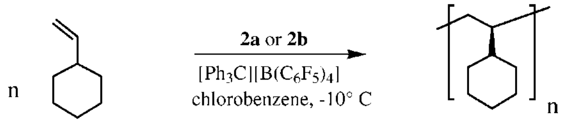
10.1021/ja0057326 CCC: $20.00

Table 1. GPC Data for Polymers Prepared from **1a** and **2a**−**c**[a]

entry	precatalyst	monomer	M_n	M_w/M_n
1	**1a**	Hex	24 600	1.05
2	**2a**	Hex	20 800	1.03
3	**2b**	Hex	23 500	1.06
4	**2c**	Hex	21 700	1.09
5	**2b**	VCH	20 400	1.10
6	**2b**	VCH(39),Hex(154),VCH(39)[b]	24 400	1.08

[a] GPC data were collected at 40 °C in THF using a 1.1 mL/min flow rate and polystyrene standards. Polymerizations were conducted using equimolar (25 μmol) amounts of precatalyst and either $[PhNMe_2H][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$ and 200 equiv of monomer at −10 °C in chlorobenzene: total volume, 10 mL. [b] Numbers in parentheses are monomer equivalents.

Scheme 2



1a system under identical conditions ($k_{obs}/[Zr]_o = 0.317$ and 0.354 $M^{-1}\,s^{-1}$ for **2c** and **1a**, respectively).

With regard to living character, the above kinetic data, along with the GPC data of Table 1, support the view that polymerizations employing **2a**−**c** are indeed living. These results stand in sharp contrast to those obtained by Schrock and co-workers[10] in which a reduction in the steric bulk of the coordinated ligands had a detrimental effect on both the activity and the livingness of their Ziegler−Natta catalysts. It can also be noted that, for **2a**−**c**, the ^{13}C NMR spectra of the poly(1-hexene) materials obtained are similar to the spectrum recorded for the poly(1-hexene) provided by the nonstereospecific system of **1b** ($R^1 = R^2 = Cy$).[1b,7] This observation indicates that the steric bulk of the Cp* group appears to be critical for establishing a stereodifferentiating environment for olefin complexation such as that found for the **1a** system which is isospecific for 1-hexene polymerization.[1a]

Given the extreme activities associated with **2a**−**c**, it was of interest to determine if these precatalysts could be used to polymerize sterically encumbered monomers in a living fashion. To our satisfaction, this proved to be the case for polymerizations of VCH conducted at −10 °C, employing **2a** and **2b** which could be taken to ~99% completion according to Scheme 2. As Figure 2 reveals, a kinetic analysis confirmed the living character of these polymerizations ($k_{obs}/[Zr]_o = 0.131\ M^{-1}\,s^{-1}$ for **2b**) which further provided narrow polydispersities for each data point (M_w/M_n = 1.04−1.10). Surprisingly, it was determined that both of these *achiral*, C_s-symmetric precatalysts produced *highly isotactic* PVCH material (mmmm >95%) as evidenced by their ^{13}C NMR spectra.[5d,7,11] These results suggest that for these systems, PVCH microstructure is under chain-end control. Finally, it is interesting to note that use of $[PhNMe_2H][B(C_6F_5)_4]$ as cocatalyst with **2b** provided identical k_{obs} values for VCH polymerization which implies that the potential reversible coordination of dimethylaniline does not seriously effect propagation.

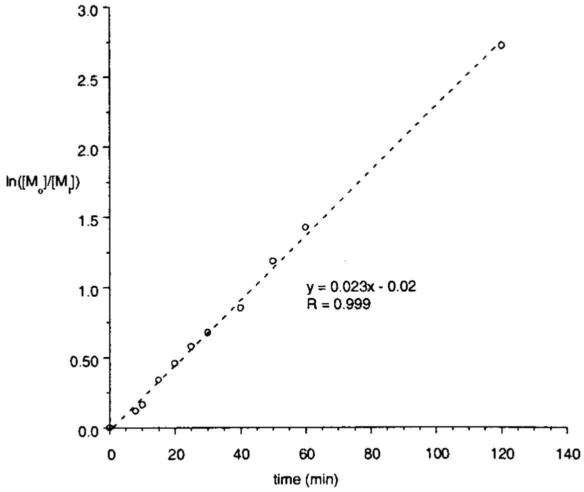


Figure 2. Kinetic analysis of the polymerization of VCH using **2b** (M_w/M_n = 1.04−1.10 for each data point). The dashed line is a linear curve fit of the data.

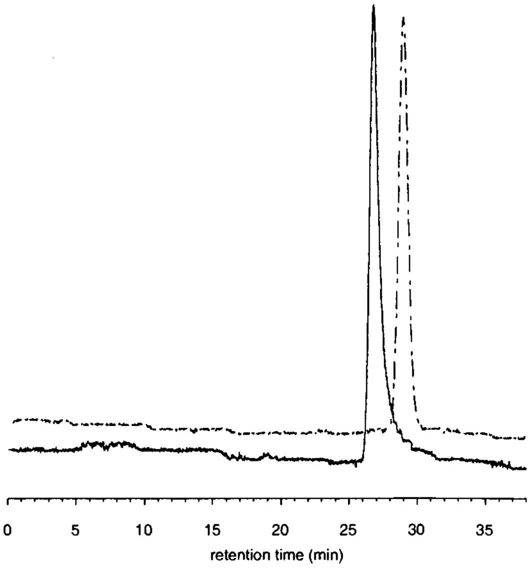


Figure 3. GPC trace of PVCH−PH−PVCH triblock (entry 6) (solid line) and a polystyrene standard (M_n; 11 300, M_w/M_n; 1.02) (dashed line).

With a living system in hand for VCH polymerization, we were interested in determining whether novel di- and triblock copolymers of isotactic PVCH could be prepared. As Table 1 indicates, this proved to be possible for the synthesis of a triblock material containing 33% *iso*-PVCH (entry 6).[7] Figure 3 shows the GPC trace for this material which consists of a monomodal molecular weight distribution possessing a narrow polydispersity of 1.08. The ability to obtain such a well-defined material after a total polymerization time of 5 h attests to the robustness of the living polymers derived from **2**.

In conclusion, the extreme activities expressed by **2** for the living polymerization of (sterically encumbered) α-olefins at low temperature should pave the way for the production of a range of new homo- and block copolymer polyolefin materials.

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Supporting Information Available: Details of precatalyst and polymer synthesis and characterization and the crystallographic analysis of **2a** and **2b** (PDF). This material is free of charge via the Internet at http://pubs.acs.org.

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(10) (a) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830−3831. (b) Baumann, R.; Stumpf, R.; Davis, W. M.; Liang, L. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 7822−7836.

(11) The C_1-symmetric precatalyst **1a** also provides isotactic PVCH at 25 °C; however, the system is not living at this temperature.