

Solid-supported stereospecific living Ziegler–Natta polymerization of α -olefins

Yonghui Zhang and Lawrence R. Sita*

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, USA.

E-mail: ls214@umail.umd.edu

Received (in Cambridge, UK) 2nd July 2003, Accepted 24th July 2003

First published as an Advance Article on the web 12th August 2003

A successful strategy has been developed for the synthesis of a cationic pentamethylcyclopentadienyl zirconium amidinate initiator on a lightly crosslinked polystyrene-divinylbenzene support that can be used to polymerize α -olefins in a living and stereospecific fashion.

The past decade has witnessed many remarkable advances in the development of well-defined ‘single-site’ catalysts for the Ziegler–Natta polymerization of ethylene and α -olefins.¹ Among these have been the discovery of nonmetallocene-based transition metal initiators that can effect olefin polymerizations in a living, and, in a few cases, highly stereoselective fashion.² In recognition of industrial needs, there has also been parallel interest and progress in the design and utilization of solid supports that can serve to ‘heterogenize’ homogeneous olefin polymerization catalysts in a well-defined manner that preserves most of their solution phase properties.^{3,4} To date, however, the heterogenization of a Ziegler–Natta initiator on a solid support for the living polymerization of olefins has not been reported. The anticipated advantages of such a system, however, are several-fold, and they include: (1) the suppression of undesired bimolecular processes involving propagating centers, (2) the ability to perform polymerizations in more inert, but for the original homogeneous model, less solubilizing solvents, (3) the separation through simple filtration of living polymer chains from dead ones leading to a narrower molecular weight distribution, and (4) the ability to prepare multiblock polyolefin copolymers in a combinatorial fashion for the rapid screening and selection of optimum physical properties. In this report, we now describe the successful synthesis of a solid-supported version of a class of cationic pentamethylcyclopentadienylzirconium amidinate initiators that have previously been shown to be highly active and stereospecific polymerization of α -olefins.⁵ Importantly, polymerizations conducted using this solid-supported initiator were found to retain both the desired living character and stereospecificity of the corresponding homogeneous process.

The synthesis of the solid-supported initiator was performed in a straightforward fashion according to the reaction sequence shown in Scheme 1. To begin, we have previously reported that deprotonation of the dichloride **1** with the highly hindered base, $\text{Ph}_3\text{SiLi}\cdot(\text{THF})_3$,⁶ quantitatively provides a lithium ‘enolate’ complex that then reacts with a range of electrophiles in a regioselective manner to generate new amidinate ligands that are substituted at the methyl position of the original acetamidinate fragment.⁷ In the present case, the *in situ* generated enolate complex was reacted with commercially available chloro-

methylated polystyrene beads (Bio-Rad, Bio-beads™ S-X1 200–400 mesh, 1.36 mmol g^{-1}) in toluene at 25°C to produce the solid-supported dichloro complex **2** that was isolated as a pale yellow solid after filtration and washing with solvent. Methylation of **2** was next carried out by treating a suspension of the material in diethyl ether (Et_2O) with methyllithium at -78°C , followed by gradually warming the mixture to room temperature. Microanalysis (%N) was then used to establish that the extent of conversion of the initial chloromethylated solid support to **3** in this two step process was in the range of 40–50% ($0.54\text{--}0.68 \text{ mmol g}^{-1}$) as based on values obtained for multiple runs. Finally, monodemethylation of **3** through protonation with the borate, $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$, in chlorobenzene at -10°C provided **4** as an orange solid in virtually a quantitative yield as established once again by microanalysis.

The ability of solid **4** to function as an initiator for the living polymerization of α -olefins is demonstrated by the data presented in Fig. 1. More specifically, in agreement with the criteria for a living polymerization system,⁸ a linear relationship between the number average degree of polymerization, M_n , for poly(1-hexene), as determined from GPC analysis, using polystyrene standards of the material obtained after standard workup, and polymer yield was established by carrying out

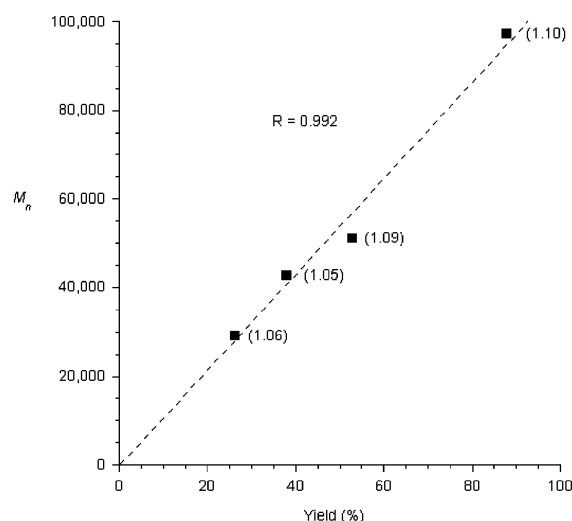
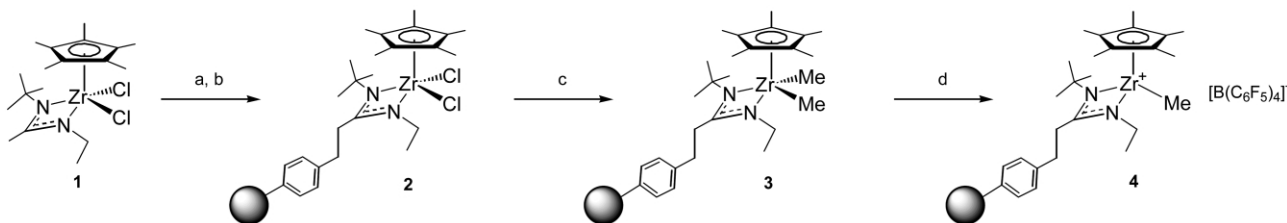


Fig. 1 Dependence of M_n and M_w/M_n (in parentheses) values (GPC, polystyrene standards) for isotactic poly(1-hexene) on yield of isolated polymer.



Scheme 1 Reagents and conditions: a, $\text{Ph}_3\text{SiLi}\cdot(\text{THF})_3$, THF, 25°C , 2 h; b, Bio-beads™ S-X1, toluene, 2 h; c, MeLi, Et_2O , -78 to 25°C , 3 h; (d) $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$, chlorobenzene, -10°C , 5 min.

separate polymerizations of a fixed amount (5 mmol) of 1-hexene in chlorobenzene (0.5 M) at $-10\text{ }^{\circ}\text{C}$ for varying periods of time. In this regard, a noticeable decrease in polymerization activity relative to the corresponding homogeneous system was observed as it required 25 h for an 88% yield of polymer to be obtained (*cf.* $\sim 100\%$ in less than 2 h for the homogeneous initiator). Nonetheless, as Fig. 1 demonstrates, even after these long periods of time, the poly(1-hexene) material obtained possessed a narrow polydispersity (M_w/M_n) value indicating that chain termination during polymerization is not occurring to any appreciable extent. In support of this statement, ^1H NMR spectroscopy of the polymeric materials showed the absence of vinyl end-groups that might arise through termination *via* β -hydride elimination, and $^{13}\text{C}\{^1\text{H}\}$ NMR confirmed that each of the poly(1-hexene) samples was purely isotactic in microstructure with no observable resonances for 2,1-misinsertions or stereoerrors resulting from a mistake in olefin face selectivity. Finally, it can be noted that from the data in Fig. 1, it was calculated that the number of 'active' centers in **4** is approximately 0.41 mmol g^{-1} which is somewhat less than the number based strictly on chemical yield established through microanalysis. Although it is likely that the latter number has a larger error associated with it, it is also possible that some of the cationic zirconium centers in **4** are too shielded to engage in productive olefin insertion and propagation as we have previously determined that the magnitude of such activity is highly, and subtly, dependent upon the steric environment about the metal.⁹ Work is now in progress to prepare other variants of **4** using more open crosslinked polymer frameworks.

In addition to the living and stereospecific polymerization characteristics of **4**, this solid-supported initiator was found to possess other notable properties and capabilities. To begin, compared to its homogeneous analogue, in dry form, **4** has a remarkably long shelf-life. For instance, after 10 days at room temperature, the initiator lost only 7% of activity and after 20 days, 55% of its activity was still retained. This loss of activity, however, is not associated with a decrease in the living or stereospecific nature of the remaining active sites. The neutral precursor **3**, which appears to have indefinite shelf-life at room temperature, can also be used for the *in situ* generation of **4** which provides identical polymerization results. Further, with the heterogenized initiator **4**, it was also possible to carry out polymerizations in solvents that are not compatible with the homogeneous system. For instance, using toluene in place of chlorobenzene provided isotactic poly(1-hexene) at a similar rate to that expressed in Fig. 1 (*cf.* $M_n = 70\,000$, $M_w/M_n = 1.10$, 78% yield after 24 h). Finally, by judiciously selecting a smaller degree of polymerization (DP), as defined by $[M]_0/[I]_0$, it was demonstrated that complete monomer conversion could be achieved in under 3 h. In this manner, the solid-supported synthesis of well-defined polyolefin block copolymers of narrow polydispersity could be accomplished. Figs. 2 and 3 present the inverse-gated $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum and GPC

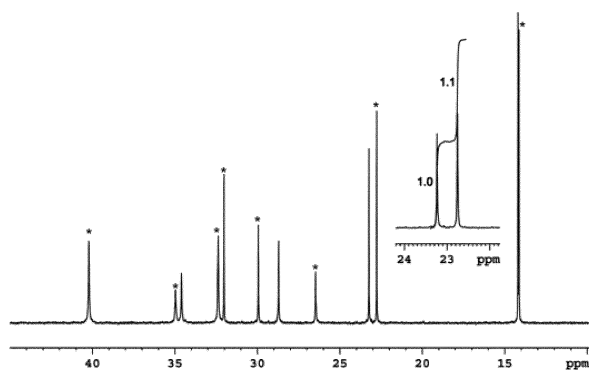


Fig. 2 Inverse gated $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , $25\text{ }^{\circ}\text{C}$) spectrum of isotactic-poly(1-hexene)-block-isotactic-poly(1-octene) block copolymer. Resonances for the poly(1-octene) block are marked with an asterisk (*).

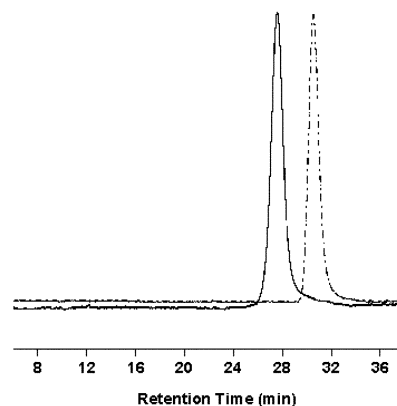


Fig. 3 GPC analyses of isotactic-poly(1-hexene)-block-isotactic-poly(1-octene) block copolymer (M_n 23 700, $M_w/M_n = 1.07$) (solid line) and an aliquot of the isotactic poly(1-hexene) block formed before addition of the 1-octene monomer (M_n 8 500, $M_w/M_n = 1.05$) (dashed line).

trace, respectively, of an isotactic poly(1-hexene)-block-isotactic-poly(1-octene) block copolymer prepared by the sequential addition of 1-hexene ($DP_{\text{calc}} = 90$) (polymerization time, $T_p = 3\text{ h}$) and 1-octene ($DP_{\text{calc}} = 90$) ($T_p = 3\text{ h}$). As Fig. 2 reveals, both blocks are highly isotactic and integration confirms a near 1 : 1 ratio as planned. The GPC trace reproduced in Fig. 3 further confirms that this diblock material is monomodal and of very narrow polydispersity.

In conclusion, a facile synthetic route to a class of solid-supported initiators for the living, stereospecific polymerization of α -olefins has been demonstrated. The full range of benefits and applications that this heterogenized variant provides over the homogeneous system are currently under investigation.

This material is based upon work supported by the National Science Foundation (CHE-0092493).

Notes and references

- For reviews, see: (a) H. H. Brintzinger, D. Fischer, R. Müllhaupt, B. Rieger and R. M. Waymouth, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1143; (b) V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283.
- For a recent review, see: G. W. Coates, P. D. Hustad and S. Reinartz, *Angew. Chem., Int. Ed. Engl.*, 2002, **41**, 2236.
- For recent reviews, see: (a) H. C. L. Abbenhuis, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 1058; (b) J. C. W. Chien, *Top. Catal.*, 1999, **7**, 23.
- (a) H. Nishida, T. Uozumi, T. Arai and K. Soga, *Macromol. Rapid Commun.*, 1995, **16**, 821; (b) S. B. Roscoe, J. M. M. Frechet, J. F. Walzer and A. J. Dias, *Science*, 1998, **280**, 270; (c) M. C. W. Chan, K. C. Chew, C. I. Dalby, V. C. Gibson, A. Kohlmann, I. R. Little and W. Reed, *Chem. Commun.*, 1998, 1673; (d) A. G. M. Barrett and Y. R. de Miguel, *Chem. Commun.*, 1998, 2079; (e) M. Stork, M. Koch, M. Klapper, K. Müllen, H. Gregorius and U. Rief, *Macromol. Rapid Commun.*, 1999, **20**, 210; (f) S. B. Roscoe, C. Gong, J. M. J. Frechet and J. F. Walzer, *J. Polym. Sci. (A), Polym. Chem.*, 2000, **38**, 2979; (g) A. G. M. Barrett and Y. R. de Miguel, *Tetrahedron*, 2002, **58**, 3785; (h) R. M. Kasi and E. B. Coughlin, *Organometallics*, 2003, **22**, 1534.
- (a) K. C. Jayaratne and L. R. Sita, *J. Am. Chem. Soc.*, 2000, **122**, 958; (b) K. C. Jayaratne, R. J. Keaton, D. A. Henningsen and L. R. Sita, *J. Am. Chem. Soc.*, 2000, **122**, 10490; (c) R. J. Keaton, K. C. Jayaratne, D. A. Henningsen, L. A. Koterwas and L. R. Sita, *J. Am. Chem. Soc.*, 2001, **123**, 6197; (d) K. C. Jayaratne and L. R. Sita, *J. Am. Chem. Soc.*, 2001, **123**, 10754; (e) Y. Zhang, R. J. Keaton and L. R. Sita, *J. Am. Chem. Soc.*, 2003, **125**, in press.
- H. G. Woo, W. P. Freeman and T. D. Tilley, *Organometallics*, 1992, **11**, 2198.
- Y. Zhang, D. A. Kissounko, J. C. Fettinger and L. R. Sita, *Organometallics*, 2003, **22**, 21.
- (a) M. Szwarc and M. van Beylen, *Ionic Polymerization and Living Polymers*, Chapman and Hall, New York, 1993; (b) K. Matyjaszewski, *J. Phys. Org. Chem.*, 1995, **8**, 197.
- D. A. Kissounko, J. C. Fettinger and L. R. Sita, *Inorg. Chim. Acta.*, 2003, **345**, 121.