

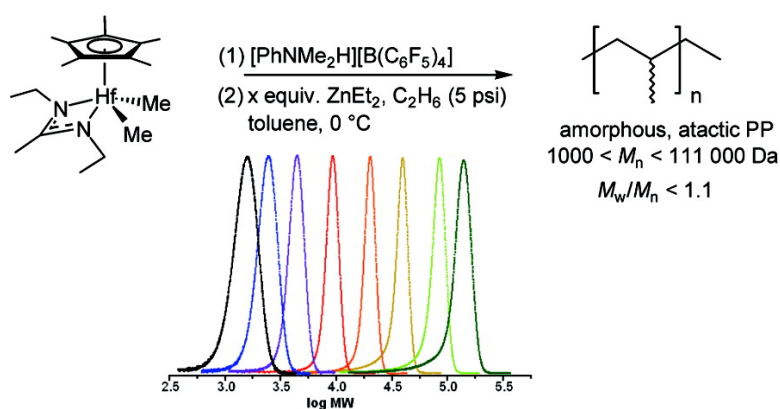
Communication

**Highly Efficient, Living Coordinative Chain-Transfer Polymerization of Propene with ZnEt: Practical Production of Ultrahigh to Very Low Molecular Weight Amorphous Atactic Polypropylenes of Extremely Narrow Polydispersity**

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# Highly Efficient, Living Coordinative Chain-Transfer Polymerization of Propene with $\text{ZnEt}_2$ : Practical Production of Ultrahigh to Very Low Molecular Weight Amorphous Atactic Polypropenes of Extremely Narrow Polydispersity

Wei Zhang and Lawrence R. Sita\*

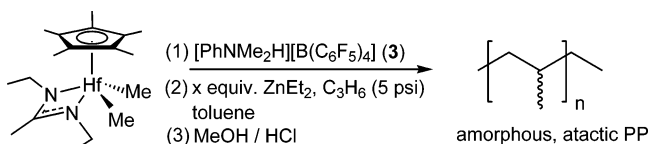
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Highly efficient, rapid and reversible chain transfer between active transition-metal-based propagating centers and main group metal alkyls, such as  $\text{ZnR}_2$  and  $\text{AlR}_3$ , also referred to as coordinative chain transfer polymerization (CCTP),<sup>1–3</sup> that can be used in conjunction with the *living* Ziegler–Natta (ZN) polymerization of ethene and  $\alpha$ -olefins,<sup>4</sup> offers a very attractive solution to the intrinsic problem of limited polymer production that this latter “one polymer chain per metal” process entails, while at the same time, potentially preserving all of its beneficial features, such as access to tight control over molecular weight indices, narrow polydispersities, polymer chain-end functionalization, and block copolymer production, to name just a few. Herein, we now report, to the best of our knowledge, the first realization of this goal for an  $\alpha$ -olefin with demonstration of highly efficient, living CCTP of propene that provides access to practical quantities of a series of amorphous atactic polypropene (a-PP) samples. These samples are distinguished by having tunable molecular weights ranging from ultrahigh, in the absence of CCTP, to very high to very low when CCTP is conducted with increasing initial equivalents of  $\text{ZnEt}_2$ —all the while, maintaining extremely narrow polydispersities.

Since 2000, we have been investigating the mechanistic details and full extent of new polyolefin materials that are accessible by the class of cationic group 4 metal complexes exemplified by the specific example  $\{\text{Cp}^*\text{Zr}(\text{Me})[\text{N}(\text{Et})\text{C}(\text{Me})\text{N}(t\text{-Bu})]\}\text{[B}(\text{C}_6\text{F}_5)_4\text{]}$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) (**1**) that can serve as highly active catalysts for the living stereospecific ZN polymerization of propene and higher  $\alpha$ -olefins.<sup>5</sup> Recent computational studies of propene polymerization by **1** as performed by others<sup>6</sup> have commented on the sterically crowded nature of the propagating metal center, and indeed initial attempts at CCTP of propene using this catalyst were not particularly promising in terms of activity. Thus, efforts were directed toward reducing steric interactions within the metal ligand sphere, and, as a result, it was gratifying to find that the *N,N*-diethyl hafnium derivative, generated in standard fashion from equimolar amounts of the newly synthesized dimethyl precursor  $\text{Cp}^*\text{Hf}(\text{Me})_2\text{-[N}(\text{Et})\text{C}(\text{Me})\text{N}(\text{Et})]$  (**2**), and the borate,  $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$  (**3**), at  $-10^\circ\text{C}$  in chlorobenzene (PhCl), was extremely active for the aspecific polymerization of propene at this temperature where ultrahigh molecular weight (UHMW) a-PP with a weight-average molecular weight index,  $M_w$ , above 2 000 kDa was produced after only a short period of time.<sup>7</sup> Detailed kinetic studies of these polymerizations further revealed linear increases in both  $M_w$  and the number-average molecular weight index,  $M_n$ , versus time that are suggestive of a quasi-living or controlled polymerization.<sup>8</sup> However, these trends were also accompanied by a steady increase in the polydispersity index ( $M_w/M_n$ ) above an initially small value of 1.12, possibly as a consequence of significant solution viscosity limitations that quickly manifest as a function of time. Finally, the atactic nature and complete lack of crystallinity in these UHMW a-PP materials were confirmed by  $^{13}\text{C}$  NMR stereochemical

## Scheme 1.



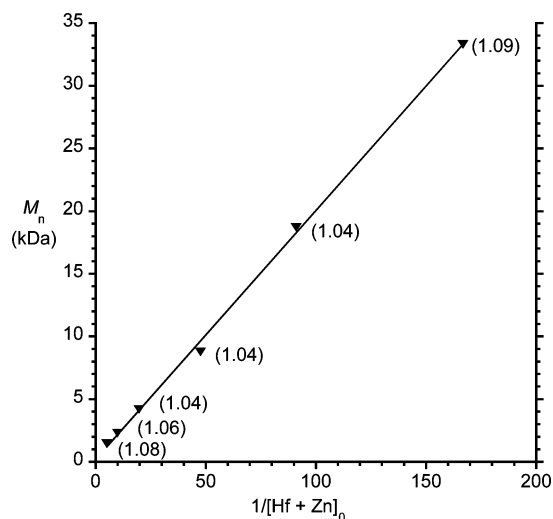
**Table 1.** Coordinative Chain-Transfer Polymerization (CCTP) of Propene with **2** and Added  $\text{ZnEt}_2$  According to Scheme 1<sup>a</sup>

run	<b>2, 3</b> ( $\mu\text{mol}$ )	$\text{ZnEt}_2$ (equiv)	$T_p$ ( $^\circ\text{C}$ )	yield (g)	$M_n$ (kDa)	$M_w / M_n$
1	20	20	-10	6.02	12.6	1.03
2	20	20	-20	7.92	15.9	1.03
3	20	20	20	1.63	3.63	1.05
4	20	200	0	4.99	1.45	1.08
5	20	100	0	4.93	2.28	1.06
6	20	50	0	4.94	4.18	1.04
7	20	20	0	4.18	8.75	1.04
8	20	10	0	4.78	18.7	1.04
9	20	5	0	4.85	33.3	1.09
10	10	10	0	10.1	71.9	1.09
11	10	5	0	9.64	111	1.15

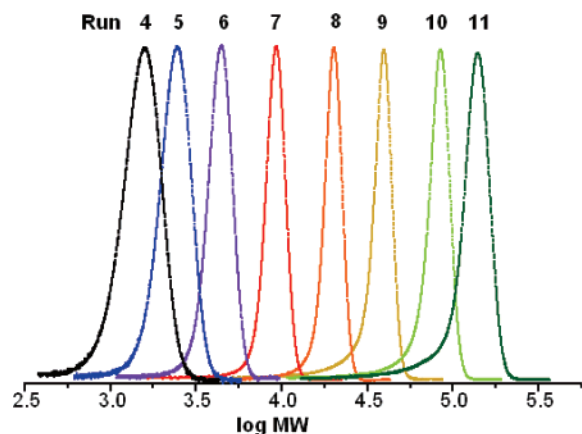
<sup>a</sup> Conditions:  $\text{ZnEt}_2$  added as 1.1 M solution in toluene, total volume (toluene) = 20 mL and  $t_p = 2$  h, except for runs 10 and 11 (50 mL, 14 h), at constant propene pressure (5 psi).<sup>7</sup>

analysis, differential scanning calorimetry (DSC), and solid-state X-ray diffraction studies.<sup>7</sup>

With the high activity and ability to prepare UHMW a-PP via living (controlled) ZN polymerization employing **2** established, it became of significant interest to determine if practical quantities of a molecular-weight-dependent series of this unique class of polyolefin material could be obtained for extended physical characterization and mechanical testing.<sup>9</sup> Toward this goal, it was first successfully determined that propene polymerizations based on **2** and the borate **3** could be conducted using toluene in place of PhCl to provide similar UHMW a-PP products possessing nearly identical molecular weight distributions and without any significant deleterious effects on activity.<sup>7</sup> Next, CCTP of propene was pursued with **2** by carrying out polymerizations in toluene in the presence of varying molar equivalents of  $\text{ZnEt}_2$  according to Scheme 1. Table 1 and Figures 1 and 2 summarize the results of these studies that serve to confirm that highly efficient living CCTP of propene can indeed be achieved. Thus, to begin, at  $-10^\circ\text{C}$ , and in the presence of an initial 20 equiv of  $\text{ZnEt}_2$ , a-PP of much lower molecular weight and extremely narrow polydispersity was obtained after 2 h (run 1). Data for runs 2 and 3 in Table 1 record the effect of temperature on CCTP, which at constant propene pressure, is easily accounted for by an apparent reduced activity due to significant differences in propene concentrations in solution at the various temperatures employed. In this respect, it is important to note that end-group analysis by  $^1\text{H}$  NMR spectroscopy of the a-PP material



**Figure 1.** Dependence of observed  $M_n$  and  $M_w/M_n$  (in parentheses) as a function of the inverse of total initial concentration of metal species, according to the polymerization conditions of Scheme 1 and Table 1.



**Figure 2.** Molecular weight distributions for a-PP samples obtained under conditions detailed in Table 1.

obtained at 20 °C, lacks any evidence of chain-termination by  $\beta$ -hydride elimination, which is in keeping with the extremely narrow polydispersity that is maintained (see Table 1).<sup>7</sup> Next, by keeping temperature constant at 0 °C, runs 4–9 in Table 1 detail the effects of varying initial molar equivalents of  $ZnEt_2$  on the outcome of CCTP of propene as mediated by the active catalyst derived from **2** and **3**. Importantly, the plot of observed  $M_n$  versus  $1/[Hf + Zn]_0$  shown in Figure 1 reveals a strictly linear relationship, which along with the constant yield and extremely narrow polydispersities of all the isolated a-PP products obtained provides strong compelling evidence that highly efficient living CCTP is being maintained throughout the entire series without suffering a setback in either overall activity, rates of reversible chain-transfer, or those for chain-termination.<sup>7,10</sup> Indeed, a detailed kinetic analysis of CCTP of propene conducted under conditions similar to run 7, provided a highly linear relationship between  $M_n$  vs time with the polydispersity index values of all the aliquots remaining extremely narrow within the range of 1.03–1.06, both features being hallmarks of a living polymerization process.<sup>4,5,8</sup> Finally, to demonstrate that even higher  $M_n$  values and larger quantities of a-PP are possible with this CCTP process, two additional polymerizations were conducted

in the presence of 10 and 5 equiv of  $ZnEt_2$  but with a larger volume of solvent and for longer time (50 mL and 14 h, respectively). As can be seen from the data presented in both Table 1 and Figure 2 (i.e., runs 10 and 11), this desired goal was indeed achieved, where even for the highest molecular weight a-PP obtained in run 11, with  $M_n = 111$  kDa, polydispersity remained within the range of being very narrow with  $M_w/M_n = 1.15$ .

In summary, the present report serves to unequivocally establish, to the best of our knowledge, the first demonstration of the coupling of highly efficient CCTP with the living ZN polymerization of an  $\alpha$ -olefin that simultaneously provides (1) practical quantities of low molecular weight oligomers [cf. in the absence of CCTP, 1.6 g (vs only 9.1 mg) of **2** would be required to prepare a comparable amount of the a-PP obtained in run 4 of Table 1], (2) regulation of molecular weight values over a very large range while maintaining extremely narrow polydispersities, and (3), in studies to be pursued, the ability to provide all of these materials as telechelic polymers and block copolymers with functionalized chain ends.<sup>1–3</sup>

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**Supporting Information Available:** Experimental details, including crystallographic analysis of **2** and polymer synthesis, characterization, and kinetic studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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