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Living Polymerization of α-Olefins by Chelating Diamide Complexes of Titanium

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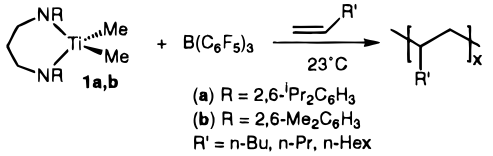
Living polymerization methods permit the preparation of polymers with well-defined structures.[1] For the coordination polymerization of an α-olefin, chain growth occurs via olefin insertion into a metal−carbon bond (Cossee−Arlman mechanism)[2,3] while β-alkyl elimination,[4] chain transfer to a cocatalyst,[5] and β-hydride elimination[6] serve as chain termination or transfer steps. In addition, some catalyst systems terminate via homolytic M−C bond cleavage concomitant with reduction of the metal.[7] It is the relative rates of these steps that determine the chain length and hence the molecular weight distribution of the polymer. Although β-alkyl elimination is negligible[8] for higher α-olefins (≥1-butene) and chain transfer to a cocatalyst can be eliminated by the use of tetraalkylborates,[9,10] it has so far proven difficult to control β-hydride elimination.

The olefin polymerization chemistry of broad classes of group 4 compounds such as Cp_2MX_2, $CpMX_3$, and linked Cp-amide derivatives have been studied extensively; thus, the search for new non-Cp ligand environments is currently of considerable interest.[11−25] Previously we have investigated the α-olefin polymerization chemistry of chelating diamide compounds of titanium.[26] Complexes of the type $[RN(CH_2)_3NR]TiMe_2$ (R = 2,6-${}^iPr_2C_6H_3$; R = 2,6-$Me_2C_6H_3$), when activated with methyl aluminoxane (MAO), are highly active catalysts for the polymerization of 1-hexene. The only chain termination mechanism operative in these systems appears to be chain transfer to aluminum ($M_n = 47\,000$, $M_w/M_n = 1.73$),[27] as we have been unable to observe olefinic resonances in the proton or carbon NMR spectra of the polymers or oligomers prepared with these catalyst systems. Hence, it seemed likely that if the aluminum cocatalyst were replaced with a borate anion,[28] a living system could be achieved. In this paper, we introduce a new living α-olefin polymerization catalyst system. To our knowledge, this is the first example of the living polymerization of an aliphatic α-olefin at room temperature.[29−34]

Equimolar amounts of the titanium dimethyl complex $[RN(CH_2)_3NR]TiMe_2$ (**1a**, R = 2,6-${}^iPr_2C_6H_3$; **1b**, R = 2,6-$Me_2C_6H_3$)[26] and $B(C_6F_5)_3$[35] catalyze the living aspecific[19] polymerization α-olefins at room temperature (eq 1). The polymerization solutions are light yellow and homogeneous. In the absence of excess monomer, attempts to spectroscopically identify the catalytically active species have been thwarted by the extreme reactivity of the catalyst system with chlorinated solvents and its insolubility in aromatic solvents. A summary of the polymerization results is shown in Table 1.[36] The catalyst systems generate high molecular weight polymers with remarkably narrow molecular weight distributions. The polymer samples are soluble in aliphatic solvents and THF. It should be noted that the titanium dimethyl complexes **1a,b** *do not* polymerize these monomers under the conditions studied, nor does $B(C_6F_5)_3$. Deuterium and carbon-13 labeling experiments are in progress to determine the mode(s) of olefin addition (2,1- vs 1,2-insertion).



(1)

A noticeable increase in activity and hence molecular weight is observed for polymerizations performed in the presence of CH_2Cl_2 (compare entries 1−3 to entries 7−9). The polarity of CH_2Cl_2 may result in greater charge separation[37−39] between the putative cationic titanium alkyl and the borate anion. Although the measured activities and polymer yields increase by a factor of about 10, the molecular weights of the polymers increase by a factor of about 30. This suggests that some of the catalyst may not be active in this solvent. Activities are suppressed when the polymerizations are performed in the presence of toluene (compare entries 1−3 to entries 4−6), as has been noted when compounds **1a,b** are activated with

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Table 1. Polymerization of α-Olefins[a]

entry	catalyst precursor	monomer and conditions	yield (mg)	M_w[b]	M_n[b]	M_w/M_n	activity[c]
1	1a	1-hexene, 10 min	50	4 300	4 100	1.05	40
2	1a	1-octene, 10 min	50	5 100	4 900	1.05	40
3	1a	1-decene, 10 min	50	5 800	5 500	1.06	40
4	1a	1-hexene/toluene,[d] 30 min	100	20 000	19 100	1.05	30
5	1a	1-octene/toluene,[d] 30 min	110	16 900	15 500	1.09	30
6	1a	1-decene/toluene,[d] 30 min	110	16 600	15 800	1.05	30
7	1a	1-hexene/CH_2Cl_2,[e] 10 min	570	176 100	164 200	1.07	490
8	1a	1-octene/CH_2Cl_2,[e] 10 min	870	148 100	138 200	1.07	750
9	1a	1-decene/CH_2Cl_2,[e] 10 min	890	131 000	121 500	1.07	760
10	1a	1-hexene, 30 min	90	12 800	12 100	1.06	30
11	1b	1-octene, 30 min	160	21 900	20 900	1.05	50
12	1b	1-decene, 30 min	150	19 200	17 300	1.11	40

[a] General conditions: 6.7 μmol of **1a** or **1b** in 0.67 mL of pentane and 6.7 μmol of $B(C_6F_5)_3$ in 0.35 mL of pentane were added to 6 mL of monomer or monomer/solvent at 23 °C. [b] By GPC in THF vs polystyrene standards. [c] g of polymer/(mmol of catalyst•h). [d] 2 mL of toluene in 4 mL of monomer. [e] 2 mL of CH_2Cl_2 in 4 mL of monomer.

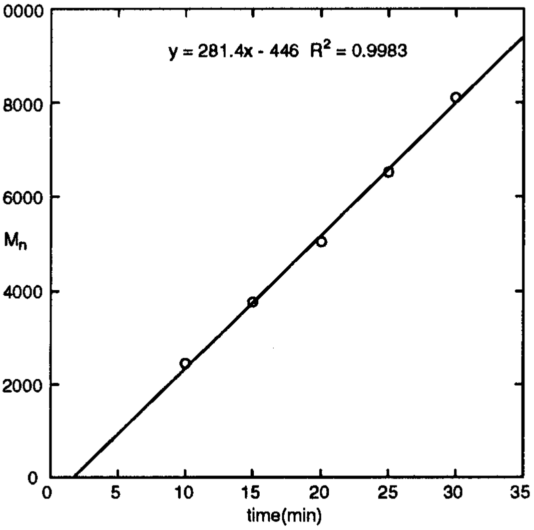
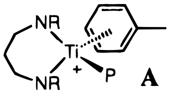


Figure 1. Time dependence on M_n for the polymerization of 1-hexene with **1b**/$B(C_6F_5)_3$ (toluene:1-hexene = 50:50). M_w/M_n = 1.06−1.07 for each data point.

MAO.[26] Assuming a cationic alkyl complex,[40] we interpret these results as competitive binding of toluene to titanium (**A**).



A

Such an interaction is possible, given the low coordination number of these diamide complexes and the spectroscopic observation of other group 4 cationic η^6-toluene species.[41−43] In addition, we have prepared the isoelectronic cyclopentadienyl complex $[RN(CH_2)_3NR]TiMe(\eta^5\text{-}C_5H_5)$ ($R = 2,6\text{-}{}^iPr_2C_6H_3$),[27] suggesting that the metal can accommodate ligands of this size. Studies are in progress to isolate an authentic η^6-toluene complex.

We have measured the time dependence of the polymerization of 1-hexene with the catalyst system **1b**/$B(C_6F_5)_3$ in a 50:50 mixture of toluene/1-hexene (Figure 1).[36] The ratio of toluene to 1-hexene permits convenient measurement of molecular weights at regular time intervals (*vide supra*) with a minimal increase in viscosity. Aliquots were removed from the solution at 5 min intervals, and the number average molecular weight (M_n) was plotted versus time. The GPC trace of each sample shows a single, narrow molecular weight peak (M_w/M_n = 1.06−1.07). A linear relationship between M_n and time indicates that the system is living.

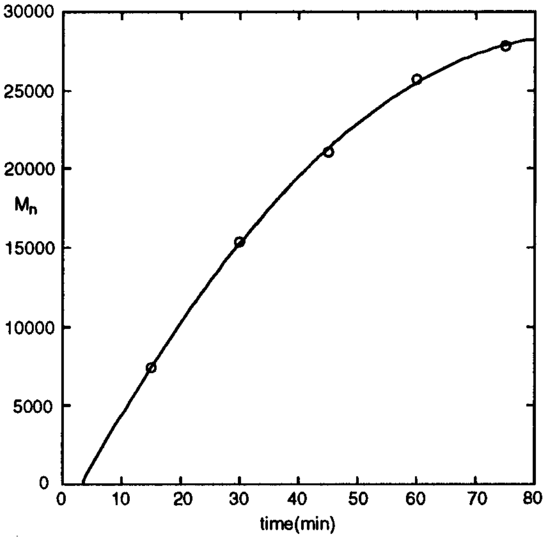


Figure 2. Time dependence on M_n for the polymerization of 1-hexene with **1b**/$B(C_6F_5)_3$ (toluene:1-hexene = 33:67). M_w/M_n = 1.05−1.08 for each data point.

In a separate experiment, the time dependence of the polymerization of 1-hexene with the catalyst system **1b**/$B(C_6F_5)_3$ in a 33:67 mixture of toluene/1-hexene was measured (Figure 2).[36] The plot of M_n versus time deviates from linearity after 30 min; however, the polydispersities remain narrow (M_w/M_n = 1.05−1.08). A significant increase in viscosity and the declining monomer to catalyst ratio are likely responsible for this observation. If additional monomer and solvent are added periodically, the molecular weights continue to increase (>500 000) with no change in the polydispersities (M_w/M_n = 1.05−1.08).

In summary, a new catalyst system for the living polymerization of α-olefins at room temperature has been introduced. There appears to be no chain termination or transfer operative in these systems even after several hours. Successful polymerization of other olefins, block polymer formation, and further ligand variations will be reported shortly.

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Supporting Information Available: Polymer synthesis and characterization (5 pages). See any current masthead page for ordering and Internet access instructions.

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