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Living Polymerization of α -Olefins at Elevated Temperatures Catalyzed by a Highly Active and Robust Cyclophane-Based Nickel Catalyst

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Received January 7, 2005

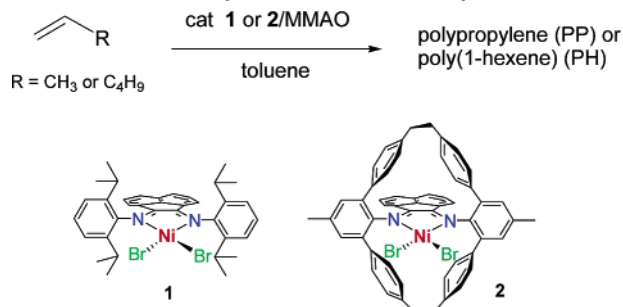
Revised Manuscript Received February 12, 2005

Living polymerization methods allow for the synthesis of polymers with precisely controlled molecular weight, narrow molecular weight distribution, end-functionalized polymers, and well-defined block copolymers.^{1,2} Whereas tremendous advances in living/controlled polymerization have been made by using anionic,³ cationic,⁴ and radical-based polymerization,⁵ there are relatively fewer examples of living olefin polymerization using transition metal catalysts.⁶ For those reported in the literature, most living olefin polymerizations were conducted at subambient temperatures to suppress potential termination and chain transfer reactions.^{6–17} The living features of active olefin polymerization catalysts were usually lost at higher temperature. For practical applications, it would be highly desirable to develop more robust living polymerization systems that can operate at higher temperatures. Herein we report the first late transition metal catalyzed living polymerizations of α -olefins at elevated temperatures.

Late transition metal olefin polymerization catalysts have received much attention recently because they can produce polyolefins with interesting new branching topologies and have better tolerance to functional groups.^{18–20} One noteworthy example is the Ni^{II}– and Pd^{II}– α -diimine complexes discovered by Brookhart and co-workers.^{21,22} The Ni^{II} systems were shown to have comparable activities to those of the early metal catalysts in polymerizing ethylene into high molecular weight (MW) polyethylenes, and the Pd^{II} systems were shown to incorporate polar olefins such as methyl acrylate.^{21,22} The branching topology of the polymers formed by the Pd^{II}– α -diimine catalysts can be controlled from linear to hyperbranched to dendritic by changing polymerization condition or catalyst structure.^{23–27} Besides ethylene polymerization, the Brookhart Ni^{II}– α -diimine catalyst (**1** in Scheme 1), once activated by methylaluminoxane (MAO), is also active for the polymerization of α -olefins.¹³ In addition, it was shown that both the Ni^{II}– and Pd^{II}– α -diimine catalysts initiate living polymerization of α -olefins and ethylene at subambient temperatures (0 to -10 °C).^{13–15} Polymerizations at higher than ambient temperatures, however, lost the living character, which was presumably caused by increased chain transfer reaction and deactivation of the catalysts at higher temperatures.^{13,14}

Recently, our laboratory developed a cyclophane-based Ni^{II}– α -diimine complex (**2** in Scheme 1) which was shown to be a highly active and robust catalyst for ethylene polymerization at high temperature.²⁸ The improved performance at high temperature was at-

Scheme 1. Catalysts for α -Olefin Polymerization



tributed to the unique cyclophane framework of the catalyst ligand, which prevents catalyst deactivation and provides efficient steric blocks at the axial sites, suppressing associative chain transfer by monomer from axial direction.²⁸ In our current investigation, we discovered that the catalyst **2** gave living polymerization of α -olefins at significantly higher temperatures as compared to its acyclic analogue. In this communication we report the living polymerizations of propylene and 1-hexene using catalyst **2**. For comparison, polymerization data of an acyclic analogue of **2**, catalyst **1**, are also included in the discussion.

Exposure of catalyst **2** to modified methylaluminoxane (MMAO) in toluene generated a highly active catalyst for polymerization of propylene (Table 1, entries 2–4). The polymerization at temperatures ranging from 25 to 50 °C gave polypropylene (PP) with molecular weight distribution of ($MWD = M_w/M_n$) values in the range 1.06–1.16. These narrow molecular weight distributions suggest living polymerization features at these temperatures. For comparison, at the same experimental conditions, the acyclic catalyst **1** at room temperature gave polypropylene with a broader MWD (Table 1, entry 1), which agrees with Brookhart's early report.¹³

The living polymerization of propylene using **2**/MMAO at elevated temperatures was further confirmed by taking aliquots of the polymerization solution with time. The number-averaged molecular weight (M_n) and MWD of PP was monitored as a function of time. As shown in Figure 1 for propylene polymerization at 50 °C, PP M_n increases linearly with time over a broad molecular weight range (32K to 133K) while the MWD remains low (~ 1.1), indicating a living polymerization. To the best of our knowledge, this is the first example of late transition metal catalyzed living polymerization of α -olefin at higher than ambient temperature. For early transition metal catalysts, living polymerization of ethylene or α -olefin above room temperature has been achieved only in rare instances.^{29,30}

Polymerization of 1-hexene with catalyst **2** was also investigated and compared with catalysts **1** (Table 1, entries 5–10). A series of polymerization of 1-hexene were carried out at 2.66 M concentration of 1-hexene in toluene at 25, 50, and 75 °C. As indicated by the narrow MWD (1.13–1.22), catalyst **2** also gave living polymerization of 1-hexene at above ambient temperatures. For comparison, polymerization at the same conditions using catalyst **1** afforded polymers with significantly broader MWD (~ 1.5). As reported by Brookhart and co-workers, living polymerization of

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Table 1. Polymerization Data for Propylene and 1-Hexene^a

entry	catalyst	reaction condition		TOF ^b	M_n^c ($\times 10^{-3}$)	M_w/M_n	polymer properties	
		temp (°C)	time (h)				branches/1000 C ^d	thermal anal. (°C) ^e
Propylene Polymerization Data								
1	1	25	2	2262	327	1.44	216	−23 (T_g)
2	2	25	2	2167	302	1.16	113	−54 (T_g)
3	2	35	1	2205	154	1.06	104	−56 (T_g)
4	2	50	1	2032	133	1.13	105	−55 (T_g)
1-Hexene Polymerization Data								
5	1	25	3	1505	543	1.50	108	−54 (T_g)
6	1	50	3	753	461	1.45	110	−57 (T_g)
7	1	75	3	341	279	1.49	111	−53 (T_g)
8	2	25	3	1331	510	1.22	57	−34 (T_g), 62 (T_m)
9	2	50	3	1901	647	1.13	58	−38 (T_g), 58 (T_m)
10	2	75	3	1822	529	1.17	52	−47 (T_g), 58 (T_m)

^a Polymerization condition: catalyst **1** or **2** (0.005 mmol) activated with 2000 equiv of MMAO; toluene (total volume of toluene and monomer equals 50 mL); propylene pressure 1 atm and 1-hexene concentration 2.66 M. ^b TOF = turnover frequency, which was calculated as the moles of monomer per mole of catalyst per hour. ^c Molecular weight data was determined by GPC using polystyrene standards. ^d Total branching was determined by ¹H NMR spectroscopy. ^e T_m and T_g were determined by differential scanning calorimetry (DSC).

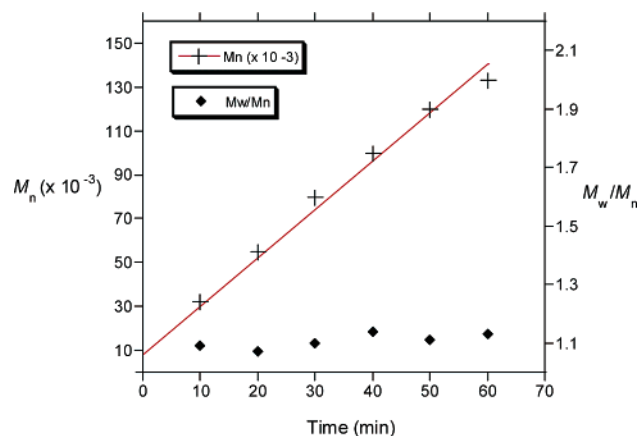


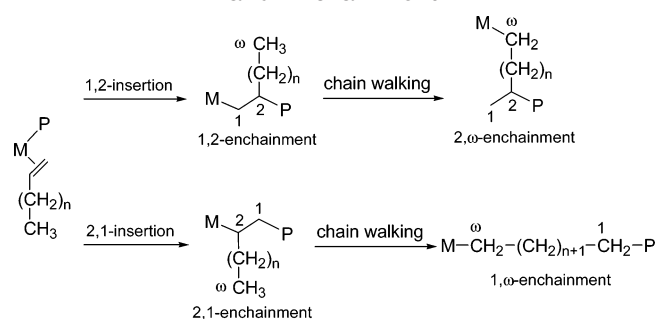
Figure 1. Plot for M_n and M_w/M_n as a function of reaction time for propylene polymerization at 50 °C using **2**/MMAO catalyst.

1-hexene using **1** could only be achieved at subambient temperature (-10 °C) and with relatively low monomer concentration.¹³

The activities of catalyst **2** are very high for propylene and 1-hexene polymerizations. Because of the relatively low thermal stability for catalyst **1**, the turnover frequency (TOF) for 1-hexene polymerization decreased with increasing temperature (Table 1, entries 5–7). On the contrary, the activity for catalyst **2** remained constant with temperature for both propylene and 1-hexene polymerizations. In our previous studies, significantly higher thermal stability was observed in ethylene polymerization for **2** than **1**.²⁸ We attribute the enhanced stability and living polymerization nature for catalyst **2** at elevated temperatures to its unique catalyst structure. The cyclophane ligand may play two critical roles here: (1) the fixed cyclophane ring prevents C–H activation of the metal center to the ligand, which was proposed to be a catalyst deactivation pathway,³¹ and (2) the cyclophane framework keeps the axial sites for the metal center fully blocked, suppressing associative chain transfer of ethylene from the axial sites.²⁸

Compared to the acyclic catalyst **1**, the cyclophane catalyst **2** also afforded polyolefins with significantly different microstructures as revealed by NMR and thermal analysis (Table 1). NMR data show that both PP and poly(1-hexene) (PH) made by **2** have only one-half of the branching density compared to the corresponding polymers made with **1**. The difference in

Scheme 2. Different Modes of Monomer Insertion and Enchainment



polymer microstructure was further reflected by the thermal analysis. Differential scanning calorimetric (DSC) analysis shows that the glass transition temperature (T_g) for PP made with **2** is ~ -55 °C as apposed to -23 °C for PP made by **1**. For PH made with **2**, in addition to lower branching density, two thermal transition temperatures, a melting temperature ($T_m \sim 60$ °C) and a T_g (~ -40 °C), were observed by DSC. For comparison, PH made by catalyst **1** exhibit much higher number of branches and only a T_g around -55 °C.

The differences in branching density and thermal properties can be explained by the insertion mode and chain walking mechanism. As proposed by Brookhart and co-workers for catalyst **1**,¹³ a fraction of α -olefin insertion proceeds in 2,1 fashion (Scheme 2). Metal migration to the terminal carbon and subsequent insertion results in enchainment of α -olefins in a 1, ω fashion. This will result in polymers containing fewer branches than expected from sequential 1,2-insertions, and linear, unbranched segments can be incorporated along the main chain resulting in crystalline domains. The significantly higher level of “chain straightening” in PP and PH made by catalyst **2** indicates that the 2,1 mode of α -olefin insertion occurs more frequently in the polymerizations. Increased 1, ω enchainment in 1-hexene polymerization using **2** leads to PH not only with reduced branching density but also having longer linear segments, resulting in crystalline domains and exhibiting T_m 's. It should be emphasized that the observed increase in “chain straightening” cannot be accounted for by a simple change in relative rates for chain walking and insertion without involving a change in the insertion mode. For example, in propylene polymerization, 1,2-insertion will not be able to lead to any “chain straightening” no matter how fast the chain walking

process is. Only 2,1-insertion followed by chain walking can result in "chain straightening" and a decrease in its total branching density. For polymerization of 1-hexene, whereas 1,2-insertion followed by chain walking can partially straighten the chain, each straightened monomeric unit should have one methyl branch which will disrupt crystal packing and should not result in significant crystalline domains. While the precise mechanism for the increased 2,1-insertion is not clear, we tentatively ascribe this to the unusual cyclophane microenvironment in catalyst **2**. Presumably, the unusual cyclophane environment lowers the activation energy of 2,1-insertion to make it more favorable.

In summary, we report the first late transition metal catalyzed living olefin polymerization at elevated temperatures. Living polymerizations of propylene and 1-hexene were achieved at 50–75 °C by using catalyst **2** developed in our laboratory. Because of the unusual cyclophane ligand framework, catalyst **2** exhibits significantly improved stability and living polymerization nature for α -olefin polymerization at elevated temperatures and gives polyolefins with different microstructures compared to the acyclic catalyst **1**. This highly active and robust living polymerization system offers exciting opportunities for practical design of various polyolefin architectures. Further studies on this living olefin polymerization system and its application to new polymer architecture designs are currently being undertaken in our laboratory and will be reported in the future.

Acknowledgment. We thank the National Science Foundation (DMR-0135233) and the University of California at Irvine for financial support.

Supporting Information Available: Details of polymerizations and polymer characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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MA050039U