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Living Polymerization of α-Olefins Using Ni$^{\text{II}}$−α-Diimine Catalysts. Synthesis of New Block Polymers Based on α-Olefins

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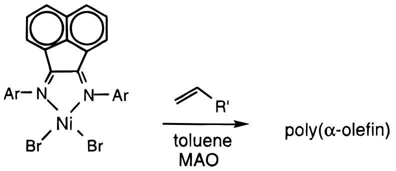
Living polymerization techniques[1] allow the synthesis of polymers with predictable molecular weights and narrow molecular weight distributions, end-functionalized polymers and well-defined block copolymers. While intense efforts have recently focused on development of homogeneous single-site, early metal d^0 and d^{0}f^n catalysts for polymerization of ethylene and α-olefins (particularly propylene),[2] rapid chain transfer processes in these systems have limited their use as living polymerization catalysts. The living polymerization of α-olefins has been achieved only in rare instances and at very low temperatures.[3,4] We describe here the development of a procedure for living polymerization of α-olefins based on recently reported Ni$^{\text{II}}$−α-diimine catalysts[5] and application of this procedure to the synthesis of diblock and triblock poly(α-olefins).[6]

As previously reported, catalysts derived from [ArN=C(R)−C(R)=NAr]NiBr$_2$ (**1**) plus methylaluminoxane (MAO) are quite active for the polymerization of α-olefins in toluene (eq 1).[5] Additional examples of polymerization at 23 °C using catalyst precursors **1a** and **1b** are shown in Table 1, entries 1, 3, 7−9, 11, 13, and 15. Polymerization of propylene (1 atm) yields polypropylene with molecular weight distribution (MWD) of 1.44 (entry 1) for **1a**/MMAO[7] and 1.59 (entry 11) for **1b**/MAO. Polymerization of 1-hexene (>2 M in toluene) gives poly(1-hexene) with M_w/M_n values in the range of 1.4−1.8 (entries 6−8). While reasonably narrow, these molecular weight distributions suggest chain transfer is significant under these conditions. However, when polymerizations are carried out at somewhat lower temperature (−10 °C) and low monomer concentrations (<1 M), poly(α-olefins) are produced with very narrow molar mass distributions suggesting a living polymerization.[8] For example, polymerization of propylene with **1a**/MMAO at −10 °C (1 atm, 60 min) yields polypropylene (M_n = 161 000) with M_w/M_n of 1.13 while polymerization of 1-hexene (0.8 M, −10 °C) yields poly(1-hexene) (M_n = 44 000) with M_w/M_n = 1.09. A GPC trace of the poly(1-hexene) prepared under these conditions is shown in Figure 1.



(1)

a) Ar = 2,6-(i-Pr)$_2$C$_6$H$_3$- ; b) Ar = 2-t-BuC$_6$H$_4$-

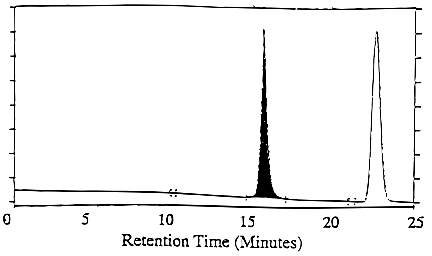


Figure 1. GPC trace of poly(1-hexene) prepared by complex **1a** + MAO at −10 °C.

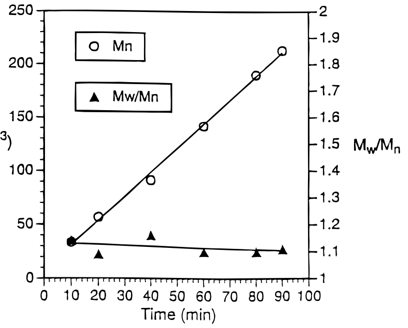
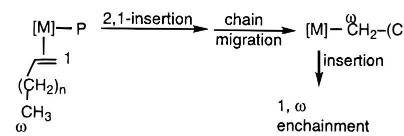


Figure 2. Plot of M_n and M_w/M_n as a function of reaction time for propylene polymerization at −10 °C.

To further confirm living polymerization, M_n and M_w/M_n values were monitored as a function of conversion for polymerization of propylene with **1a**/MMAO at −10 °C. As shown in Figure 2, number average molecular weight increases linearly with time over a broad molecular weight range (25K to 225K) while the molecular weight distribution remains low (ca. 1.1), clearly indicative of a living polymerization.[1]

During polymerization, a significant fraction of α-olefin insertions occur in a 2,1 fashion. Metal migration to the terminal carbon and subsequent insertion results in enchainment of α-olefins in a 1,ω fashion (eq 2).[5,9] This process has several consequences. The resulting polymers contain fewer branches than expected from sequential 1,2-insertions[10] and linear, unbranched segments can be incorporated along the main chain resulting in crystalline domains. The length of the linear



(2)

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[4] For examples of living polymerization of ethylene, see: (a) Brookhart, M.; DeSimone, J. M.; Grant, B. E.; Tanner, M. J. *Macromolecules* **1995**, *28*, 5378−5380 and references therein. (b) Mashima, K.; Fujikawa, S.; Urata, H.; Tanaka, Y.; Urata, H.; Oshiki, T.; Tanaka, E.; Nakamura, A. *Organometallics* **1995**, *14*, 2633−2640.

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[6] This work was reported in part at 211th National ACS Meeting New Orleans, LA; Inorganic Division, Abstr. 261.

[7] MMAO is a modified methylaluminoxane activator containing 25% isobutyl aluminoxane.

[8] For ethylene homopolymerization under these conditions chain transfer is significant. Polyethylene prepared at −20 °C using **1a** has a MWD of 1.48, while polyethylene prepared at −40 °C has a MWD of 1.39.

[9] Details of the microstructure of the poly(α-olefins) and the mechanism of α-olefin polymerization will be the subject of a future publication: S. J. McLain, E. McCord, M. Brookhart, D. J. Tempel, L. K. Johnson, C. M. Killian.

[10] Exclusive 1,2-enchainment would result in polypropylene with 333 branches/1000 carbons, poly(1-hexene) with 167 branches/1000 carbons, and poly(1-octadecene) with 56 branches/1000 carbons.

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Table 1. α-Olefin Polymerization Data

			reaction conditions			polymer properties			
entry	catalyst[a]	monomer[e]	time (min)	temp (°C)	TOF (per h)	$10^{-3}M_n$[b]	M_w/M_n	branches/1000 C[c]	therm anal. (°C)[d]
1	**1a**/MMAO	P (1atm)	60	23	3000	190	1.44	272	−24 (T_g)
2	**1a**/MMAO	P (1atm)	60	−10	2500	160	1.13	297	−16 (T_g)
3	**1a**/MMAO	H (0.8 M)	60	23	1400	92	1.55	120	−57 (T_g), −17 (T_m)
4	**1a**/MMAO	H (0.8 M)	60	−10	560	36	1.18	145	−49 (T_g)
5	**1a**/MAO	H (0.8 M)	60	−10	530	44	1.09	135	−51 (T_g)
6	**1a**/MAO	H (6.4 M)	30	−10	1400	91	1.42	160	−44 (T_g)
7	**1a**/MAO	H (3.2 M)	30	23	2800	84	1.54	126	−52 (T_g)
8	**1a**/MAO	H (6.0 M)	30	23	2500	71	1.80	125	−51 (T_g)
9	**1a**/MMAO	O (0.3 M)	60	23	300	87	1.20	45	56 (T_m)
10	**1a**/MMAO	O (0.3 M)	60	0	180	45	1.09	50	33 (T_m)
11	**1b**/MAO	P (1atm)	60	23	1300	60	1.59	159	−55 (T_g)
12	**1b**/MAO	P (1atm)	60	−10	660	36	1.27	214	−50 (T_g)
13	**1b**/MAO	H (0.8M)	60	23	1000	70	1.62	73	−49 (T_g), 34 (T_m)
14	**1b**/MAO	H (0.8M)	60	−10	260	26	1.15	118	−61 (T_g)
15	**1b**/MAO	O (0.3 M)	60	23	310	68	1.22	33	78 (T_m)
16	**1b**/MAO	O (0.3 M)	120	−10	25	19	1.14	39	32 (T_m), 60 (T_m)[f]

[a] Ni complex (0.017 mmol) activated with 100 equiv of MAO or MMAO; toluene (entries 1−6 and 9−10 total volume toluene and monomer equals 50 mL; entries 7−8 and 11−16 total volume toluene and monomer equals 100 mL). [b] Molecular weight data was determined by GPC vs polystyrene standards. [c] Total branching was determined by ^{1}H NMR spectroscopy (accurate to *ca*. 2%). [d] T_m and T_g were determined by differential scanning calorimetry (DSC). [e] Propylene (P), 1-hexene (H), and 1-octadecene (O). [f] Two melt transitions have been verified for poly(1-octadecene) by dynamic mechanical analysis.

Table 2. Synthesis of α-Olefin Block Polymers (A-B and A-B-A)

entry	catalyst[a] precursor	block polymer[b]	reaction time (block-min)	$10^{-3}M_n$[c]	M_w/M_n	therm anal. (°C)[d]
1	**1a**	P-*b*-H	A-30/B-30	159	1.11	−18 (T_g)
2	**1a**	P-*b*-H	A-30/B-60	163	1.13	−42 (T_g), −25 (T_g)
3	**1a**	O-*b*-P-*r*-O-*b*-O	A-40/B-20/A-40	60	1.09	9 (T_m), 37(T_m)
4	**1a**	O-*b*-P-*r*-O-*b*-O	A-95/B-60/A-150	253	1.17	−11 (T_m), 40 (T_m), −38 (T_g)
5	**1b**	O-*b*-P-*r*-O-*b*-O	A-130/B-30/A-140	56	1.24	8 (T_m), 53 (T_m)
6	**1b**	O-*b*-P-*r*-O-*b*-O	A-250/B-60/A-260	112	1.43	0 (T_m), 69 (T_m), −52 (T_g)

[a] Complex (0.017 mmol) activated with 100 equiv of MMAO; toluene; entries 1 and 2 temperature is −15 °C, entries 3−6 temperature is −10 °C. [b] Propylene (P), 1-hexene (H), and 1-octadecene (O). [c] Molecular weight data was determined by GPC vs polystyrene standards. [d] T_m and T_g were determined by differential scanning calorimetry (DSC).

segments increases with the chain length of the α-olefin and results in increasing melt transition temperatures in these semicrystalline polymers.[11] Furthermore, the ratio of 1,2- versus 2,1-insertion is sensitive to the nature of the α-diimine ligand. Catalyst **1b**/MAO exhibits a higher fraction of 2,1-insertions than **1a**/MAO. Poly(1-octadecene) produced by **1b**/MAO at 23 °C (entry 15) exhibits fewer branches (33 branches/1000 carbon atoms) and a higher T_m (78 °C) than the polymer produced by **1a**/MMAO (entry 9, 45 branches/1000 carbon atoms, $T_m = 56$ °C).

The living nature of these polymerizations, coupled with the variation in polyolefin properties as a function of α-olefin chain length and ligand structure, permits the synthesis of a variety of unique diblock and triblock polymers. Several examples are shown in Table 2. Sequential monomer addition of propylene and 1-hexene at −15 °C to catalyst **1a**/MMAO results in polypropylene-*b*-poly(1-hexene) with a MWD of 1.13. An overlay of the monomodal GPC elution curves for the polypropylene A block ($M_n = 85\,000$, $M_w/M_n = 1.12$) and the final polypropylene-*b*-poly(1-hexene) A-B diblock ($M_n = 163\,000$, $M_w/M_n = 1.13$) clearly shows a shift to shorter retention times, indicating the clean preparation of a diblock polymer under these conditions (see Supporting Information).

The preparation of α-olefin based A-B-A triblock copolymers where the semicrystalline A block is based on a long-chain α-olefin and the amorphous B block is derived from propylene provides a methodology for the synthesis of elastomeric polyolefins. For example, treatment of catalyst **1a**/MMAO with 1-octadecene at −10 °C for 95 min and then addition of 1 atm of propylene followed by the formation of a second block of poly(1-octadecene) results in the formation of a well-defined high molecular weight elastomeric A-B-A triblock copolymer (see Table 2, entry 4).[12] An analogous preparation using catalyst precursor **1b** + MMAO results in a triblock copolymer in which the A blocks have a melt transition temperature of 69 °C, illustrating the increase in 1,ω-insertion for this catalyst system (entry 6). These triblock polymers are highly elastic and qualitatively show good elastic recovery.

In summary, we have developed procedures for using α-diimine Ni^{II}-based catalysts for the living polymerization of α-olefins. In addition, this work has been extended to the development of a new synthetic strategy for the preparation of near monodisperse elastomeric α-olefin-based block copolymers. The microstructures of these polymers are unique, and they exhibit physical properties unlike those of poly(α-olefins) made by early metal catalysts. Details of the physical properties of these polymers along with additional strategies for preparation of elastomeric polyolefins will be the subject of a future paper.

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Supporting Information Available: Details of catalyst and polymer synthesis and characterization (9 pages). See any current masthead page for ordering and Internet access instructions.

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(11) Incorporation of linear segments also lowers T_g relative to atactic polymers prepared from Ziegler−Natta catalysts. For example, “normal” atactic polypropylene exhibits a T_g of −18 °C, whereas the T_g of polypropylene prepared from these catalysts ranges from −16 to −55 °C.

(12) Since 1-octadecene is not removed during formation of the B block, this block is actually a random polypropylene/octadecene block. Propylene is much more reactive than 1-octadecene thus a much higher fraction of propylene relative to 1-octadecene is incorporated into the polymer. This random block exhibits a low T_m (see Table 2) whereas polypropylene prepared under these conditions exhibits no T_m (see Table 1).