1140 *Macromolecules* **2001,** *34,* 1140−1142

Living Polymerization of Ethylene Using Pd(II) α-Diimine Catalysts

Amy C. Gottfried and Maurice Brookhart*

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290

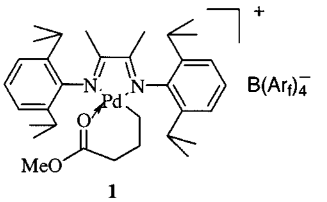
Received September 12, 2000

Revised Manuscript Received December 28, 2000

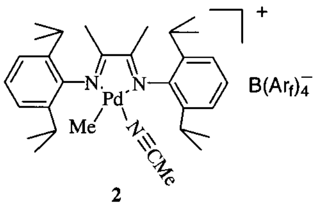
Living polymerizations of α-olefins have been achieved using several catalysts based on the early transition metals, including tris(2,4-pentanedionate)vanadium catalysts activated with diethylaluminum chloride,[1] chelating diamide titanium complexes,[2] zirconium complexes containing $[(t\text{-BuN-}o\text{-}C_6H_4)_2O]^{2-}$ diamido donor ligands,[3] $[t\text{-BuNSiMe}_2\text{Flu}]TiMe_2/B(C_6F_5)_3$ catalysts,[4] Cp_2MMe_2 (M = Zr, Hf) and *rac*-(et)Ind_2ZrMe_2,[5] and dimethylmonocyclopentadienylzirconium acetamidinates,[6] the latter two systems exhibiting living stereospecific polymerization. We have shown that certain late metal-based nickel aryl α-diimine systems polymerize α-olefins in a living fashion and that di- and triblock poly(α-olefins) can be prepared.[7] To date, none of these systems have been shown to catalyze living ethylene polymerization. Two systems known to carry out living ethylene polymerization are $C_5Me_5M(butadiene)X_2/MAO$ (M = Nb, Ta) complexes reported by Mashima[8] and the colbalt(III) system $C_5Me_5(P(OMe)_3\overline{Co{-}CH_2CH(H})R^+$ which we have used to prepare end-functionalized polyethylene.[9]

Aryl α-diimine palladium catalysts, initially reported by us,[10] polymerize ethylene to yield high molecular weight, highly branched amorphous material.[10−19] Molecular weight distributions reported range from 1.4 to 3.9 depending on the reaction conditions,[10,14−17,19] and a bimodal behavior is often observed.[19] In this communication, we report conditions under which the palladium diimine catalysts can be used to carry out living ethylene polymerization to yield amorphous polyethylene with controlled molecular weights and exceptionally narrow molecular weight distributions.

Catalysts **1** and **2**, shown below, were used in the current study. Syntheses of both catalysts have been previously reported.[19]



1



2

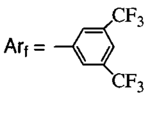


Table 1. Polymerization of Ethylene by 1 at 5 °C, 400 psig in Chlorobenzene[a]

entry	time (h)	M_n ($\times 10^{-3}$)[b]	M_w/M_n[b]	branches/ 1000C[c]
1	1	13	1.09	108
2	2	27	1.06	101
3	3	39	1.05	109
4	4	49	1.05	86
5	5	59	1.05	93
6	6	71	1.04	96
7	14.9	164	1.06	
8	24.2	236	1.06	

[a] Catalyst **1** (5.0×10^{-5} M) in chlorobenzene, total volume 100 mL. [b] Molecular weight data were determined by GPC vs polystyrene standards. [c] Total branching was determined by ^1H NMR spectroscopy.

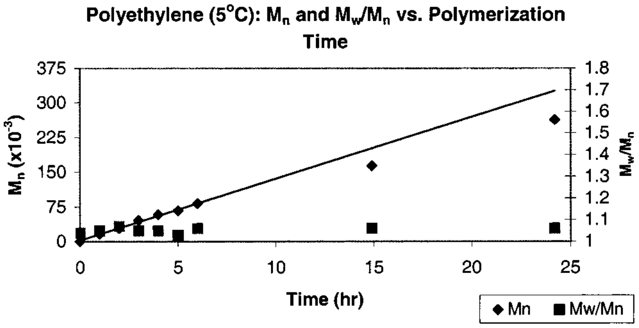


Figure 1. Plot of M_n and M_w/M_n as a function of reaction time for the polymerization of polyethylene at 5 °C and 400 psig of ethylene; catalyst **1** (Table 1, entries 1−8).

Living polymerization of ethylene using catalyst **1** was carried out in chlorobenzene at 5 °C under 400 psig of ethylene. Polymer solutions were quenched with Et_3SiH prior to polymer isolation (eq 1).

$$C_2H_4\ (400\ \text{psig}) \xrightarrow[(2)\ Et_3SiH]{(1)\ \mathbf{1},\ C_6H_5Cl,\ 5\ °C} \text{amorphous polyethylene} \qquad (1)$$

Results are summarized in Table 1, and a plot of M_n and M_w/M_n vs time is shown in Figure 1. The M_n values shown are those determind by GPC using polystyrene standards. As shown in Figure 1, the M_n value increases linearly with time, and the molecular weight distribution remains well under 1.1 up to M_n values of 250K. The M_n values at 15 and 24 h are slightly lower than expected and may signal slight catalyst decomposition.[20] Further proof that this system is living was established by stopping the polymerization at 1 h intervals by removing the ethylene via an argon purge for an hour and then restarting the polymerization by pressurizing it again with 400 psig of ethylene. At the end of each 2 h cycle, an aliquot of polymer was taken, quenched with Et_3SiH, and analyzed by GPC. Despite the absence of monomer during the argon purge cycles, the polyethylene grew in a living manner analogous to that observed in Figure 1 with a linear increase in M_n vs polymerization time. GPC analysis showed monomodal distribution with the MWD remaining below 1.08.

All of the polymers synthesized using the palladium α-diimine catalysts are highly branched with ca. 100 branches/1000 carbons in the polymer (Tables 1 and 2). This branching number is independent of polymerization conditions and is similar to branching numbers previously reported.[10−14] A turnover frequency of 216/h

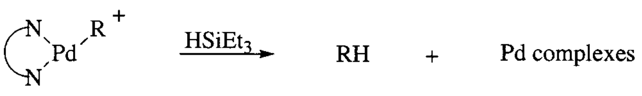
Table 2. Living Ethylene Polymerization: Pressure, Concentration, and Catalyst Adduct Effects[a]

entry	cat.	mol of cat. ($\times 10^{-6}$)	ethylene press. (psig)	yield (g)	M_n ($\times 10^{-3}$)[b]	M_w/M_n[b]	branches/ 1000C[c]
1	1	5.0	400	0.151	58	1.05	102
2	1	5.0	300	0.174	66	1.05	96
3	1	5.0	200	0.167	59	1.06	96
4	1	5.0	100	0.130	51	1.08	94
5	1	5.0	1 atm[d]	0.044	25	1.27	98
6	1	2.5	400		59	1.06	92
7	1	5.0	400	0.151	58	1.05	102
8	1	7.5	400	0.248	57	1.06	96
9	1	15	400	0.474	61	1.05	93
10	2	5.0	400	0.228	64	1.04	93
11	2	5.0	200	0.302	69	1.03	99
12	2	5.0	100	0.225	63	1.03	95
13	2	5.0	1 atm[d]	0.1211	22	1.15	

[a] All polymerizations run for 5 h at 5 °C, in chlorobenzene, total volume 100 mL. [b] Molecular weight data were determined by GPC vs polystyrene standards. [c] Total branching was determined by ^{1}H NMR spectroscopy. [d] Run under 1 atm of ethylene in glass.

at 5 °C was calculated on the basis of moles of catalyst employed and the weight of polymer produced per hour. The resting state of the catalyst is known to be the alkyl olefin complex, (diimine)Pd(C_2H_4)R$^+$ (**3**); thus, the TOF is independent of the pressure of ethylene and controlled by the rate of migratory insertion of **3**.[10,18c] The rate of migratory insertion measured by low-temperature NMR spectroscopy and extrapolated to 5 °C is in good agreement with the observed TOF of 216/h. M_n values calculated on the basis of the TOF are about 2.5 times lower than these shown in Table 1 and indicate that the use of polystyrene standards substantially overestimates the M_n. For example, the predicted M_n at 2 h is 11.4K vs 27K estimated using polystyrene standards.

A critical factor in generating polymer with low polydispersities is the method of quench. When polymer solutions were quenched by removal of monomer and solvent followed by dissolution in hexanes and precipitation in acidified methanol or by addition of methanol directly to the polymerization solution, polymers exhibited a bimodal distribution. The high molecular weight peak was a minor and variable component, and its peak M_n was twice that of the major low molecular weight fraction. This clearly indicates that some chain coupling takes place using this quenching procedure, but the mechanism of such coupling is unknown. We have established that the Pd−alkyl bond in this and related systems is rapidly cleaved by triethylsilane as shown in eq 2.[21]



(2)

Thus, when polymer solutions are quenched with Et_3SiH, the palladium−carbon bond is converted cleanly to a saturated end group, and no high molecular weight fractions are observed. In low molecular weight polymers, the ester end groups can be detected by ^{1}H NMR spectroscopy and, consistent with the reaction shown in eq 2, no unsaturated end groups are visible.

Results of 5 h polymerization runs at various pressures using catalyst **1** are summarized in Table 2, entries 1−5. In the 100−400 psig range, there is no significant change in $M_n$values or in the MWDs of the polymers produced. However, at 1 atm, the molecular weight distribution is substantially broadened (1.27), and the $M_n$value has fallen to 25K. We have previously established that, in the presence of ethylene, chelate complex **1** is in equilibrium with the alkyl ethylene complex **4**, and the equilibrium strongly favors the chelate at low C_2H_4 concentrations (eq 3).[19]

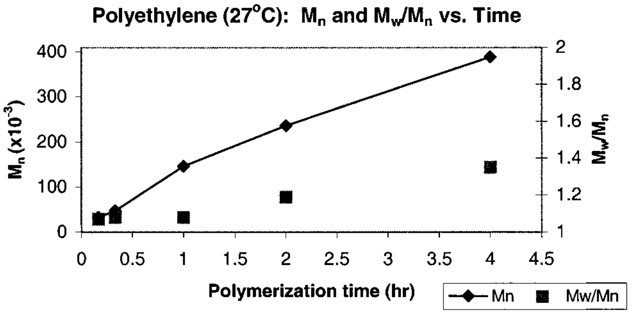
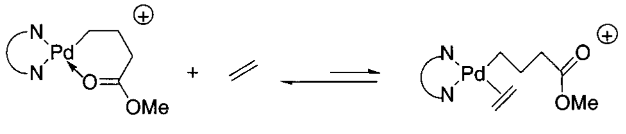


Figure 2. Plot of M_n and M_w/M_n as a function of reaction time for the polymerization of polyethylene at 27 °C and 400 psig of ethylene; catalyst **1**.



1 **4**

(3)

Since initiation occurs by migratory insertion of **4**, at low ethylene pressures where **1** is highly favored the rate of insertion will be very slow relative to the rate of propagation. (Once one insertion occurs from **4**, formation of larger chelates is no longer favored.) Thus, we propose that the broadened molecular weight distribution at 1 atm is due to a very slow rate of initiation relative to the rate of propagation. This is supported by observation of a low molecular weight tail in the GPC trace and a reduced polymer yield (0.044 g at 1 atm vs 0.151 g at 400 psig; see Table 2, entries 1−5). Entries 6−9 show that there is no change in behavior with catalyst concentration, and entries 10−13 show that the acetonitrile adduct, catalyst **2**, behaves as expected, nearly identical to **1**. Using catalyst **2**, the polyethylene produced no longer possesses ester end-caps.

Results of polymerizations carried out at 27 °C, 400 psig, using catalyst **1** are summarized in Figure 2. The increased temperature results in a more rapid rate of propagation, but this is accompanied by a nonlinear increase in M_n and broadening polydispersities. For example, at 1 h the M_n is 146K and the PDI is 1.08, while at 2 h, M_n is 237K and PDI has risen to 1.19. The turnover frequency drops off rapidly beginning at 4460 turnovers/h for a 10 min run and dropping to an average of 2670 turnovers/h for a 2 h run. This drop clearly indicates catalyst decay under these conditions, and the GPC trace at 2 h indicates a substantial low molecular weight tail. While molecular weight and dispersity are controlled early in the reaction, clearly nonliving behavior is observed at extended times.

In summary, we have developed conditions under which living polymerization of ethylene can be carried out using palladium α-diimine catalysts to yield amorphous polyethylene with controlled and very narrow molecular weight distributions. In the case of catalyst **1**, polymers with ester end groups are produced, whereas with **2**, saturated hydrocarbon polymers are formed. Future reports will address synthesis of telechelic and block polymers using these catalysts and other combinations of monomer.

Acknowledgment. This work was supported by the National Science Foundation (CHE-9710380) and by DuPont. A.C.G. thanks the University of North Carolina for a graduate fellowship.

Supporting Information Available: Details of polymerizations and polymer characterization, including GPC traces, illustrating the effects of time, pressure, and temperature on the polymer. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Doi, Y.; Suzuki, S.; Soga, K. *Macromolecules* **1986**, *19*, 2896−2900. (b) Doi, Y.; Koyama, T.; Soga, K. *Makromol. Chem.* **1985**, *186*, 814−819. (c) Doi Y.; Ueki, S.; Keii, T. *Macromolecules* **1979**, *12*, 814−819.

(2) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008−10009.

(3) (a) Schrock, R. R.; Baumann, R.; Reid, S. M.; Goodman, J. T.; Stumph, R.; Davis, W. M. *Organometallics* **1999**, *18*, 3649−3670. (b) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830−3831. (c) Baumann, R.; Schrock, R. R. *J. Organomet. Chem.* **1998**, *557*, 69−75.

(4) Hagihara, H.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 3184−3188.

(5) Fukui, Y.; Murata, M.; Soga, K. *Macromol. Rapid Commun.* **1999**, *20*, 637−640.

(6) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 958−959.

(7) Killian, C.; Temple, D.; Johnson, L.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664−11665.

(8) Mashima, K.; Fujikawa, S.; Tanaka, Y.; Urata, H.; Oshiki, T.; Tanaka, E.; Nakamura, A. *Organometallics* **1995**, *14*, 2633−2640.

(9) (a) Brookhart, M.; DeSimone, J. D.; Grant, B. E.; Tanner, M. J. *Macromolecules* **1995**, *28*, 5375−5380. (b) Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 1443−1444. (c) Brookhart, M.; Volpe, A. F., Jr.; Lincoln, D. M.; Horvath, I. T.; Millar, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 5634−5636. (d) Brookhart, M.; Volpe, A. F., Jr.; DeSimone, J. D.; Lamanna, W. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32*, 461. (e) The living nature of the polymerization has been confirmed by spectroscopic characterization of initiating and propagating (i.e., resting state) species[9b−d] and by linear plots of M_n vs conversion: Volpe, A. F., Jr. PhD Dissertation, University of North Carolina at Chapel Hill, 1991.

(10) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414−6415.

(11) Brookhart, M. S.; Johnson, L. K.; Killian, C. M.; Arthur, S. D.; Fledman, J.; McCord, E. F.; McLain, S. J.; Kreutzer, K. A.; Bennett, A. M. A.; Coughlin, E. B.; Ittel, S. D.; Parthasarathy, A.; Wang, L.; Yang, Z. Processes of Polymerizing Olefins. U.S. Patent 5,866,663, Feb 2, 1999.

(12) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **1999**, 1169−1203.

(13) McLain, S. J.; McCord, E. F.; Johnson, L. K.; Ittel, S. D.; Nelson, L. T. J.; Arthur, S. D.; Halfhill, M. J.; Teasley, M. F.; Tempel, D. J.; Killian, C.; Brookhart, M. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *38* (1), 772−772.

(14) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999**, *283*, 2059−2062.

(15) Heinemann, J.; Mulhaupt, R.; Brinkman, P.; Luinstra, G. *Macromol. Chem. Phys.* **1999**, *200*, 384−389.

(16) Held, A.; Baurers, F. M.; Mecking, S. *Chem. Commun.* **2000**, 301−302.

(17) de Vries, T. J.; Duchateau, R.; Vorstman, A. G.; Keurentjes, J. T. F. *Chem. Commun.* **2000**, 263−264.

(18) For theoretical and mechanistic studies on polymerization by the Pd(II) α-diimine catalysts, see: (a) Michalak, A.; Zeigler, T. *Organometallics* **2000**, *19*, 1850−1858. (b) Tempel, D. J.; Brookhart, M. *Organometallics* **1998**, *17*, 2290−2296. (c) Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, in press.

(19) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888−899.

(20) Longer runs (48 h) exhibit a decrease in turnover frequency indicative of catalyst decay and broadened molecular weight distribution (1.3) with a low molecular weight tail.

(21) (a) LaPoint, A. M.; Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1997**, *119*, 906−917. (b) Huff, R. L.; Brookhart, M. University of North Carolina at Chapel Hill. Unpublished results, 2000.

MA001595L