

Palladium(II)- and Nickel(II)-Catalyzed Olefin Polymerization

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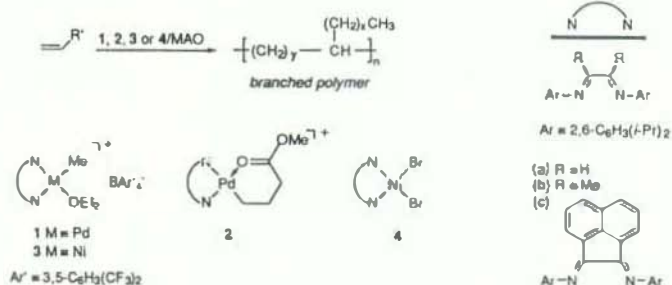
Introduction

The study of homogeneous single-site transition metal d^0 and lanthanide d^{0f} complexes as catalysts for the polymerization of ethylene and α -olefins has been of intense recent interest. These well-defined initiators serve as mechanistic models for the traditional Ziegler-Natta catalysts. In addition, structural variation and careful catalyst design in these homogeneous systems allow for control of polymer microstructure and molecular weight. However, one limitation of these early metal catalysts is their incompatibility with functionalized comonomers due to their highly oxophilic nature. Late transition metal catalysts are less oxophilic, but they most often dimerize or oligomerize olefins rather than form high molar mass polymers.

Results and Discussion

We have recently reported¹ that cationic palladium and nickel complexes with sterically bulky α -diimine ligands polymerize ethylene and α -olefins to high molar mass polymers of unique microstructure² (Scheme 1).

Scheme 1



With the palladium-ether adducts 1, or the much more stable and thus more conveniently applicable chelate complexes 2 as catalyst precursors, highly branched amorphous polyethylene is obtained, with branches of variable length randomly distributed throughout the polymer. Variation of the ethylene concentration over a wide range has a relatively small effect on the overall number of branches and the polymer molecular weight, as well as the catalyst activity (Table 1, entries 1 and 2). Polymerization of α -olefins results in polymers with less branches than expected for chain-growth by 1,2-insertion, thus a significant portion of 2,1-insertions followed by migration of the metal center to the terminal carbon atom must occur.

Table 1. Summary of Olefin Polymerization Data

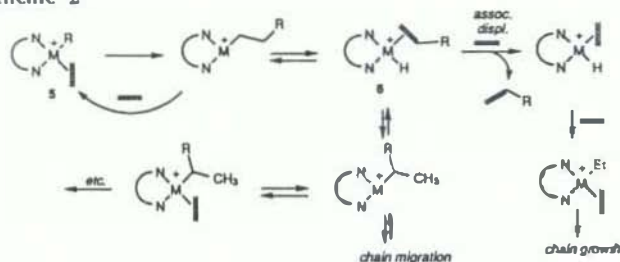
Catalyst	mol cat. $\times 10^6$	Monomer ^c	TOF (h ⁻¹)	\bar{M}_n^a ($\times 10^{-3}$)	\bar{M}_w/\bar{M}_n	Branching ^b
1 2b	10.4	E (2 atm)	1630	297	3.5 ^d	102
2 2b	10.1	E (29 atm)	1540	496	3.0 ^d	98
3 2a	9.9	E (29 atm)	640	36/1.3 ^d	-	93
4 2c	9.8	E (29 atm)	560	82	3.5 ^d	107
5 1b	50	P (1 atm)	580	15	4.3	213
6 1b	100	1-H	650	31	2.5	88
7 4c/MAO	0.83	E (1 atm)	2×10^5	650	2.4	24
8 4c/MAO	0.83	E (4 atm)	2×10^5	610	2.3	5
9 4c/MAO	0.83	E (1 atm)	2×10^5	190	2.2	71
10 4a/MAO	1.7	E (1 atm)	5×10^5	31	2.5	38
11 4a/MAO	1.7	E (15 atm)	2×10^6	32	2.8	<5
12 4b/MAO	1.6	E (1 atm)	1×10^5	520	1.6	48
13 4c/Et ₂ AlCl	17	1-H (10 v%)	2000	140	2.2	100
14 4a/MAO	17	P (1 atm)	3000	74	2.0	275

temperature: 0 °C (entries 7,8,12, and 13); 25 °C (entries 1-6, 9-11, and 14); reaction times: 18.5 h (entries 1-4), 16 h (entry 5), 2h (entries 6 and 13), 30 min (entries 7-9), 10 min (entries 10-12), 1 h (entry 14); solvent (50-200 mL): CH₂Cl₂ (entries 1-6), toluene (entries 7-14); Al:Ni = 100-1000 (entry 13; 10); ^a determined by GPC vs. polystyrene standards; ^b CH₃ groups/1000 carbon atoms; ^c ethylene (E), propylene (P), 1-hexene (1-H); ^d bimodal distribution.

The isolable nickel diethyl ether complexes 3 also catalyze the polymerization of ethylene and α -olefins, exhibiting much higher activities than the analogous palladium complexes (see Table 1). In addition, the nickel catalysts are more conveniently generated *in situ* by the methylaluminoxane (MAO) activation of the diimine nickel dibromide complexes 4 in the presence of olefins. The polyethylene produced by these nickel catalysts ranges from highly linear to moderately branched, as determined by NMR spectroscopy. The extent of branching in the polyethylene prepared using the nickel-based catalysts can be rigorously controlled by variation in reaction conditions (ethylene pressure and temperature) and catalyst structure. At higher ethylene pressures, decreased branching is observed, but polymer productivity and molecular weight are similar (compare entry 7 with 8, and 10 with 11). At higher temperatures, the degree of branching increases significantly (compare entry 7 with 9). Increasing the steric bulk of the α -diimine ligand results in the formation of more highly branched polymer (compare entry 7 with 12). The nickel catalysts exhibit extremely high activities which are comparable to those reported for the group IV metallocene-based catalysts. Turnover frequencies of 2×10^6 , corresponding to a productivity of 100,000 kg of PE mol⁻¹ of Ni h⁻¹ have been observed. The nickel complexes are also highly efficient catalysts for the polymerization of α -olefins. For example, propylene is polymerized by 4a + MAO at 25 °C in toluene to produce amorphous polypropylene (3000 TO/h, $\bar{M}_n = 74,000$), while 1-hexene is polymerized by 4c + Et₂AlCl at 0 °C to produce amorphous poly(1-hexene) (2000 TO/h, $\bar{M}_n = 140,000$).

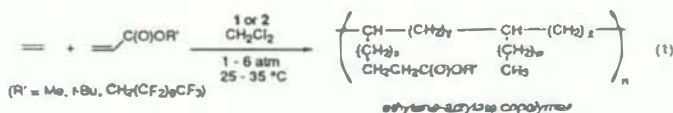
Low temperature NMR-spectroscopic studies support the mechanistic rationale outlined in Scheme 2.

Scheme 2



The alkyl olefin complex 5 was established as the catalyst resting state. Chain transfer in these systems is believed to occur from complex 6 by an associative exchange of free ethylene for the growing polymer chain. The measurement of ethylene exchange rates in these systems suggests that the rate of associative exchange is retarded by the steric bulk of the α -diimine ligands.

Copolymers of ethylene or α -olefins with alkyl acrylates and other functionalized vinyl monomers can also be obtained employing the palladium catalysts (Table 2 and equation 1).



GPC analysis, using simultaneous refractive index and UV detection, indicates that the fraction of acrylate comonomer is equally distributed over all molecular weights of the monomodal distribution. Like the corresponding homopolymers, the ethylene-copolymers are highly branched. The ester-groups are incorporated predominantly at the ends of branches in the mode shown in equation 1 ($x \geq 0$), resulting from 2,1-insertion of acrylate into the Pd-C bond.

Table 2. Summary of Olefin Copolymerization Data

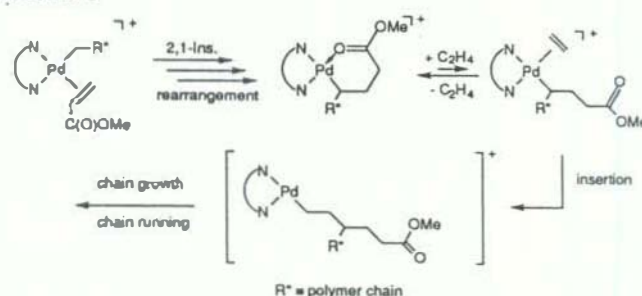
Cat.	Monomers ^d	conc. Comon.	p (atm)	Comon. incorp. ^b	TON E re. P	TON Comon. (x10 ⁻³)	\bar{M}_n^a	\bar{M}_w/\bar{M}_n	
1	2b	E/MA	0.6 M	2	1.0%	7710	78	88	1.8
2	2b	E/MA	2.9 M	2	6.1%	1296	84	26	1.6
3	2b	E/MA	5.8 M	2	12.1%	455	63	11	1.6
4	2b	E/MA	5.8 M	6	4.0%	3560	148	42	1.8
5	2a	E/MA	5.8 M	6	5.0%	355	19	0.3 ^c	-
6	2c	E/MA	5.8 M	6	4.7%	364	18	10	1.8
7	2b	E/ <i>t</i> BuA	3.4 M	6	0.7%	956	7	25	1.6
8	1b	E/FOA	0.6 M	1	0.6%	8928	54	106	3.1
9	2b	E/MVK	3.0 M	6	1.3%	626	8	7	1.5
10	2b	P/MA	0.6 M	6	1.1%	1179	13	37	1.8
11	2b	P/FOA	1.8 M	2	5.6%	145	9	18	1.8

0.1 mmol catalyst; solvent: CH₂Cl₂ (total volume CH₂Cl₂ and comonomer, 100 ml., entry 8: 60 ml.); temperature: 35 °C (entry 8: 25 °C); reaction time: 18.5 h (entry 8: 24 h); ^a determined by GPC vs. polystyrene standards; ^b mol-%; ^c determined by ¹H NMR spectroscopy of the non-volatile product fraction; ca. 0.5 g of volatile products were formed additionally; ^d ethylene (E), propylene (P), methyl acrylate (MA), *t*-butyl acrylate (*t*BuA), H₂C=CHC(O)OCH₂(CF₂)₆CF₃ (FOA), methyl vinyl ketone (MVK).

Accordingly, in low-temperature NMR studies, reacting the ether-complexes 1 with methyl acrylate (MA), 2,1-migratory insertion is observed with ca. 95% regioselectivity, followed by rearrangement to yield the six-membered chelate complexes 2 as the final products. The overall number of methyl- and ester-ended branches per 1000 carbon atoms (excluding atoms of C(O)OR groups) resembles the branching of the corresponding ethylene- or α -olefin-homopolymers.

Productivities of the copolymerizations are greatly reduced relative to those of homopolymerizations. As expected, the fraction of acrylate incorporation is directly proportional to its concentration in the reaction solution (Table 2, entries 1 - 3) and productivity falls correspondingly. Variation of the diimine backbone substituents R does not significantly effect the percentage of acrylate incorporation in the copolymer (entries 4 - 6). Productivities, however, are dependent upon the nature of R (Me > H \approx naphthene) and follow the same trend as observed for the palladium-catalyzed ethylene homopolymerizations.

Scheme 3



NMR studies and the structure of the copolymers support the mechanistic pathway for the copolymerization of ethylene and MA depicted in Scheme 3. During the copolymerization, a six-membered chelate is formed after insertion of MA. Further chain-growth requires coordination of ethylene by displacement of the chelating carbonyl group, and under the conditions of entries 1 - 4 in Table 2, this is the turnover limiting step. Therefore, the chelate complex is the catalyst resting state. In accord with this proposed mechanism, raising the ethylene pressure results in an increase in ethylene- and MA-turnovers (entry 4 vs. 3).

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References

- (1) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* 1995, *117*, 6414-6415.
- (2) The polymer microstructure was derived from ¹H and ¹³C NMR data. Detailed characterization of these polymers by ¹³C NMR spectroscopy confirms the proposed structure; McCord, E.; McLain, S., unpublished results.