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Copolymerization of Ethylene and Propylene with Functionalized Vinyl Monomers by Palladium(II) Catalysts

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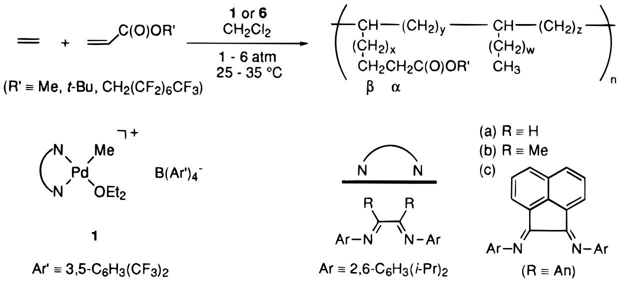
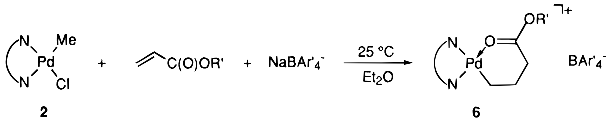
Ziegler−Natta and related catalysts based on early transition metal d^0 complexes are extensively used for the coordination polymerization of nonpolar olefins such as ethylene and propylene.[1] However, due to their highly oxophilic nature, these catalysts are incompatible with functionalized vinyl monomers.[2] Late transition metal catalysts are less oxophilic, but they most often dimerize or oligomerize olefins[3] rather than form high molar mass polymers.[4] Thus, ethylene−acrylate or ethylene−vinyl acetate copolymers are still exclusively produced by radical routes, which often require high pressure.[5,6] Recently we reported the development of highly active Ni(II)- and Pd(II)-based catalysts of the general type $[(ArN{=}C(R){-}C(R){=}NAr)M(CH_3)(OEt_2)]BAr'_4$ (*cf.* Scheme 1) that *polymerize* ethylene *and* α-olefins.[7] The bulky substituents on the aryl groups of the diimine ligand block associative olefin exchange and thus effectively retard chain transfer. We report here the first examples of metal-catalyzed copolymerizations of nonpolar olefins (ethylene and propylene) with alkyl acrylates to give high molar mass polymers.

Scheme 1



The copolymerization reactions were initiated by the diethyl ether adducts **1** or the more stable chelate complexes **6**, which were easily prepared from [(N∧N)PdMeCl] (**2**), acrylate, and $NaBAr'_4$ (eq 1) and isolated as air- and temperature-stable solids.[8] Exposure of **1** or **6** to ethylene or propylene in the presence of alkyl acrylates results in the formation of high molar mass random copolymers (Table 1). Using simultaneous refractive index and UV detection, GPC analysis indicates that the fraction of acrylate comonomer is equally distributed over all molecular weights of the monomodal distribution.[8] Similar to the corresponding ethylene homopolymers,[7] the ethylene copolymers are amorphous, highly branched materials with ∼100 branches/1000 carbon atoms.[9] Typical T_g values fall in the range of −67 to −77 °C. The ester groups are predominantly located at the ends of branches in the manner shown in Scheme 1 ($x \geq 0$). Evidence of this structural feature, which requires a 2,1-insertion of acrylate into the Pd−C bond, comes from observation of a triplet for H_α at 2.2−2.4 ppm and a multiplet for H_β at 1.6 ppm.[10] Similar properties were also determined for an ethylene−methyl vinyl ketone copolymer (entry 12) and for the amorphous propylene−acrylate copolymers (entries 14 and 15).[11]



(1)

Productivities of the copolymerizations are greatly reduced relative to those of the homopolymerizations (entry 13). As expected, the fraction of acrylate incorporation is directly proportional to its concentration in the reaction solution (entries 1−3), and productivity falls correspondingly. Gas solubility experiments[12] show that the ethylene/methyl acrylate (MA) molar ratio is ∼1:6 under the conditions of entry 4, which implies relative rates of incorporation of ethylene and MA of ∼150:1 at equal molar concentrations. Variation of the diimine backbone substituents R does not significantly affect the percentage of acrylate incorporation in the copolymer (entries 4−6). Productivities, however, are dependent upon the nature of R (Me > An ≈ H) and follow the same trend as observed for the ethylene homopolymerizations.[7]

Low-temperature NMR studies provide insight into the mechanism of the copolymerization. The reaction of the ether adduct **1a** with MA at −80 °C produces the π-acrylate complex **3a**, which undergoes 2,1-migratory insertion with ∼95% regioselectivity to yield the four-membered chelate **4a** (eq 2). At −80 to −60 °C, complex **4a** isomerizes to the five-membered chelate complex **5a**, which rearranges to the six-membered chelate complex **6a** at −20 °C. Insertion of fluorinated octyl acrylate (FOA) also yields predominantly the six-membered chelate **6** as the final product. In contrast, with *tert*-butyl acrylate, a significant percentage of 1,2-insertion to give a second five-membered chelate $[(N{\wedge}N)PdCH_2CHMeC(O)O\text{-}t\text{-}Bu]^+$ (**5′**) also occurs.[8]

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[1] As leading references, see: (a) Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217−219. (b) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015−10031. (c) Coughlin, E. B.; Bercaw, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 7606−7607. (d) Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455−1457. (e) Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507−508. (f) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355−6364.

[2] Polymerization of olefins containing functional groups in a position remote from the vinyl group by early transition metal catalysts has been reported: (a) Chung, T. C. *Macromolecules* **1988**, *21*, 865−869. (b) Chung, T. C.; Rhubright, D. *Macromolecules* **1993**, *26*, 3019−3025. (c) Kesti, M. R.; Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 9679−9680.

[3] (a) Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 1137−1138. (b) Peuckert, M.; Keim, W. *Organometallics* **1983**, *2*, 594−597. (c) Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185−206.

[4] Polymerization of ethylene has been described: (a) Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 1443−1444. (b) Brookhart, M.; Volpe, A. F., Jr.; Lincoln, D. M.; Horvath, I. T.; Millar, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 5634−5636. (c) Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466−467. (d) Klabunde, U.; Ittel, S. D. *J. Mol. Catal.* **1987**, *41*, 123−134. (e) Wang, L.; Lu, R. S.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1993**, *115*, 6999−7000. Certain Ni(II) catalysts convert α-olefins to oligomers with degrees of polymerization of ∼4−20: (f) Möhring, V. M.; Fink, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1001−1003.

[5] Doak, K. W. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Ed.; John Wiley and Sons: New York, 1986; Vol. 6, pp 386−429.

[6] For polymerization of olefins containing functional groups in a position remote from the olefinic function, *cf.* refs 2 and 4d. A palladium-catalyzed reaction of ethylene with methyl acrylate has been claimed to give low molecular weight materials ($M_n \leq 4100$), but no detailed product characterizations were given: Drent, E.; Pello, D. H. L.; Jager, W. W. Eur. Pat. Appl. 589527, 1994.

[7] Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414−6415.

[8] For complete data, *cf.* supporting information.

[9] C(O)OR carbon atoms are excluded.

[10] Detailed characterization of these polymers by ^{13}C NMR spectroscopy supports the proposed copolymer structure: McCord, E.; McLain, S., unpublished results.

[11] The propylene−acrylate copolymers possess ∼210 methyl groups/1000 carbon atoms.[9] This implies 2,1-insertion of propylene and subsequent “chain straightening” by chain migration to the terminal carbon atom.

[12] Mecking, S.; Brookhart, M., unpublished results.

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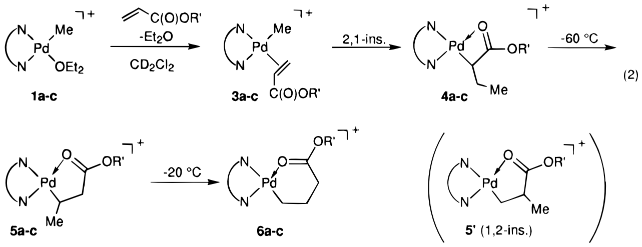
Table 1. Olefin Polymerization Data[a]

			reaction conditions		results				polymer properties	
							TON[e]			
entry	cat.[b]	monomers[c]	concn comon (M)	P (atm)	polymer mass (g)	comon incorp[d] (%)	E *re.* P	comon	$\bar{M}_n$[f] ($\times 10^{-3}$)	$\bar{M}_w/\bar{M}_n$
1	**6b**	E/MA	0.6	2	22.2	1.0	7710	78	88	1.8
2	**6b**	E/MA	2.9	2	4.3	6.1	1296	84	26	1.6
3	**6b**	E/MA	5.8	2	1.8	12.1	455	63	11	1.6
4	**6b**	E/MA	5.8	6	11.2	4.0	3560	148	42	1.8
5	**6a**	E/MA	5.8	6	1.2	5.0	355	19	0.3[g]	
6	**6c**	E/MA	5.8	6	1.2	4.7	364	18	10	1.8
7	**6b**	E/tBuA	3.4	6	2.8	0.7	956	7	25	1.6
8	**6b**	E/tBuA	0.4	1	1.9	0.4	665	3	6	1.8
9	**1a**	E/FOA	0.6	1	1.5	0.3	506	2	3	1.6
10	**1b**	E/FOA	0.6	1	27.5	0.6	8928	54	106	3.1
11	**6b**	E/FOA	1.8	1	9.5	0.9	2962	27	95	2.7
12	**6b**	E/MVK	3.0	6	1.8	1.3	626	8	7	1.5
13	**6b**	E		6	10.3		37127		384	3.1
14	**6b**	P/MA	0.6	6	5.0	1.1	1179	13	37	1.8
15	**6b**	P/FOA	1.8	2	1.0	5.6	145	9	18	1.8

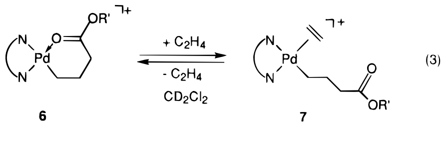
[a] Conditions: 0.1 mmol of catalyst (entry 13, 0.01 mmol); solvent, CH_2Cl_2 (total volume CH_2Cl_2 and comonomer, 100 mL; entries 9 and 10, 60 mL); temperature, 35 °C (entries 8−11 and 13, 25 °C); reaction time, 18.5 h (entries 8−10, 24 h; entry 11, 37 h). [b] Complexes **6**: R′ ≡ Me (entry 8, R′ ≡ *t*Bu). [c] Ethylene (E), propylene (P), methyl acrylate (MA), *tert*-butyl acrylate (*t*BuA), $H_2C{=}CHC(O)OCH_2(CF_2)_6CF_3$ (FOA), methyl vinyl ketone (MVK). [d] In mol %. [e] Turnover number ≡ moles of substrate converted per mole of catalyst. [f] Determined by GPC *vs* polystyrene standards, uncorrected. [g] Determined by ^{1}H NMR spectroscopy of the nonvolatile product fraction; ~0.5 g of volatile products formed additionally.



(2)

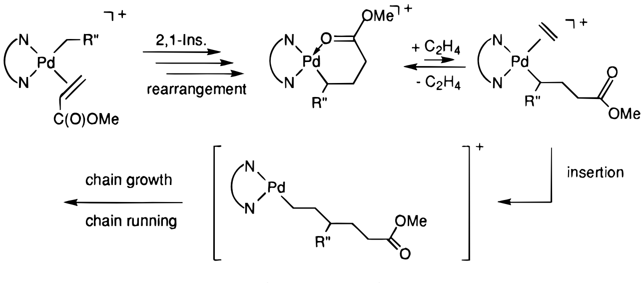
Exposure of the ether adduct **1a** to 5 equiv each of ethylene and MA at −80 °C results in selective formation of the ethylene complex $[(N\wedge N)PdMe(C_2H_4)]^+$.[7] After complete consumption of ethylene occurs at −30 °C, 1 equiv of MA is incorporated to form a chelate complex analogous to **6a** by insertion into the $Pd{-}(CH_2)_{2n}Me$ bond. The much more rapid insertion of acrylates into the Pd−R bond (−80 °C) than ethylene insertion (−30 °C)[7] clearly shows that the predominant incorporation of ethylene into the copolymers is due to the low relative binding constant of MA to the electrophilic metal center.

Reversible substitution of the chelating carbonyl group of **6** by ethylene was observed at low temperatures for both the MA and FOA chelates (eq 3). In contrast to the former, the FOA chelates open readily at −80 °C in the presence of 1 equiv of ethylene.[8,14] For the MA chelates, study of the temperature dependency of the equilibria **6** + C_2H_4 ⇌ **7** at −100 to −58 °C gave, for **6a**, $\Delta H° = -8.1 \pm 0.2$ kcal/mol, $\Delta S° = -34 \pm 1$ eu; for **6b**, $\Delta H° = -5.3 \pm 0.3$ kcal/mol, $\Delta S° = -31 \pm 2$ eu; and for **6c**, $\Delta H° = -5.7 \pm 0.1$ kcal/mol, $\Delta S° = -27 \pm 1$ eu. Extrapolation to the conditions of entry 4 in Table 1 gives a ratio of the chelate to the ethylene complex, **6b**/**7b**, of ~1000:1. Warming **6** (R′ ≡ Me) to temperatures above −30 °C results in ethylene polymerization. The only organometallic species observed during this process is **6**, indicating that initiation to form the active species for polymerization is much slower than chain propagation.



(3)

Scheme 2



R" ≡ polymer chain

The NMR studies and the structure of the copolymers support the mechanistic pathway depicted in Scheme 2. During the copolymerization, a six-membered chelate is formed after insertion of MA. Further chain growth requires coordination and insertion of ethylene,[13] and under the conditions of entries 1−4 in Table 1, 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).

In conclusion, these are the first transition metal catalysts capable of copolymerizing ethylene and propylene with polar-functionalized vinyl monomers to high molar mass polymers by a coordination-type polymerization.

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Supporting Information Available: Details of catalyst and polymer synthesis and characterization and descriptions of low-temperature NMR experiments (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[13] Insertion of acrylate at this point is unlikely, as complexes **6** react only slowly (days) with excess acrylate.[8]

[14] The more facile substitution of the carbonyl group of the fluorinated chelate by ethylene may be partially responsible for the higher productivities in the FOA copolymerizations.