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Insertion Polymerization of Acrylate

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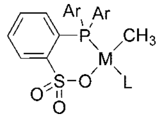
Catalytic insertion polymerization of ethylene and propylene is employed for the production of more than 60 million tons of polyolefins annually.[1] An insertion polymerization of electron deficient polar-substituted vinyl monomers has remained elusive, however. For example, polyacrylates are not accessible by insertion polymerization.[2]

A major advance was the finding by Brookhart et al. that cationic Pd(II) diimine complexes can copolymerize ethylene and 1-olefins with acrylates.[3] Due to “chain walking” of the catalyst, the highly branched copolymers contain acrylate units preferentially at the end of branches. Linear ethylene-acrylate copolymers are obtained with neutral Pd(II) phosphinosulfonate complexes, which do not “chain walk”.[4] These catalyst are also compatible with a broad scope of functional vinyl monomers.[5,6] The polymers obtained contain ethylene (or 1-olefin) as the major component (≥75 mol %), and no consecutive insertions of electron deficient vinyl monomer into the polymer chain have been accounted for. An acrylate unit inserted in the polymer chain can *κ-O* coordinate to the metal center via the carbonyl group. Further chain growth requires opening of this chelate by ethylene. This mechanism has been demonstrated for the diimine complexes[3] and is also suggested for the phosphinosulfonate complexes.[4]

We report on multiple insertion of acrylate in homo- and copolymerizations, employing appropriately labile-substituted catalyst precursors.

The aforementioned neutral catalysts have been studied as in situ mixtures of metal sources and ligands,[4,7] and employing well-defined single-component catalyst precursors [(P∧O)PdMe(L)] (L = pyridine, PPh_3, ½ tmeda (tmeda = $Me_2NCH_2CH_2NMe_2$)).[8−11] However, these N- and P-based ligands L are relatively strong σ-donors, and it must be anticipated that they severely compete with the monomer for coordination at the metal center, rendering a large portion of the metal centers in a dormant inactive state. This not only adds complexity to studies of the polymerization reaction, but limits the range of acrylate incorporation as a certain ethylene concentration is required to achieve any substantial polymerization rate.



1a-L: M = Ni, Ar = 2-$MeOC_6H_4$
2a-L: M = Pd, Ar = 2-$MeOC_6H_4$
2b-L: M = Pd, Ar = 2-[2,6-$(MeO)_2C_6H_3$]C_6H_4

As a potentially more labile ligand, dimethylsulfoxide (dmso) was studied. Complexes **1**,**2-dmso** were obtained in high yield from the respective phosphine sulfonic acid and [(tmeda)MMe_2] in dmso as a solvent. While tertiary amines bind more strongly to the Ni(II) and Pd(II) centers than dmso (vide infra), the high boiling point of dmso enables dynamic removal of tmeda under vacuum and finally formation of the dmso complexes.

In the solid state, **1a-dmso** and **2b-dmso** possess a distorted square planar coordination geometry around the metal center, with the methyl and the phosphine ligands mutually cis to each other. While **1a-dmso** exhibits *κ-O* coordination of dmso to the Ni(II) center, in **2b-dmso** coordination to the less electrophilic Pd(II) center occurs via the sulfur atom (Figure 1 and Supporting Information, SI).

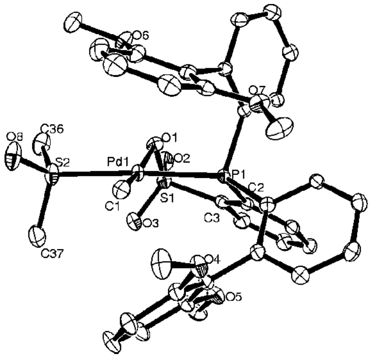


Figure 1. ORTEP plot of **2b-(*κ-S*)-dmso**. Ellipsoids are shown with 50% probability. Hydrogen atoms are omitted for clarity.

The relative binding strength of dmso to the Pd(II) center in comparison to N-donor ligands was assessed by ^1H NMR spectroscopy at 25 °C for **2a-dmso**. Upon addition of 1.5 equiv of NMe_2nBu, pyridine or lutidine, the Pd-Me resonances of **2a-NMe₂*n*Bu** (δ 0.03), **2a-pyr** (δ 0.24), and **2a-lut** (δ −0.04), respectively, appeared along with free dmso (δ 2.54), while the characteristic resonances of **2a-dmso** disappeared completely (cf. SI). This corresponds to equilibrium constants for [(P∧O)PdMe(dmso)] + L ⇄ [(P∧O)PdMe(L)] + dmso of $K_{eq} \geq 10^2$ ($L = NMe_2nBu$, pyridine, or 2,6-lutidine).

In line with this labile binding of dmso, **1,2-dmso** were found to be highly active single component catalyst precursors for the polymerization of ethylene. **1a-dmso** produces oligomers with an average activity approaching 10^6 TO h^{-1} (cf. SI) which is among the highest values reported for neutral Ni(II) catalysts to date.[12] For the less electrophilic Pd(II) analogues **2-dmso** high activities are observed at

Table 1. Ethylene Polymerization[a]

entry	catalyst precursor	p [bar]	average TOF [mol (C_2H_4) mol (Pd)$^{-1}$ h^{-1}]	PE yield [g]	M_n[b] [10^3 g mol^{-1}]	M_w/M_n[b]	branching[c] [/1000 C]
1−1	**2a-dmso**	2	4.1×10^4	1.99	6.3	2.3	8
1−2	**2a-dmso**	5	1.0×10^5	4.92	12.6	2.2	3
1−3	**2a-dmso**	7.5	1.0×10^5	4.94	18.2	1.9	1
1−4	**2a-dmso**	10	1.0×10^5	5.04	13.1	1.9	1
1−5	**2a-pyr**	2	2.2×10^4	1.05	11.2	2.1	4
1−6	**2a-pyr**	5	3.0×10^4	1.49	16.6	2.2	2
1−7	**2a-pyr**	10	4.0×10^4	1.95	19.5	1.9	1
1−8	**2b-dmso**	2	1.1×10^5	1.59	11.3	1.9	<1

[a] Reaction conditions: 100 mL of toluene; 80 °C, 3.5 μmol of Pd(II) (entry 1-8: 90 °C, 1 μmol); 30 min polymerization time. [b] Determined by GPC at 160 °C vs linear PE. [c] By ^{13}C NMR at 130 °C; only methyl branches observed.

Table 2. Ethylene-MA Copolymerization[a]

entry	catalyst precursor	p [bar]	MA concn [mol L^{-1}]	polymer yield [g]	TOF C_2H_4	TOF MA	X_{MA}[d]	M_n [10^3 g mol^{-1}]	M_w/M_n
2−1	**2a-pyr**	5	0.6	0.82	1128	120	9.6%	2.4[b]	1.8[b]
2−2	**2a-dmso**	5	0.6	2.57	3545	368	9.4%	2.5[b]	2.3[b]
2−3	**2a-dmso**	5	1.2	1.36	1317	391	23%	4.3[c]	2.0[c]
2−4	**2a-dmso**	5	2.5	0.74	493	268	35%	3.1[c]	1.8[c]
2−5	**2a-dmso**	5	5	0.36	149	161	52%	1.8[c]	1.6[c]
2−6	**2a-dmso**	10	5	0.66	433	243	36%	2.8[c]	1.8[c]
2−7	**2a-dmso**	15	7.5	0.72	496	258	34%	3.0[c]	1.8[c]

[a] Reaction conditions: total volume toluene + MA, 50 mL; 95 °C; 20 μmol Pd(II); 1 h reaction time. [b] From GPC at 160 °C in 1,2,4-trichlorobenzene vs linear PE. [c] From GPC at 40 °C in THF, vs polystyrene standards. [d] From ^1H NMR at 130 °C.

low ethylene pressure. Activities are independent of monomer concentration at $p(C_2H_4) \geq 5$ bar for **2a-dmso** (Table 1). This saturation behavior suggests that dmso does not compete effectively with ethylene for binding to the metal center even at these low pressures. By contrast, activities observed with **2a-pyr** and **2a-lut** are lower and saturation kinetics require $p(C_2H_4) > 10$ bar (Table 1 and SI).[8]

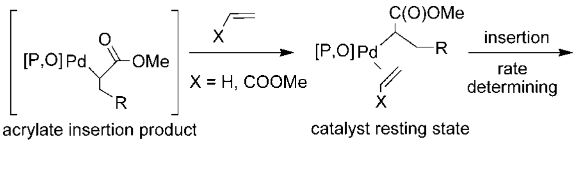
Ethylene-methyl acrylate (MA) copolymerization with **2a-dmso** also proceeds with substantially higher activity than with **2a-pyr** (at only 5 atm C_2H_4; Table 2). Under otherwise identical reaction conditions, molecular weight and MA-content of the obtained materials is virtually identical (entries 2−1 and 2−2). This confirms that the same catalytically active species are operative in both cases, which however are in an unfavorable equilibrium with dormant pyridine complexes in the case of **2a-pyr**.

The reactivity of **2a-dmso** facilitates copolymerizations at high [MA]:[C_2H_4] ratios. An acrylate incorporation of 52 mol % MA was observed at $p(C_2H_4) = 5$ bar, [MA] = 5 mol L^{-1} (entry 2−5). ^{13}C NMR analysis (cf. SI) of copolymers with $X_{MA} > 30$ mol-% reveal, in addition to isolated acrylate repeat units,[4] "alternating" acrylate−ethylene−acrylate sequences and consecutive acrylate units in the polymer chain.

At a given $p(C_2H_4)$, acrylate incorporation increases with increasing [MA] as expected. This is primarily due to a decrease in rate of ethylene incorporation, while the overall rate of MA incorporation is similar (entries 2−2 to 2−4).[13] This implies that monomer insertion after an acrylate insertion is rate determining.

In polymerizations at different $p(C_2H_4)$ and with an approximately constant ratio of [MA]:[ethylene], not only the copolymer composition but also activities are found to be virtually independent of the reaction conditions (entries 2−4, 2−6, and 2−7). This suggests that the rate determining step is insertion of monomer into the palladium alkyl bond of [(P∧O)Pd{CH(COOMe)CH_2R}(monomer)]. Contrary to current suggestions,[4] opening of four-membered chelates formed by *κ-O* coordination of an inserted acrylate unit appears not to be the major decisive limiting factor. This is also supported by the finding that reaction of MA with **2a-dmso** does not afford such a chelate complex, but [(P∧O)Pd{CH(COOMe)CH_2CH_3}(dmso)] (30 equiv MA, 25 °C, in CH_2Cl_2; SI). In combination with the above finding that under polymerization conditions dmso does not compete substantially with ethylene binding, this suggests that copolymerization rates are significantly retarded by an intrinsically slow insertion of monomer into the α-carbonyl substituted alkyl (Scheme 1).[14]

Scheme 1. Rate Limiting Step of Copolymerization



The reaction of **2a-dmso** with MA alone at elevated temperature resulted in multiple consecutive insertions. Reaction of 2 g MA in toluene (4 mol L^{-1}) with 80 μmol **2a-dmso** at 95 °C for 4 h yields 0.70 g nonvolatile oligomers (TON ≈ 100). FAB-MS analysis of this sample reveals formation of up to MA-heptamers obtained by MA insertion into a Pd−H bond; a number average degree of polymerization DP_n = ca. 5 was estimated by NMR analysis. NMR analysis (cf. SI) of the product mixture confirms that most chains were formed by MA-insertion into a Pd−H bond and that 2,1-insertion is predominant over the 1,2-modus. Analysis of olefinic and aliphatic endgroups confirms that chain transfer occurs exclusively by β-H elimination.

In summary, copolymers with unprecedented acrylate incorporations have been prepared. The homooligomerization of acrylate reported has all mechanistic features of an acrylate insertion polymerization, namely multiple insertions before chain transfer occurs. The rate of acrylate copolymerization with the catalyst system studied appears to be retarded by an intrinsically slow monomer insertion into the alkyl species resulting from acrylate insertion.

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Supporting Information Available: Detailed experimental procedures and analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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