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Copolymerization

Incorporation of Vinyl Chloride in Insertion Polymerization**

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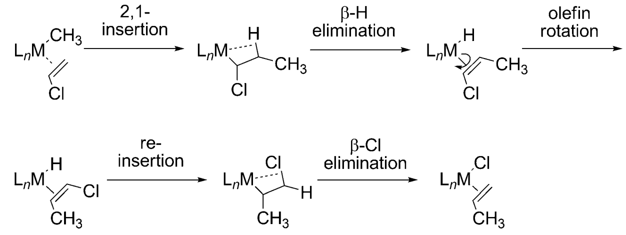
Dedicated to Pierre Braunstein on the occasion of his 65th birthday

Catalytic polymerizations of ethylene and propylene are practiced industrially on a large scale. Vinyl chloride (VC) is the monomer produced on the largest scale after ethylene and propylene.[1] However, the incorporation of VC into (co)polymers by insertion polymerization has remained elusive, and VC even inhibits polyethylene formation.[2] The origin of this reactivity is believed to be very specific for VC. Unlike for other vinyl monomers, such as acrylates,[3–5] acrylonitrile,[6] and others,[7–12] inhibition of polymerization by coordination of the functional groups of the free monomer and of repeat units formed from its incorporation into the polymer chain is not considered to be problematic for VC. Vinyl chloride is a weak κ-Cl donor (comparable, for example, to methylene chloride). Extensive studies with early- and late-transition-metal catalysts have revealed that a different more fundamental problem prohibits the catalytic polymerization of vinyl chloride.[2a–d] Thermodynamically favorable β-chloride elimination occurs subsequently to the incorporation of VC into the growing chain to afford inactive metal chloride complexes, and thus irreversibly deactivates the catalyst.

The ß-chloro substituted alkyl species that undergo this detrimental reaction are formed by a net 1,2-insertion of VC into the growing chain. For an insertion of VC into late-transition-metal–carbon bonds, DFT calculations[2a,b,d] and experimental evidence point to an initial insertion in a 2,1-fashion. However, the propensity of late-transition-metal polymerization catalysts for "chain-walking" results in a net 1,2-incorporation of VC (Scheme 1). This unfavorable outcome has been observed for α-diimine palladium complexes, bis(imino)pyridine iron and cobalt complexes, and for salicylaldiminato, and phosphine–enolato nickel complexes.[2c,d,13]

Owing to the low propensity of neutral phosphine–sulfonato palladium complexes for chain walking,[14] we decided to study their polymerization properties towards vinyl chloride. Most recently, related cationic phosphine–phosphine oxide palladium catalysts have been reported to exhibit reduced activity for ethylene polymerization in the presence of VC. However, an ethylene homopolymer that has no detectable chlorine content is formed by these catalysts.[2e] We now report, that among complexes **L1**Pd to **L4**Pd studied (Figure 1), complexes [**L2**PdCH$_3$(dmso)], [{**L2**PdCH$_3$}$_2$], [**L2**PdH(P*t*Bu$_3$)], and [**L4**PdCH$_3$(dmso)] catalyze the formation of chlorinated copolymers from ethylene and VC owing to a partial suppression of chain walking after monomer insertion.



Scheme 1. 2,1-Insertion of VC into a metal methyl bond, net-1,2-insertion by chain walking, and β-Cl elimination.

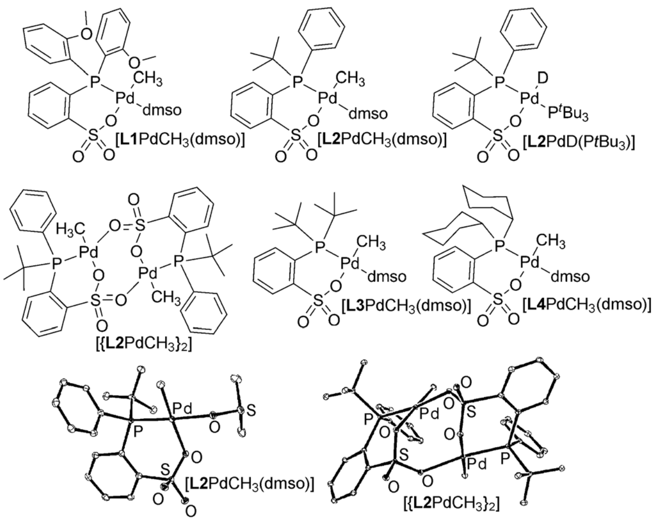


Figure 1. Catalyst precursors **L1**Pd to **L4**Pd and ORTEP plots of [**L2**PdCH$_3$(dmso)] and [{**L2**PdCH$_3$}$_2$] with hydrogen atoms omitted for clarity and thermal ellipsoids set at 50% probability.[15]

Prior to copolymerization experiments, the reactivity of [**L1**PdCH$_3$(dmso)] toward VC was assessed by monitoring experiments by NMR spectroscopy (caution: VC is carcinogenic and requires special safety measures, see the Supporting Information). VC (4.3 equiv) insertion into [**L1**PdCH$_3$(dmso)] occurs, albeit slowly, at 298 K in [D$_2$]methylene chloride solution. A chloroalkyl palladium complex is not detected, but formation of propylene (by β-Cl elimination)

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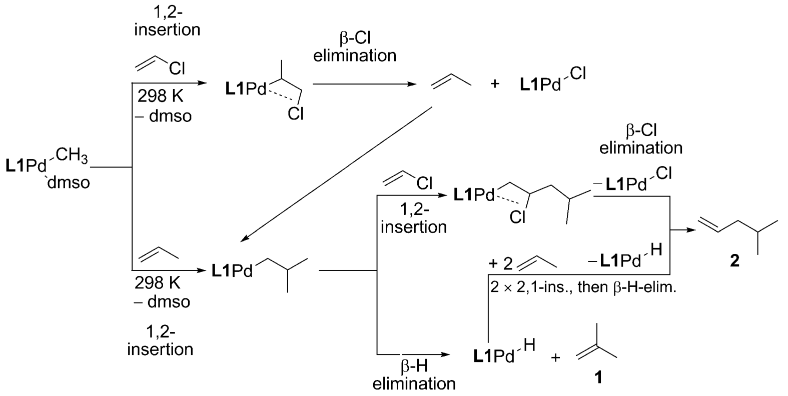


Scheme 2. Formation of propylene, *iso*-butene (**1**), and 4-methyl-pent-1-ene (**2**) by reaction of VC with [**L1**PdCH$_3$(dmso)]. [**L1**PdCH$_2$CH(CH$_3$)$_2$], propylene, **1**, and **2** were all identified by NMR spectroscopy.

after net 1,2-insertion of VC is evident after 5 min. The propylene formed reacts faster than VC with the remaining [**L1**PdCH$_3$(dmso)] to form a palladium isobutyl complex, [**L1**PdCH$_2$CH(CH$_3$)$_2$], by 1,2-insertion (Scheme 2). [**L1**PdCH$_2$CH(CH$_3$)$_2$] undergoes β-H elimination to afford *iso*-butene (**1**), as identified by comparison to genuine samples of **1**. In addition, 4-methylpentene (**2**) forms either by VC insertion into [**L1**PdCH$_2$CH(CH$_3$)$_2$] followed by β-Cl elimination, or by double insertion of propylene into a palladium hydride followed by β-hydride elimination. Furthermore, acetaldehyde slowly forms by (catalyzed) hydrolysis of VC owing to the presence of traces of water.

Given the known higher propensity for ethylene insertion into [**L1**PdCH$_3$(dmso)] than for propylene insertion, these results suggest that ethylene–VC copolymerizations need to be conducted at moderate (3–4 bar) ethylene pressure to facilitate significant VC insertion. Except for the control experiments in the absence of catalyst or ethylene, all experiments resulted in the formation of a polymer, which was analyzed by NMR spectroscopy and gel permeation chromatography (GPC; Table 1; for details see the Supporting Information). During these polymerizations the color of the reaction mixture changes from nearly colorless to the pale yellow color that is indicative of decomposed catalyst. Based on this observation the catalyst half-life time under polymerization conditions is estimated to approximately 20 min (see the Supporting Information). Generic catalyst decomposition pathways have been recently identified.[14b] However, we believe that net 1,2-insertion of VC followed by β-chloride elimination as observed in the experiments monitored by NMR spectroscopy (see above) constitutes a major decomposition route.

NMR analyses of the polymers obtained indicate that CHCl units have not been incorporated in a mid-chain fashion in detectable amounts.[16] However, signals typical of (long-chain) 2-chloroalkanes were present in the ^{1}H and ^{13}C NMR spectra, indicating up to 0.1 % incorporation of VC when complexes [**L2**PdCH$_3$(dmso)], [{**L2**PdCH$_3$}$_2$], or [**L4**PdCH$_3$(dmso)] were used (Figure 2 and Table 1). Most characteristic, the CH$_3$C*H*ClCH$_2$-R proton resonates at 4.08 ppm as a virtual sextet with $J_{HH} = 6.3$ Hz, which is correlated to a ^{13}C signal at 58.44 ppm through $^1J_{CH}$. This C*H*Cl signal couples to a doublet ($^3J_{HH} = 6.6$ Hz) at 1.56 ppm (C*H*$_3$CHClCH$_2$-R; ^{13}C NMR: 25.16 ppm) and to a multiplet at $\delta = 1.78$ ppm (CH$_3$CHClC*H*$_2$-R; ^{13}C NMR: 40.54 ppm), as deduced from ^{1}H homodecoupling, 1D ^{1}H TOCSY-, ^{1}H,^{1}H gCOSY, and ^{1}H,^{13}C gHSQC experiments. Furthermore, these resonances match the respective resonances of 2-chloroheptane, 2-chlorodecane, and 12-chlorotridecan-1-ol (for details see the Supporting Information).[17]

Table 1: Ethylene–VC copolymerizations with catalyst precursors **L1**Pd to **L4**Pd.[a]

entry	catalyst precursor	T [K]	cat. [µmol]	p(C$_2$H$_4$) [bar]	VC [g]	n_{VC}:n_{cat}	yield [mg]	TON[b] C$_2$H$_4$	inc. VC [mol %][c]	n[PE]/n-[mCPE][d]	M_n (NMR) [g mol^{-1}][f]	M_n (GPC) [g mol^{-1}][g] (M_w/M_n)
1	[**L1**PdCH$_3$(dmso)]	353	50	4	2.2	704	123	88	–	n.a.[e]	4700	2600 (1.8)
2	[{**L2**PdCH$_3$}$_2$]	353	42	4	1.9	724	100	85	0.084	3.3:1	8000	4200 (2.4)
3	[{**L2**PdCH$_3$}$_2$]	343	45	4	1.5	533	179	142	0.066	4.6:1	8000	4400 (2.6)
4	[{**L2**PdCH$_3$}$_2$]	313	45	4	0.4	142	177	140	0.029	9.8:1	8400	4000 (1.6)
5	[{**L2**PdCH$_3$}$_2$]	313	45	–	0.5	178	–	–	–	n.a.[e]	–	–
6	[**L2**PdCH$_3$(dmso)]	343	47	4	3.2	1089	127	96	0.106	5.0:1	4500	2600 (2.2)
7	[**L2**PdCH$_3$(dmso)]	323	47	4	1.2	409	268	203	0.049	2.4:1	14 400	8000 (1.5)
8	[**L2**PdCH$_3$(dmso)]	343	45	4	1.8	640	282	223	0.063	5.2:1	7100	5500 (1.8)
9	[**L3**PdCH$_3$(dmso)]	303	45	4	2.8	996	315	250	–	n.a.[e]	5900	6600 (1.6)
10	[**L4**PdCH$_3$(dmso)]	333	45	4	2.3	818	298	236	0.048	3.4:1	13 400	6000 (2.5)
11	–	343	–	4	3.6	–	–	–	–	n.a.[e]	–	–
12	[**L2**Pd^{13}CH$_3$(dmso)]	343	47	4	2.6	885	215	163	0.082	3.2:1	8100	5300 (1.8)
13	[**L2**Pd^{13}CH$_3$(dmso)]	343	47	3	2.6	885	151	115	0.096	3.6:1	6100	3000 (2.2)
14	[**L2**PdH(P*t*Bu$_3$)]	358	19	3.2	1.7	1432	15	28	0.399	1.8:1	3900	n.d.[h]

[a] For 2 h in 100 mL toluene, see the Supporting Information. [b] Turnover number (TON): polymerized C$_2$H$_4$ per Pd present (mol/mol). [c] Incorporated VC determined by integration of the CH$_3$C*H*ClCH$_2$-R ^{1}H NMR signal versus polyethylene (PE) backbone signals in C$_2$D$_2$Cl$_4$ at 373–383 K. [d] Ratio of PE chains/monochlorinated PE chains (mCPE) determined by ^{1}H NMR spectroscopy from the ratio of olefinic group versus CH$_3$C*H*Cl group signals. [e] Not applicable. [f] Determined by integration of the olefinic versus backbone ^{1}H NMR signals. [g] Determined by high temperature GPC in trichlorobenzene at 403 K versus linear PE standards. [h] Not determined.

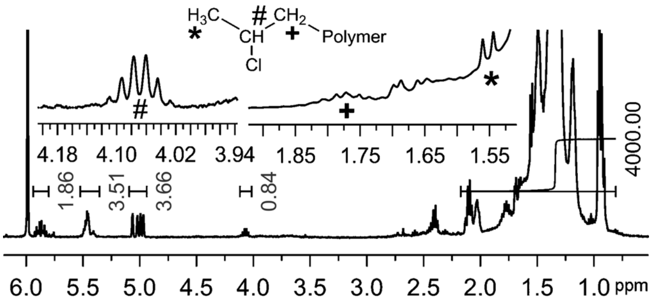


Figure 2. ^{1}H NMR spectrum of ethylene–VC copolymer (entry 2, Table 1) with characteristic $CH_3CHClCH_2$ end group signals.

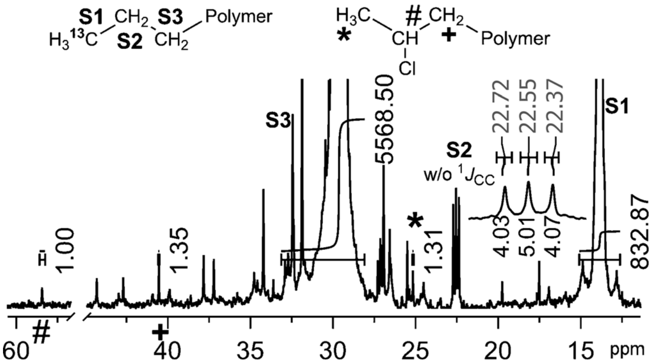
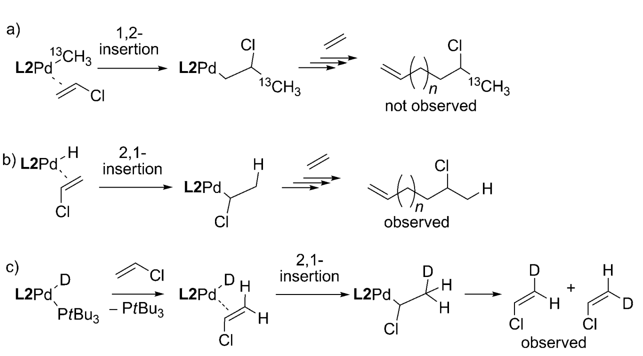


Figure 3. ^{13}C NMR spectrum of ethylene–VC copolymer (entry 13, Table 1) obtained with [**L2**Pd$^{13}CH_3$(dmso)], indicating $^1J_{CC}$-coupled S2 end groups, whereas the CH_3CHCl end group has natural abundance ^{13}C.

These $CH_3CHClCH_2$-R groups may be formed either by 1,2-insertion of VC into the palladium methyl bond of [**L2**PdCH$_3$(dmso)], [{**L2**PdCH$_3$}$_2$], or [**L4**PdCH$_3$(dmso)] and subsequent ethylene insertion (also cf. Scheme 3 a), or by 2,1-insertion into a palladium hydride complex and subsequent ethylene insertion (also cf. Scheme 3 b).[18] To determine which of these insertion modes is occurring, ^{13}C-labeled [**L2**Pd$^{13}CH_3$(dmso)] was used as a catalyst precursor. Analysis of the polymers formed (Table 1, entries 12 and 13) indicates that the ^{13}C-labeled methyl group is located in > 95 % in the unfunctionalized polymer end group as evidenced by the natural abundance $^{13}CH_3\mathit{C}H_2CH_2$ (S2) end group signal split into a doublet with $^1J_{CC} = 34.8$ Hz and the ^{13}C-labeled $^{13}\mathit{C}H_3CH_2CH_2$ (S1) signal in comparison to the $\mathit{C}H_3CHClCH_2$ signals (no $^1J_{CH}$, no $^1J_{CC}$, and no signal enhancements as a result of the ^{13}C label were detected; Figure 3 and the Supporting Information). That is, the observed CH_3CHCl group in the polymer is formed by 2,1-VC insertion into a palladium hydride species [**L2**PdH(VC)] (Scheme 3 b) and not by 1,2-insertion into [**L2**Pd$^{13}CH_3$(VC)] (Scheme 3 a).



Scheme 3. Experimentally excluded 1,2-insertion of VC in [**L2**Pd$^{13}CH_3$(VC)] (a), and 2,1-insertion of VC into palladium hydride species as a source of $^{12}CH_3\mathit{C}HClCH_2$-R units found in ethylene VC copolymers (b) and of 2-deuterated VC in a scrambling experiment (c).

This result is fully corroborated by a reaction (NMR tube) of palladium deuteride complex [**L2**PdD(P*t*Bu$_3$)] with VC: this reaction results in scrambling of the deuterium label into the 2-position of VC to yield 2-deuterated VC by 2,1-insertion and β-hydride elimination, but not into the 1-position to yield 1-deuterated VC (Scheme 3 c; for experimental details see the Supporting Information). It is noteworthy, that the use of [**L2**PdD(P*t*Bu$_3$)] also enables ethylene–VC copolymerization with incorporation of $CH_3CHClCH_2$ groups reaching 0.4 mol % (Table 1, entry 14), although the yield is lower than for reactions using [**L2**PdCH$_3$(dmso)], [{**L2**PdCH$_3$}$_2$], or [**L4**PdCH$_3$(dmso)].

Having established that VC incorporation into the copolymer proceeds after β-hydride elimination by insertion into the resultant palladium hydride species, it is evident that the materials obtained are mixtures of ethylene homopolymer chains, initiated by palladium methyl complexes, and of monochlorinated polyethylene (mCPE) chains, initiated by palladium hydride complexes. The ratio of olefinic/CH_3CHCl groups enables a rough estimate of the portion of all polymer chains that consist of chlorinated chains. For example, for entry 2 in Table 1 this ratio indicates that approximately every fourth chain is chlorinated and that therefore approximately 30 % of all palladium hydride complexes that initiate chain growth produce VC-containing chains.[19] These results are summarized for all polymerizations in Table 1, column 11.

In conclusion, for the first time an insertion copolymerization of VC with ethylene has yielded chlorine-containing copolymers. NMR analysis of the polymers, labeling, and stoichiometric insertion studies reveal that incorporation of CHCl units proceeds by 2,1-insertion of VC into palladium hydride species. After this 2,1-insertion of VC, ethylene insertion resulting in monochlorinated polyethylene is competitive to chain walking (which through the net 1,2-insertion of VC would result in a detrimental β-chloride elimination).

Regardless of the limited incorporation of vinyl chloride, this first isolation of chlorine-containing polymers in combination with a mechanistic understanding represents a significant impetus to a long-standing challenge. Future studies will focus on further suppression of chain walking, which results in the problematic net 1,2-insertion of VC, and on facilitating in-chain incorporation of VC into polymers.

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Keywords: homogeneous catalysis · insertion · palladium · polymerization · vinyl compounds

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[19] This estimate accounts for formation of one ethylene homopolymer chain by palladium methyl complexes [**L2**PdCH$_3$(dmso)], [{**L2**PdCH$_3$}$_2$], and [**L4**PdCH$_3$(dmso)] prior to formation of mCPE chains by palladium hydrides. Note that when starting from [**L2**PdH(P*t*Bu$_3$)] (entry 14, Table 1) approximately 36% of all palladium hydride species form mCPE chains.