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Copolymerization of Ethylene and Vinyl Fluoride by (Phosphine-bis(arenesulfonate))PdMe(pyridine) Catalysts: Insights into Inhibition Mechanisms

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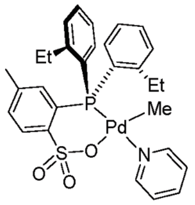
The insertion copolymerization of ethylene and polar vinyl monomers by Pd^{II} catalysts has been studied extensively.[1] Vinyl halides are particularly challenging substrates for copolymerization because they compete poorly with ethylene for binding to Pd^{II} catalysts, and for vinyl chloride and vinyl bromide, rapid β-halide elimination of $PdCH_2CHXR$ species generated by 1,2 vinyl halide insertion or 2,1 insertion followed by chain-walking results in catalyst deactivation.[2] We previously reported that (PO)PdMe(py) (py = pyridine) catalysts based on ancillary 2-PAr_2-4-Me-benzenesulfonate ligands (PO^-; Ar = 2-Et-Ph, 2-OMe-Ph, or Ph, Chart 1) copolymerize ethylene and vinyl fluoride (VF) to linear copolymers that contain a small amount of VF (< 0.5 mol %).[3,4] VF significantly reduced the polymer yield and slightly reduced the molecular weight compared to ethylene homopolymerization under the same conditions. The only detectable placements of VF in the copolymer were the in-chain $-CH_2CHFCH_2-$ unit and a trace amount of $-CH_2CHFCH_3$ chain end units.

We recently reported a new type of Pd^{II} catalyst (Li-OPO)-PdMe(L) (L = py (**1a**); 4-(5-nonyl)-py) (**1b**), Chart 1) based on the phosphine-bis(arenesulfonate) ligand PPh(2-SO_3Li-4-Me-Ph)(2-SO_3-4-Me-Ph)$^-$ ([Li-OPO]$^-$).[5] **1a** and **1b** self-assemble into tetramers in which four (Li-OPO)PdMe(L) units are linked by Li−O bonds that form a central $Li_4S_4O_{12}$ cage (Chart 1). Both **1a** and **1b** produce linear polyethylene (PE) with a very high molecular weight and broad molecular weight distribution, characteristic of multisite catalysis. Under conditions where the tetrameric structure remains substantially intact, the PE contains a substantial high molecular weight fraction, while under conditions where fragmentation is more extensive, the PE contains a large low molecular weight fraction. These results suggest that the tetrameric assembly gives rise to the high molecular weight polymer. Here we report that **1a**,**b** catalyze the copolymerization of ethylene with VF to yield copolymers with a significantly higher level of VF incorporation than observed for conventional (PO)-PdMe(py) catalysts, which enables the characterization of previously unobserved VF placements in the copolymer and provides insights into the mechanism by which VF inhibits polymerization.

Ethylene/VF copolymerizations were carried out using **1a**,**b** as the catalysts at 80 °C in toluene or hexanes. These results and results for the conventional phosphinesulfonate catalyst (2-P(2-Et-Ph)$_2$-4-Me-benzenesulfonate)Pd(Me)(py) (**2**) are shown in Table 1. **1a**,**b** yield highly linear (< 5 Me branches/1000 C) copolymers that contain up to 3.6 mol % VF (eq 1). The copolymers produced by **1a** in toluene display broad molecular weight distributions, indicative of partial fragmentation of the tetranuclear species and similar to results for ethylene homopolymerization.[5] The copolymers produced by **1b** in toluene display narrower molecular weight distributions, indicative of more extensive catalyst fragmentation, possibly resulting from the greater solubility of **1b** vs **1a**. However, the VF incorporation level is similar for both **1a**,**b**. Additionally, the copolymers produced by **1b** in hexanes, in which **1b** is insoluble and cage fragmentation is less significant than in toluene, also contain a high VF incorporation level (3.6 mol %, Table 1, entry 10). Collectively, these results suggest that both the tetrameric forms of **1a**,**b** and mononuclear species generated by cage fragmentation incorporate more VF than conventional (PO)PdMe(py) catalysts.

Chart 1. Structures of Catalysts



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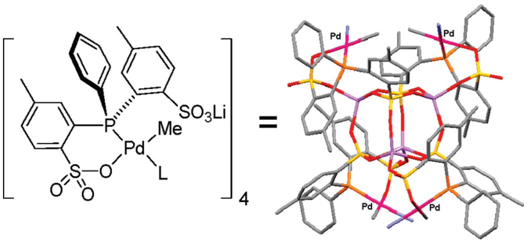
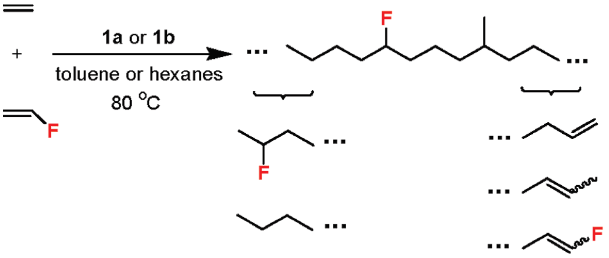


L = pyridine, **1a**
L = 4-(5-nonyl)-pyridine, **1b**



(1)

The addition of VF invariably results in a significant reduction in the polymer yield (Table 1, entry 5 vs 6 and entry 7 vs 9). However, as shown in Figure 1, the yield of copolymer produced by **1a** increases linearly with reaction time, suggesting that VF inhibits but does not deactivate the catalyst.

The microstructure of the copolymers was established by ^1H and ^{19}F NMR and FT-IR spectroscopy.[6] Four VF units were detected in the copolymer by NMR (Figures 2 and 3): $-CH_2CHFCH_2-$ (major), $-CH_2CHFCH_3$ (minor), *cis*-$CH_2CH{=}CHF$ (minor), and *trans*-$CH_2CH{=}CHF$ (very minor).[7] The FT-IR spectra contain an aliphatic ν_{CF} stretching band at 1068 cm^{-1} for the $-CH_2CHFCH_2-$ and $-CH_2CHFCH_3$ units, along with a vinyl ν_{CF} stretching band at 1162 cm^{-1} and a $\nu_{C=C}$ band at 1672 cm^{-1} for the $-CH_2CH{=}CHF$ units.

To exclude the possibility of radical copolymerization, control copolymerizations in the presence of excess galvinoxyl (10 equiv vs Pd) were carried out. The copolymer yields, VF incorporation,

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Table 1. Representative Ethylene/VF Copolymerization Results with Catalysts 1a,b and 2[a,b]

entry	catalyst	P_{VF} (psi)	$P_{C_2H_4}$ (psi)	time (h)	yield (g)	M_n[c] (10^3)	M_w[c] (10^3)	PDI[c]	VF incorp[d] (mol %)	T_m[e] (°C)
1	**1a**	60	240	2	0.146	6.45	173	27	0.8	133.6
2	**1a**	100	200	2	0.129	3.00	29.6	9.8	1.1	130.2
3	**1a**	100	100	4	0.036	1.76	85.0	48	2.5	122.4
4[f]	**1a**	100	100	4	0.044	1.32	62.8	47	2.6	123.7
5	**1a**	100	100	1	0.013	1.32	26.2	19	3.0	126.8
6	**1a**	0	100	2	0.795	2.13	71.3	33		129.4
7	**1b**	120	130	2	0.038	1.77	4.20	2.4	2.4	126.7
8[f]	**1b**	120	130	2	0.047	2.26	9.16	4.0	1.9	129.4
9	**1b**	0	130	2	3.09	3.09	6.51	2.1		129.0
10[g]	**1b**	120	130	2	0.028	1.60	494	310[h]	3.6	127.8
11	**2**	120	130	2	0.142	9.90	18.1	1.9	0.6	129.0

[a] Conditions: toluene, 50 mL, 10 μmol catalysts, 80 °C. [b] Copolymerization procedure: reactor charged with catalyst and solvent in the glovebox, connected to vacuum line and briefly exposed to vacuum, pressurized with VF at 25 °C, and then connected to gas manifold, pressurized with ethylene (on demand) to the desired total pressure at 25 °C, heated to 80 °C and kept at this temperature for the desired reaction time. [c] GPC. [d] VF incorporation in copolymer determined by NMR. [e] DSC. [f] Polymerization in the presence of galvinoxyl (100 μmol). [g] Hexanes used as the solvent. [h] Bimodal molecular weight distribution. For the higher molecular weight fraction, M_w = 1 120 000, M_n = 233 000, PDI = 4.8; for the lower molecular weight fraction, M_w = 1300, M_n = 736, PDI = 1.8. See Supporting Information for details.

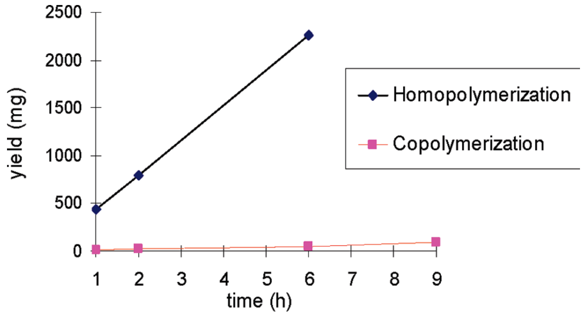


Figure 1. Plots of yield vs reaction time for ethylene homopolymerization and ethylene/VF copolymerization using **1a** as the catalyst. Conditions: toluene, 50 mL, [cat.] = 0.2 mM, $P_{C_2H_4}$ = 100 psi for homopolymerization, and $P_{C_2H_4}$ = P_{VF} = 100 psi for copolymerization, 80 °C. See Supporting Information for details.

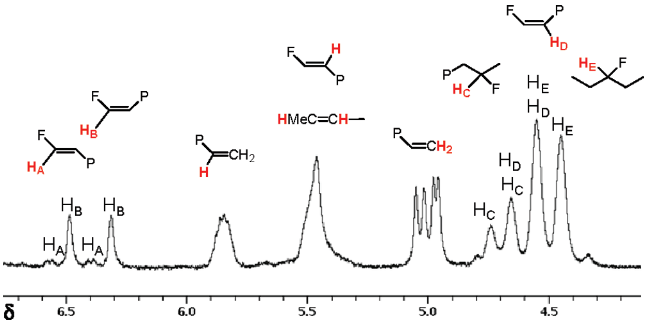


Figure 2. ^{1}H NMR spectrum (o-dichlorobenzene-d_4, 120 °C) of ethylene/VF copolymer produced by **1a** (Table 1, entry 3).

and VF placements were similar to those obtained in the absence of galvinoxyl, and analysis of the polymerization mixture showed that the galvinoxyl was not consumed (Table 1, entries 3, 4 and entries 7, 8). Also, the linear microstructure of copolymers produced by **1a**,**b** is significantly different from the branched microstructure of copolymers produced by AIBN-initiated radical ethylene/VF copolymerization.[3] These results indicate that the ethylene/VF copolymerization does not proceed by a radical mechanism.

The microstructure of the ethylene/VF copolymers is consistent with the polymerization mechanism in Scheme 1. The in-chain $-CH_2CHFCH_2-$ unit can be generated by either 1,2 or 2,1 VF insertion into growing Pd−R species. The $-CH_2CHFCH_3$ chain ends are most likely formed by β-H elimination to generate a Pd−H species, followed by 2,1 VF insertion, or by chain

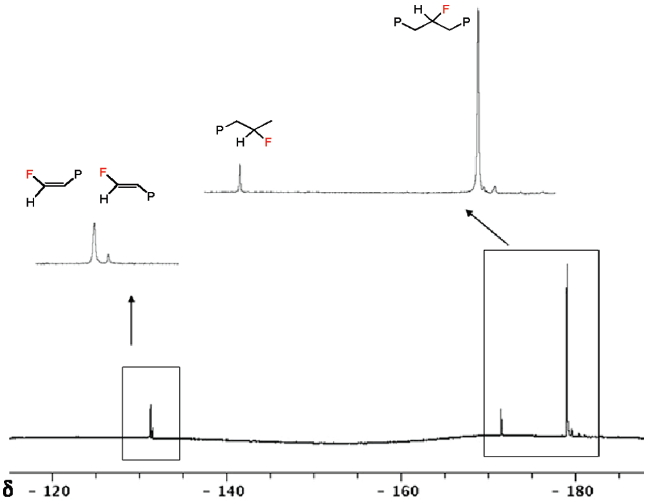
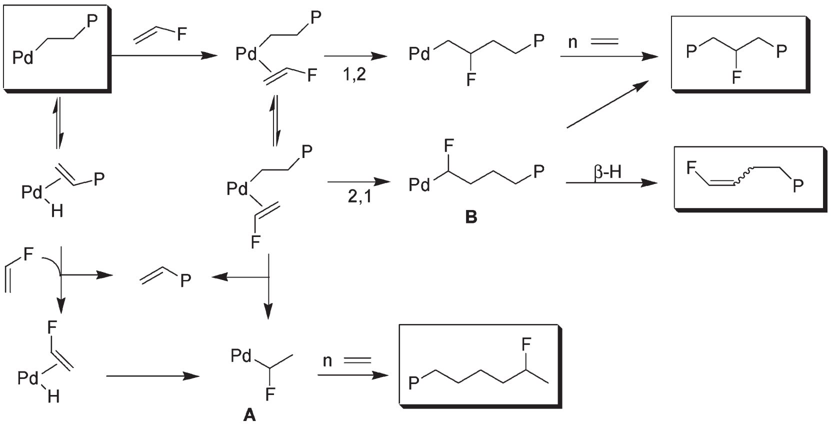


Figure 3. ^{19}F{^{1}H} NMR spectrum (o-dichlorobenzene-d_4, 120 °C) of ethylene/VF copolymer produced by **1a** (Table 1, entry 3).

transfer to bound VF, producing in both cases a $PdCHFCH_3$ intermediate (**A**), which undergoes ethylene insertion. The $-CH_2CH{=}CHF$ chain ends are most likely formed by 2,1 VF insertion into Pd−R species to generate a $PdCHFCH_2R$ intermediate **B**, followed by β-H elimination. Similar 2,1 insertion/β-H elimination processes were observed in (phosphine-enolate)NiR-catalyzed ethylene/methyl methacrylate and (PO)PdR-catalyzed ethylene/acrylonitrile copolymerizations.[4d,8] The observation of the $-CH_2CHFCH_3$ and $-CH_2CH{=}CHF$ chain ends is strong evidence that α-F-alkyl-Pd species are formed in the copolymerization reaction. Such species are expected to have high barriers to ethylene or VF insertion due to the strong electron-withdrawing effect of the α-F, which explains the observed inhibition by VF.[4d,9] The observation of sustained catalytic activity for long reaction times (Figure 1) argues against termination by β-F elimination being a significant process.

This work shows that (phosphine-bis(arenesulfonate))PdMe(pyridine) catalysts **1a**,**b** copolymerize ethylene and VF to linear copolymers that contain a significantly higher level of VF incorporation (up to 3.6 mol %) than observed for conventional (PO)PdMe(L) catalysts (< 0.5 mol %). High VF incorporation levels are observed for **1a**,**b** under conditions where the tetrameric cage structure remains substantially intact (**1b** in hexanes) and where significant cage fragmentation to form monomeric catalyst species occurs (**1a**,**b** in toluene). VF strongly inhibits the activity of the catalysts, probably due to the formation of α-fluoroalkyl

Scheme 1



Pd(CHFR) (R = H or polymeryl) intermediates, which have high barriers to ethylene or VF insertion due to the electron-withdrawing effect of the α-F substituent. Studies to probe the origin of the high VF incorporation by **1a,b** and the speciation of these catalysts under copolymerization conditions are in progress.

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Supporting Information Available: Experimental procedures, NMR spectra, and GPC traces of selected copolymer samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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