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Catalytic Copolymerization of Ethylene with Vinyl Sulfones

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An incorporation of polar moieties in polyolefins is desirable with regard to key properties such as adhesion to polar substrates, barrier and transport properties, or solvent resistance. Sulfone groups are of particular interest, as they possess an unusually high dipole moment (4.49 D), which much exceeds most other functional groups.[1] Vinyl sulfones, however, are in general difficult substrates for any type of polymerization. By contrast to other polar vinyl monomers $H_2C{=}CHX$, common free-radical polymerization is problematic, and the same holds for ionic polymerizations.[2,3]

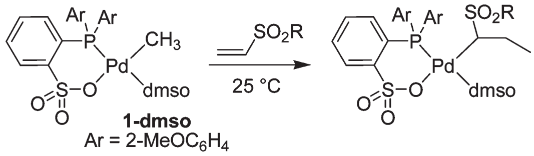
While insertion polymerizations of ethylene and propylene are employed industrially on a large scale, the incorporation of polar vinyl comonomers is challenging due to unfavorable interactions of the free monomer or resulting repeat units with the electrophilic active metal sites and specific deactivation routes.[4,5] These obstacles can be met, however, with certain d^8 metal catalysts as illustrated by ethylene and 1-olefin copolymerization with acrylates by cationic Pd(II) and Ni(II) catalysts.[6,7] Most recently, neutral Pd(II) phosphinesulfonato catalysts[8] have been demonstrated to copolymerize ethylene with a broad scope of functional vinyl monomers,[8−13] including even acrylonitrile[14] and vinyl acetate.[15]

Pd(II) phosphinesulfonato complexes **1-dmso** have been found to enable exceptionally high incorporations of acrylate in insertion polymerizations due to the comparatively labile nature of the dmso ligand.[16] This encouraged studies of the generally difficult vinyl sulfones as monomers, insertion polymerization of which hitherto is unknown.

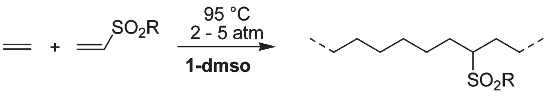
Exposure of a CD_2Cl_2 solution of **1-dmso** to methyl vinyl sulfone (MVS, 7 equiv) or phenyl vinyl sulfone (PVS, 14 equiv) at room temperature resulted in insertion into the Pd−Me bond, as evidenced by disappearance of the Pd−Me ^{1}H NMR resonance (Scheme 1). Pseudo-first-order rate constants of $k_{\text{obs}} = 6.7 \times 10^{-5}\ \text{s}^{-1}$ (MVS) and $k_{\text{obs}} = 7.8 \times 10^{-5}\ \text{s}^{-1}$ (PVS) are 1 order of magnitude lower by comparison to the insertion of methyl acrylate (Supporting Information). Insertion occurs selectively in a 2,1-fashion, resulting in the ingrowth of a characteristic triplet at δ 0.71 ppm (see Supporting Information for comprehensive NMR data of the insertion products). The absence of a signal corresponding to free dmso (δ: 2.54 ppm) suggests the insertion products to be dmso-coordinated complexes $[(\text{PO})\text{Pd}(\text{CH}(C_2H_5)SO_2R(\text{dmso})]$ (R = Me, Ph). Insertion of sulfone is also demonstrated by ESI-MS (Supporting Information).

In line with this stoichiometric study, **1-dmso** indeed catalyzes the copolymerization of ethylene with vinyl sulfones (Table 1, Scheme 2). Comparison of a 1 h and a 4.5 h polymerization experiment (entries 1 and 4) under otherwise identical conditions (5 atm, 95 °C) shows that the catalyst is stable for hours under polymerization conditions. At a given ethylene pressure, vinyl sulfone incorporation increases with increasing comonomer concentration, as expected. At the same time, catalyst activity decreases (entries 2−4 and 6). Copolymers with a methyl vinyl sulfone incorporation of up to 14 mol % (54 wt %) were obtained.

Scheme 1. Stoichiometric Insertion of Vinyl Sulfone into the Pd−Me Bond



Scheme 2. Copolymerization of Ethylene with Vinyl Sulfones



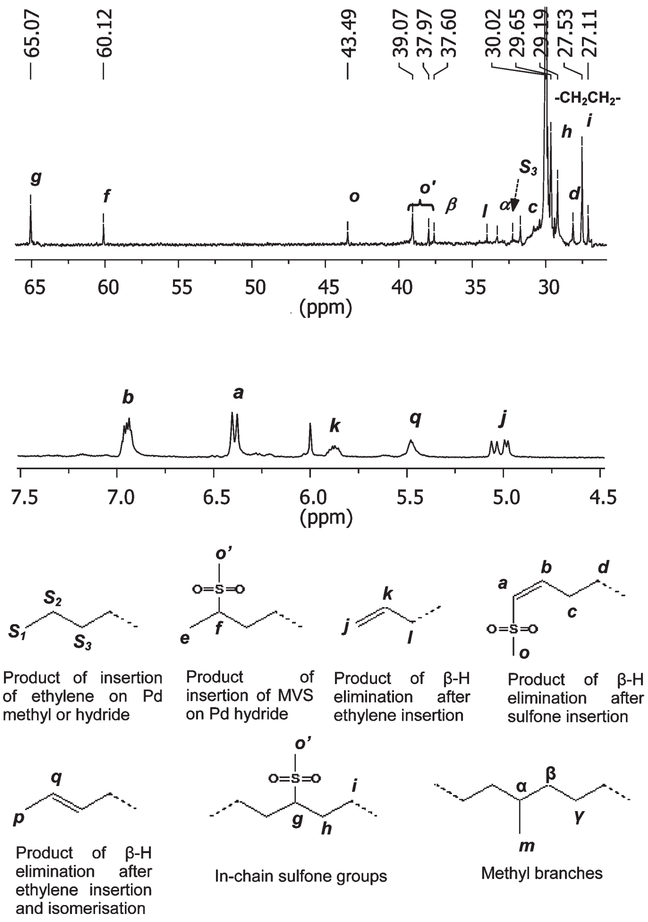


Figure 1. ^{13}C NMR spectrum ($C_2D_2Cl_4$, 130 °C) of copolymer (top; copolymer with 8.1 mol % incorporated methyl vinyl sulfone from entry 4). Olefinic ^{1}H resonances (bottom).

Polymer molecular weights determined by NMR spectroscopy are in reasonable agreement with apparent molecular weights determined by GPC vs polystyrene standards (Table 1). Narrow molecular weight distributions M_w/M_n are indicative of a well-behaved single-site nature of the polymerization.

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Table 1. Copolymerization of Vinyl Sulfones (VS) with Ethylene[a]

entry	VS	p [bar]	VS concn [mol L^{-1}]	polymer yield [g]	TOF C_2H_4	TOF VS	X_{VS} [%][b,c]	M_n [g mol^{-1}][d]	M_w/M_n[d]	M_n (NMR) [g mol^{-1}][c]
1[e]	MVS	5	1.2	0.06	73	7	8.2	2000	1.4	1400
2	MVS	5	0.1	3.2	1035	32	3	3600[f]	2.1[f]	3000
3	MVS	5	0.6	0.54	153	11	6.6	2350	1.6	1900
4	MVS	5	1.1	0.33	89	8	8.1	2000	1.6	1700
5	MVS	2	1.1	0.09	20	3	13.9	1800	1.4	1300
6	MVS	5	2.3	0.16	39	5	11.4	3200	1.5	2500
7	PVS	5	1.0	0.26	61	5	7.2	4550	1.5	3400

[a] Reaction conditions: total volume toluene + VS: 40 mL; 95 °C; 22 μmol of **1-dmso**; 4.5 h reaction time. [b] Molar incorporation in copolymer. [c] From ^{1}H NMR at 130 °C. [d] From GPC at 40 °C in THF, vs polystyrene standards. [e] 1 h reaction time. [f] From GPC at 160 °C in 1,2,4-trichlorobenzene vs linear polyethylene.

Detailed ^{1}H and ^{13}C NMR analyses (Figure 1 and Supporting Information) reveal that the majority of sulfone units are incorporated in the polymer main chain of the essentially linear copolymers (≤3 methyl branches/1000 carbon atoms) and in addition also contribute to end groups to a significant extent. Ethylene and vinyl sulfone-based unsaturated end groups are formed as a result of β-hydride elimination as the relevant chain transfer mode. The latter is comparatively favored after a vinyl sulfone incorporation, as observed previously also for other electron-deficient vinyl monomers.[14,16,17] An analysis of the saturated chain ends, resulting from monomer insertion into a Pd−H moiety, shows that chain initiation by 2,1-insertion of vinyl sulfone also occurs to a considerable extent. Overall, this results in a ca. 1:1 to 1:2 ratio of vinyl sulfone units incorporated as unsaturated and saturated end groups, and in the main chain, respectively.

These findings demonstrate that vinyl sulfones, a class of compounds generally problematic to polymerize in any type of polymerization, are amenable to catalytic insertion polymerization. This affords access to ethylene−vinyl sulfone copolymers, which represent novel polyolefins with exceptionally polar sulfone moieties.

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Supporting Information Available: Experimental procedures and characterization data of polymers and complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The extent of chain transfer after an MVS insertion (4:1 MVS vs ethylene-based end groups; 13.9 mol % MVS incorporation) is similar to the behaviour observed in methyl acrylate (MA) copolymerization affording a copolymer of comparative composition (3:1 MA vs ethylene-based end groups; 12.7 mol % MA incorporation).