Communication

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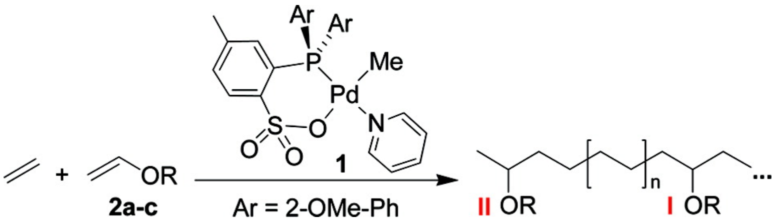

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Copolymerization of Ethylene and Alkyl Vinyl Ethers by a (Phosphine-sulfonate)PdMe Catalyst

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The direct synthesis of functionalized linear polyolefins by insertion copolymerization of olefins and polar $CH_2{=}CHX$ monomers is a challenging goal.[1] Brookhart et al. discovered that (α-diimine)PdR^+ species catalyze the copolymerization of alkyl acrylates with olefins to highly branched copolymers with acrylate units located primarily at branch ends.[2] Pugh et al. reported that in-situ-generated neutral (phosphine-sulfonate)PdR species catalyze acrylate/ethylene copolymerization to linear copolymers with significant in-chain acrylate incorporation.[3] We recently reported that (α-diimine)$PdMe^+$ catalyzes the copolymerization of olefins and silyl vinyl ethers.[4] However, the resulting copolymers are highly branched with comonomer units located mostly at branch ends. Moreover, due to the electrophilic character of (α-diimine)PdR^+ species, attempted olefin/alkyl vinyl ether copolymerizations failed due to fast cationic homopolymerization of the alkyl vinyl ether and associated decomposition of the catalyst to Pd^0, and olefin/aryl vinyl ether copolymerizations failed because (α-diimine)-$PdCH_2CHR(OAr)^+$ species undergo fast β-OAr elimination. Here we report that the discrete catalyst (PO−OMe)PdMe(pyridine) (**1**, Scheme 1, PO−OMe = 2-[bis(2-methoxyphenyl)phosphino]-4-methylbenzenesulfonate)[5,6] copolymerizes ethylene and alkyl vinyl ethers ($CH_2{=}CHOR$, **2a**−**c**: R = ^{t}Bu (**a**), Et (**b**), Bu (**c**)) to linear copolymers that contain in-chain $-CH_2CH(OR)-$ comonomer units.

We first investigated ethylene homopolymerization by **1**. Representative results are listed in Table 1(entries 1, 3, and 5). At low ethylene pressure (20 psi) in toluene at 80 °C, **1** produces low molecular weight polyethylene with ca. 10 branches/10^3 C (predominately Me branches, entry 1). The unsaturated end groups are primarily vinyl groups ($-CH_2CH{=}CH_2$) and 2-olefins ($-CH_2CH{=}CHMe$). At higher pressures (entries 3 and 5), the polymer is more linear and the molecular weight is higher. These polymerizations proceed by repetitive ethylene insertion into (PO−OMe)$PdCH_2$-CH_2P species (P = growing chain) with chain transfer by β-H transfer. Chain walking is slow relative to growth.

We then studied **1**-catalyzed copolymerization of ethylene with vinyl ethers **2a**−**c** under conditions similar to the ethylene homopolymerization conditions. As shown in Scheme 1 and Table 1, 1−7 mol % of vinyl ether is incorporated into the polyethylene. The copolymers were isolated by filtration and purified by washing or Soxhlet extraction with $CHCl_3$. The results in Table 1 show that addition of $CH_2{=}CHOR$ lowers the polymerization rate and the polymer molecular weight (entry 1 vs 2, 3 vs 4, and 5 vs 6). The presence of H_2O does not affect the copolymer structure but reduces the yield and molecular weight slightly.[7]

Scheme 1. Ar = 2-OMe−Ph; R = ^{t}Bu (**a**), Et (**b**), Bu (**c**)

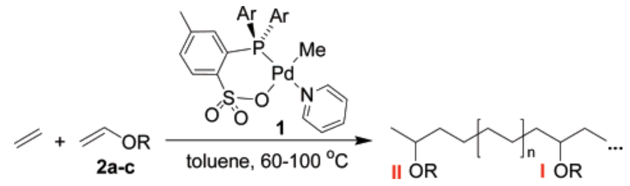

Table 1. Copolymerization of Ethylene and $CH_2{=}CHOR$ (**2a**−**c**)[a]

entry	1	2	3	4	5	6	7	8
1 (μmol)	5	5	10	5	10	10	5	5
T (°C)	80	80	80	80	80	100	80	80
$P_{CH_2CH_2}$ (psi)	20	20	74	80	294	300	20	20
$CH_2{=}CHOR$		**2b**		**2b**		**2b**	**2c**	**2a**
2 (mmol)	0	19	0	84	0	258	60	35
time (h)	19	19	1	19	1	21	19	19
yield (g)	1.4	0.06	1.5	0.28	3.6	2.1	0.1	0.09
M_n (10^3)	4.0[b]	0.9[b]	13.5[b]	0.9[b]	17.6[b]	4.8[b]	3.1[c]	1.9[c]
PDI[b]	3.2	1.8	2.5	2.0	2.1	2.0		
Me br/10^3 C	9.9	3.4	4.1	4.0	2.0	1.4	3.2	9.2
incorp. of **2** (mol %)		4.9		4.2		2.0	6.9	1.2
I (mol %)		3.5		2.7		1.4	4.8	0.2
II (mol %)		1.4		1.5		0.6	2.1	1.0

[a] Toluene, 25 mL (50 mL for entries 3,5, and 6), [**1**] = 0.2 mM. [b] GPC. [c] Determined by NMR assuming that each chain contains one unsaturated end group.

The following lines of evidence establish that the poly(ethylene-*co*-$CH_2{=}CHOR$) products are copolymers and do not contain $-[CH_2CHOR]_n-$ homopolymer. (i) Control experiments establish that $CH_2{=}CHO^t$Bu is not polymerized by **1** under these conditions. (ii) Control experiments confirm that the $-[CH_2CHOR]_n-$ homopolymers would be removed by the workup procedure (since these poly(vinyl ether)s are soluble in $CHCl_3$). (iii) NMR spectra of the crude and purified copolymers do not contain the characteristic resonances of the $-[CH_2CHOR]_n-$ homopolymer, and (iv) HMBC NMR data establish that the −CHOEt− units of the ethylene/**2b** copolymer are covalently linked to the polyethylene chain.

The NMR spectra of the ethylene/$CH_2{=}CHOR$ copolymers are similar to spectra for polyethylene produced under similar conditions, consistent with similar linear structures and end groups. Additionally, the copolymer spectra contain resonances for in-chain $-CH_2CH(OR)CH_2-$ (**I**) and chain-end $CH_3CH(OR)CH_2-$ (**II**) comonomer units, which were identified by 1- and 2-D NMR. For example, for the ethylene/**2b** copolymer, the $CH_3\boldsymbol{CH}(OEt)CH_2-$ (δ ^{1}H 3.40 (m); ^{13}C 74.8), $-CH_2\boldsymbol{CH}(OEt)CH_2-$ (δ ^{1}H 3.23 (quintet); ^{13}C 79.1), $-CH(O\boldsymbol{CH_2}CH_3)-$ (δ ^{1}H 3.50 (q); ^{13}C 63.7), and $-CH(OCH_2\boldsymbol{CH_3})-$ (δ ^{1}H 1.20 (t); ^{13}C 15.6) resonances were assigned by HMQC (Figure 1), DEPT, and COSY spectra and comparison with data for model compounds.[8] The HMBC spectrum contains a $-\boldsymbol{C}H_2CH_2C\boldsymbol{H}(OEt)CH_2\boldsymbol{C}H_2-$ correlation (δ ^{1}H/δ ^{13}C 3.23/25.4), which confirms that unit **I** is covalently linked to the polyethylene chain.

The ethylene/vinyl ether copolymers can be converted to other functionalized polyethylenes. Thermolysis of the ethylene/**2a** copolymer ($CDCl_2CDCl_2$, 120 °C, 48 h) or reaction with HCl ($CDCl_2CDCl_2$, 100 °C, 24 h) results in quantitative conversion of the $-O^t$Bu groups to −OH groups and isobutene or ^{t}BuCl,

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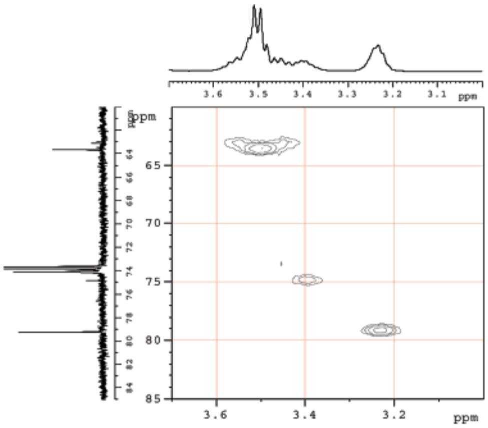


Figure 1. $^1H{-}^{13}C$ HMQC NMR spectrum ($CDCl_2CDCl_2$, 70 °C) of ethylene/**2b** copolymer (4.2 mol % of **2b**, Table 1, entry 4).

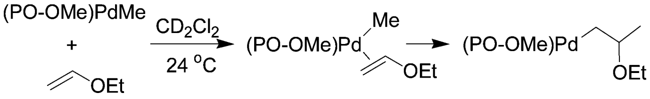
respectively. NMR spectra of the resulting hydroxy-polyethylene (i.e., ethylene/$CH_2{=}CHOH$ copolymer) contain resonances for $CH_3CH(OH)CH_2{-}$ and $-CH_2CH(OH)CH_2{-}$ units.[8a] Some isomerization of the vinyl end groups to 2-olefins occurs during thermolysis, and partial hydrochlorination of the vinyl ends to $CH_3CHClCH_2{-}$ groups occurs in the HCl reaction. The reaction of the ethylene/**2b** copolymer with HBr ($CDCl_2CDCl_2$, 80 °C, 48 h) yields the corresponding bromo-polyethylene (86% conv. of −OEt to −Br groups). Isomerization (to 2-olefins) and hydrobromination of the vinyl ends are observed in this case. The characterization of these hydroxy- and bromo-polyethylenes confirms the NMR assignments for the ethylene/$CH_2{=}CHOR$ copolymers.

Control experiments provide strong evidence against radical and cationic mechanisms for Scheme 1. The reaction of ethylene/**2b** mixtures with $H(OEt_2)_2^+$, Ph_3C^+, or $Li(OEt_2)_{2.8}^+$ (as the $B(C_6F_5)_4^-$ salts) in CH_2Cl_2 at 80 °C results in cationic homopolymerization of **2b** but no ethylene incorporation. The NMR spectra of the products are essentially identical to those of $-[CH_2CH(OEt)]_n-$ generated by other cationic initiators.[9] The reaction of ethylene/**2b** mixtures with AIBN in toluene at 80 °C gives only trace quantities of $-[CH_2CH(OEt)]_n-$ oligomers with no ethylene incorporation.[10] In contrast, under these conditions, **1** copolymerizes ethylene and **2b** and the reactivity of ethylene is much higher than that of **2b**.

In **1**-catalyzed ethylene/vinyl ether copolymerization, the in-chain units **I** can form by 1,2- or 2,1-insertion of $CH_2{=}CHOR$ into active (PO−OMe)$PdCH_2CH_2P$ species, followed by ethylene insertion. Plausible pathways to the chain-end units **II** include (i) 1,2-insertion of $CH_2{=}CHOR$ followed by chain walking and growth, and (ii) chain transfer from (PO−OMe)$PdCH_2CH_2P$ to $CH_2{=}CHOR$ followed by ethylene insertion.[11] The total level of vinyl ether incorporation and the ratio of in-chain to chain-end placements (**I**/**II**) is higher for **2b**,**c** than for **2a** under similar polymerization conditions. Steric crowding may inhibit $CH_2{=}CHO^tBu$ insertion of (PO−OMe)$PdCH_2CH_2P$ species and ethylene insertion of (PO−OMe)$PdCH_2CH(O^tBu)P$ or (PO−OMe)$PdCH(O^tBu)CH_2P$ species.

The base-free species (PO−OMe)PdMe was generated by the reaction of **1** and $B(C_6F_5)_3$, and its reactivity with vinyl ethers was explored.[12] NMR monitoring experiments show that (PO−OMe)PdMe reacts with excess (16 equiv) **2b** in CD_2Cl_2 to form (PO−OMe)$PdMe(CH_2{=}CHOEt)$, which undergoes fast exchange of free and coordinated $CH_2{=}CHOEt$ on the NMR time scale at 24 °C (Scheme 2). (PO−OMe)$PdMe(CH_2{=}CHOEt)$ undergoes 1,2-insertion to give (PO−OMe)$PdCH_2CH(OEt)Me$ as the major product (52%; k_{obs} for consumption of (PO−OMe)$PdMe(CH_2{=}CHOEt)$ = $3.01(4) \times 10^{-4}$ s^{-1}, 24 °C). NMR data for the Pd*CH₂CH(OEt)Me* group are very similar to data for (α-diimine)$PdCH_2CH(OEt)Me^+$. Neither the possible chain walk isomer (PO−OMe)$PdCMe_2OEt$ nor the 2,1-insertion product (PO−OMe)$PdCH(OEt)CH_2Me$ were observed.[4] The ethylene/vinyl ether copolymerization behavior of (PO−OMe)PdMe is similar to that of **1**.

Scheme 2



Catalyst **1** also copolymerizes ethylene and $CH_2{=}CHOPh$ to a copolymer that contains $-CH_2CH(OPh)CH_2-$ (**I**) and $CH_3CH(OPh)CH_2-$ (**II**) units. However, **1** does not incorporate $CH_2{=}CHOSiPh_3$ in ethylene polymerization.

In summary, the neutral catalyst (PO−OMe)PdMe(py) (**1**) copolymerizes ethylene and alkyl vinyl ethers to linear copolymers with in-chain and chain-end vinyl ether units. The key features of **1** that enable this chemistry are the neutral charge, which disfavors initiation of competing cationic polymerization of the vinyl ether, and the high barrier to chain walking,[13] which results in linear polymers. We are investigating the mechanisms of the reactions of **1** with vinyl ethers and the performance of modified (PO)PdR catalysts to enhance the scope, activity, and polymer molecular weights in olefin/vinyl ether copolymerization.

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

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