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Insertion Polymerization of Divinyl Formal

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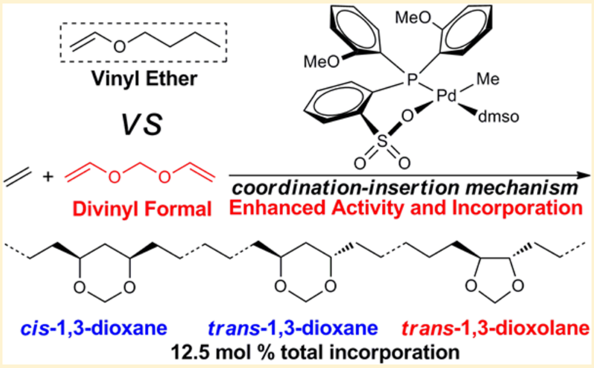
Ⓢ *Supporting Information*

ABSTRACT: Copolymerization of ethylene and divinyl formal by $[\{\kappa^2\text{-}P,O\text{-}(2\text{-MeOC}_6\text{H}_4)_2\text{PC}_6\text{H}_4\text{SO}_3\}\text{PdMe(dmso)}]$ (**1**) by a coordination–insertion mechanism affords highly linear polyethylenes with a high (12.5 mol %) incorporation of divinyl formal. This significantly exceeds the thus far relatively low incorporation (6.9 mol %) and activity with vinyl ether monomer in insertion polymerization. The resulting ethylene–divinyl formal copolymers exclusively (>98%) contain five-membered (*trans*-1,3-dioxolane) and six-membered (*cis-*/*trans*-1,3-dioxane) cyclic acetal units in the main chain, and also in the initiating ends of this functionalized polyethylene. Comprehensive NMR analysis of the microstructure of these copolymers revealed that under pressure reactor conditions consecutive 2,1–1,2-insertion of divinyl formal into a Pd–H bond is preferred, but consecutive 1,2–1,2-insertion of divinyl formal into more bulky Pd–alkyls (growing polymer chain) is favored. Moreover, homopolymerization of divinyl formal yielded a non-cross-linking poly(divinyl formal) with degrees of polymerization of $\text{DP}_n \approx 26$.



■ INTRODUCTION

Catalytic polymerizations of ethylene or propylene are among the largest scale synthetic chemical reactions performed today. By contrast, an insertion (co)polymerization of polar vinyl monomers for the direct synthesis of functionalized polyolefins remains a long-standing challenge. A first significant breakthrough was not made until 40 years after Ziegler's and Natta's seminal discoveries. In the 1990s, Brookhart et al. discovered that cationic α-diimine palladium species catalyze the insertion copolymerization of acrylates with ethylene or 1-olefins to generate highly branched copolymers with acrylate units at the end of branches preferentially.[1] Drent et al. reported that neutral phosphinesulfonato palladium complexes catalyze the insertion copolymerization of acrylates with ethylene to afford highly linear copolymers with incorporation of acrylate into the main chain.[2] In the past decade, these phosphinesulfonato palladium catalysts have been found to promote the formation of linear copolymers of ethylene with a broad scope of polar vinyl monomers.[3]

Among these available polar vinyl comonomers, vinyl ethers ($\text{CH}_2{=}\text{CHOR}$) have been comparatively neglected. The coordination–insertion polymerization of vinyl ethers is always difficult due to the following fundamental limitations and problems: (i) electron-rich vinyl ethers are highly susceptible to undesired cationic polymerization in the presence of electrophilic metal catalysts;[4] (ii) the –OR ether group can compete with vinyl groups for coordination to the metal center; (iii) due to the electron-donating ability of the –OR group, insertion barriers of vinyl ethers are generally high;[5] (iv) the insertion products generated by 1,2-insertion of vinyl ethers may be an O-chelated species, which may undergo β-OR elimination reaction, thus resulting in the termination of the growing chain. To overcome these limitations, the structure of –OR groups in vinyl ether monomers and catalysts have been revealed to be crucial.

The copolymerization of 1-hexene and $\text{CH}_2{=}\text{CHOSiPh}_3$ was achieved using a cationic α-diimine palladium catalyst (α-diimine)PdMe^+ to yield copolymers with comonomer units located mostly at the ends of branches (Chart 1a).[6] The key to the success is the presence of a bulky $-\text{OSiPh}_3$ moiety in vinyl ether monomers, which not only hinders cationic homopolymerization of vinyl ethers but also slows down the β-OSiPh_3 elimination of 1,2-insertion species of vinyl ethers. As a result, multiple insertions of $\text{CH}_2{=}\text{CHOSiPh}_3$ and other bulky vinyl silyl ethers like $\text{CH}_2{=}\text{CHOSiMe}_2\text{Ph}$ and $\text{CH}_2{=}\text{CHOSiMePh}_2$ into (α-diimine)PdMe^+ were observed (Chart 1b).[7] It should be noted that another $\{(\alpha\text{-diimine})\text{PdCl}^+\}_2$ species was also found to catalytically dimerize vinyl ethers to β,γ-unsaturated acetals and cyclize divinyl ethers to analogous β,γ-unsaturated cyclic acetals (Chart 1c).[8] A significant advance in the insertion copolymerization of vinyl ethers and olefin was the finding that neutral phosphinesulfonato palladium catalysts (P^O)PdMe(pyridine) copolymerize ethylene and less bulky vinyl ethers such as $\text{CH}_2{=}\text{CHOR}$ (R = Et, Bu, ^{t}Bu, Ph) to give highly linear copolymers with incorporation of vinyl ether units into both the main chain and the initiating chain ends, although the

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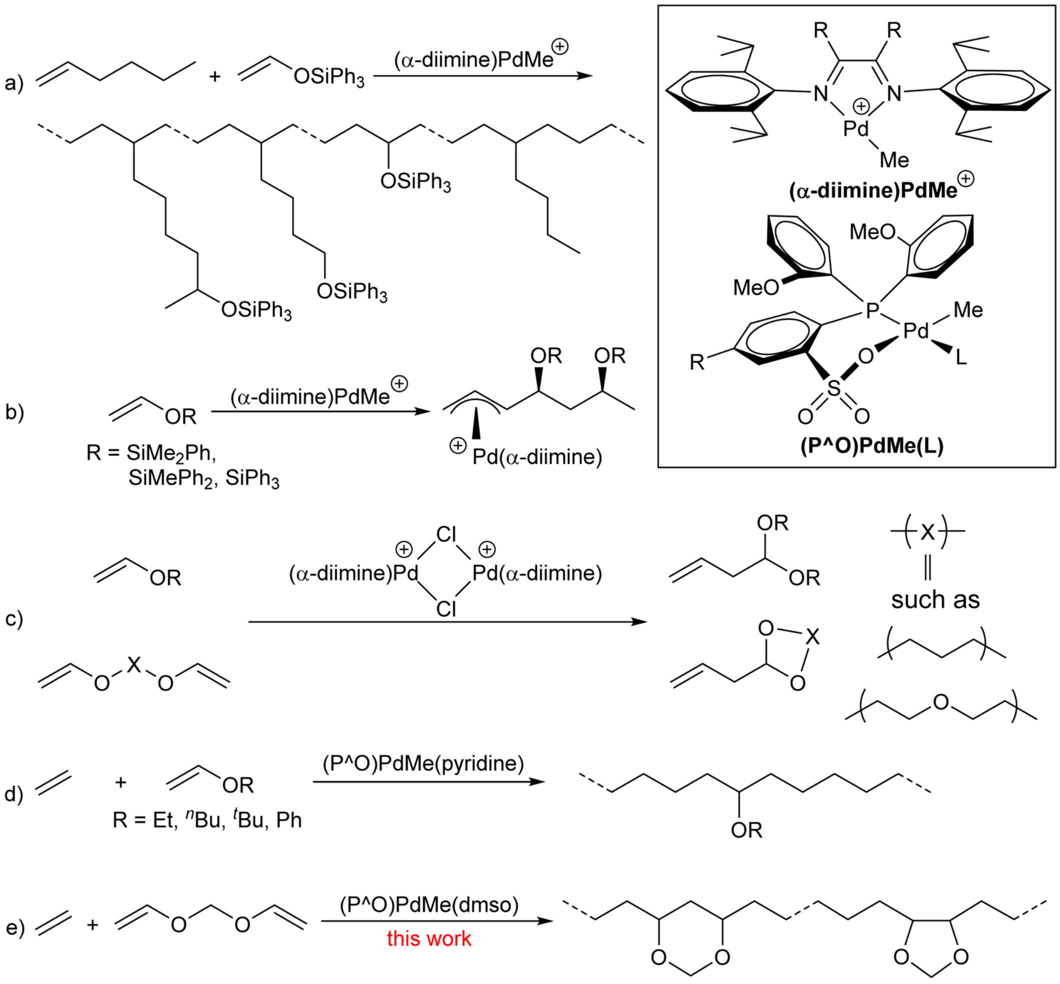
Chart 1. Insertions and Polymerizations of Vinyl Ethers



catalytic activity is limited and the comonomer incorporation is relatively low (1.2−6.9 mol %) as well (Chart 1d).[9]

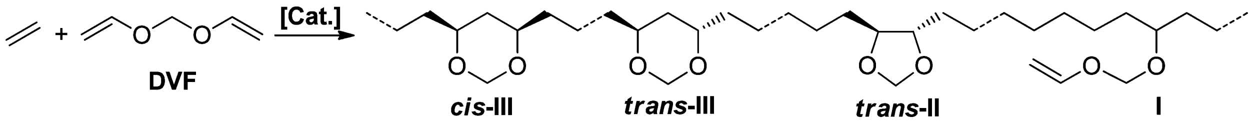
We now report how incorporation and productivity in the insertion polymerization of vinyl ether-type monomers can be much enhanced by promoting a second intramolecular insertion with divinyl formal as a monomer. This provides access to novel polyethylenes with incorporated dioxolane and dioxane cyclic acetal units.

■ RESULTS AND DISCUSSION

To provide back-to-back comparative data, copolymerizations of ethylene (E) and monovinyl ether monomers such as *n*-butyl vinyl ether (BVE) were performed using the benchmark (dianisyl)phosphinesulfonato palladium methyl catalyst precursor (P^O)PdMe(dmso) (**1**: R = H, L = dmso, Chart 1) which is well-established for polar vinyl monomer insertion polymerizations.[10] By comparison to its pyridine coordinated analogue (P^O)PdMe(pyridine), the dmso ligand in **1** is more labile which is beneficial for catalyst activation and catalyst activity and cyclopolymerization of divinyl monomers.[11,12] Under pressure-reactor conditions, exposure of **1** to 2.5 bar of E and 0.3 mol L^{-1} of BVE at 95 °C resulted in the formation of an E−BVE copolymer with a BVE incorporation of 2.1 mol % (Table 1, entry 1). As expected, at a given E pressure (2.5 bar), the incorporation of BVE in the copolymers increases with increasing concentration of the comonomer in the reaction mixture to reach 6.9 mol % at an initial concentration [BVE] = 1.8 mol L^{-1} (Table 1, entries 2−4). This limited incorporation compares to the BVE incorporation (6.9 mol %, [BVE] = 2.4 mol L^{-1}, E: 1.4 bar) in an analogous E−BVE copolymer reported previously with the catalyst precursor (P^O)PdMe(pyridine) (R = Me, L = pyridine, Chart 1).[9] According to ^{1}H and ^{13}C NMR spectra (Figure S3), these E−BVE copolymers possess a highly linear polyethylene backbone. BVE is incorporated not only into the main chain $-CH_2CH(OBu)CH_2-$ but also into the initiating chain-end $CH_3CH(OBu)CH_2-$ in a ratio of 4:3. Compared to initiating chain-ends $CH_3CH_2CH_2-$ derived from insertion of ethylene into a Pd−H or Pd−Me bond, $CH_3CH(OBu)CH_2-$ units originating from 2,1-insertion of BVE into a Pd−H bond (and possibly to a minor extent from 1,2-insertion of BVE into the Pd−Me bond of the catalyst precursor) are preferred (5:2). Note that the BVE unit is not detected at terminating chain-ends as reported previously.[9] These results reveal that copolymer chains are predominantly initiated by insertion of vinyl ether and are terminated by β-H elimination after insertion of ethylene and/or β-OBu elimination after insertion of vinyl ether.

We have shown recently that the utilization of polar divinyl compounds as a comonomer allows for enhanced polymer molecular weights, comonomer incorporations and catalyst activities in insertion copolymerization of ethylene and polar vinyl monomers. This is a result of a rapid secondary intramolecular insertion, which forms a more reactive metal alkyl intermediate.[12] To probe this concept for vinyl ethers,

Table 1. Copolymerization of Ethylene with Butyl Vinyl Ether or Divinyl Formal[a]

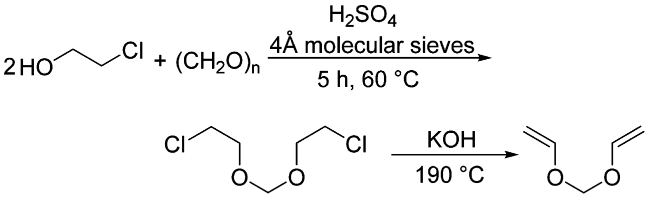


				TOF[b]			microstructure[c] (%)							
entry	concn (mol L^{-1})	t (h)	yield (mg)	E	BVE/DVF	incorp[c] (mol %)	I	*cis*-II	*trans*-II	*cis*-III	*trans*-III	M_n[d] (g mol^{-1})	M_w/M_n[d]	T_m[e] (°C)
1	BVE (0.3)	1.5	280	310	6.6	2.1	–	–	–	–	–	1900	1.7	116
2	BVE (0.6)	2.5	250	159	5.4	3.3	–	–	–	–	–	1600	1.5	111
3	BVE (1.2)	5	180	53	3.1	5.4	–	–	–	–	–	1300	1.3	103
4	BVE (1.8)	5	100	28	2.1	6.9	–	–	–	–	–	1300	1.3	98
5[f]	DVF (0.3)	1	2300	3920	52	1.3	1.1	–	65.5	26.7	6.7	3000	1.9	123
6	DVF (0.3)	1.5	1100	1190	33	2.7	1.0	–	62.2	30.4	6.4	1700	1.7	114
7	DVF (0.6)	2.5	560	337	18	5.0	1.6	–	48.0	43.1	7.3	1400	1.5	107
8	DVF (1.2)	5	350	95	8.3	8.0	2.0	–	46.5	43.4	8.1	1300	1.4	103
9	DVF (1.8)	5	100	24	3.4	12.5	2.0	–	36.8	50.0	11.2	1200	1.2	63
10[g]	DVF (0.6)	2.5	600	366	18	4.6	1.4	–	52.3	38.3	8.0	1500	1.5	110
11[h]	DVF (0.3)	1	4700	8120	74	0.9	1.7	–	61.7	29.9	6.7	4700	2.3	127
12[i]	DVF (0.3)	1	40	–	5	>99	–	–	–	–	–	<500	–	–
13[j]	DVF (0.3)	1	800	–	200	>99	–	–	–	–	–	–	–	–

[a] Reaction conditions: toluene + monomer = 50 mL; 95 °C; catalyst precursor **1** = 20 μmol; ethylene = 2.5 bar; 1000 rpm; unless stated otherwise. [b] Units: mol mol_{Pd}^{-1} h^{-1}. [c] Determined by ^1H NMR in $C_2D_2Cl_4$ at 90−130 °C. [d] Determined by GPC in 1,2,4-trichlorobenzene at 160 °C vs linear polyethylene. [e] Determined by DSC. [f] Ethylene: 5.0 bar. [g] 150 mg of butylated hydroxytoluene (BHT) was added. [h] Ethylene: 5.0 bar; 80 °C. [i] Comparative free-radical polymerization: AIBN = 80 μmol; ethylene = 5.0 bar; 80 °C. [j] Comparative cationic polymerization: $[Ph_3C][B(C_6F_5)_4]$ = 40 μmol; ethylene = 5.0 bar; 80 °C.

divinyl formal (DVF) containing a 1,6-diene structure was synthesized. DVF was obtained from dehydrochlorination of β,β′−dichloroethyl formal, that in turn was obtained from the reaction of paraformaldehyde and 2-chloroethanol (Scheme 1).

Scheme 1. Synthesis of Divinyl Formal Monomer



In pressure reactor experiments with DVF as a comonomer, under identical reaction conditions (0.3 mol L^{-1}) catalyst activities (TOF_E and TOF_{DVF}) in the reaction with E are enhanced significantly versus the monovinyl ether monomer BVE, and the comonomer incorporation increased as well (Table 1, entries 1 vs 6). As anticipated, at a given E pressure (2.5 bar), the incorporation of DVF in the copolymers increases with increasing concentration of the comonomer in the reaction mixture to reach 12.5 mol % at an initial concentration [DVF] = 1.8 mol L^{-1}, but at the expense of catalytic activity (Table 1, entries 7−9). This highest observed DVF incorporation (12.5 mol %) is ca. twice higher than the BVE incorporation (6.9 mol %) under otherwise identical reaction conditions (Table 1, entries 4 vs 9). As reported previously, the use of an electron-rich difunctional allyl ether in the copolymerization with ethylene also significantly enhances the comonomer incorporation and catalytic activity.[12b] Note that incorporations are given on the basis of molecules of DVF incorporated, that is, the amount of vinyl moieties incorporated (*vide infra*) is twice as high due to the difunctional character of DVF. Under otherwise identical conditions, a higher E pressure in the polymerization reaction results in a higher catalyst activity, but goes along with a decreased incorporation of DVF (Table 1, entries 5 vs 6). Likewise, it is worth noting that decreasing the polymerization temperature from 95 to 80 °C affords a very high catalytic activity, which is the highest reported in the insertion copolymerization of ethylene and vinyl ethers, although the incorporation of DVF slightly decreases again as expected (Table 1, entries 5 vs 11). This suggests that the coordination−insertion ability of DVF is enhanced at a higher temperature in the reaction of E and DVF, but at the same time the species formed by insertion of DVF slows down the polymerization rate.

To exclude other possible polymerization mechanisms, control experiments were carried out. Under otherwise identical reaction conditions, the presence of butylated hydroxytoluene (BHT) radical inhibitor in the reaction mixture of E and DVF did not alter the catalytic activity and comonomer incorporation significantly (Table 1, entries 7 vs 10). Moreover, without addition of catalyst precursor **1**, the reaction of E and DVF with free radical initiator (AIBN) in toluene at 80 °C gave an oligomer with a much lower productivity (Table 1, entries 11 vs 12).[13] ^1H NMR and IR spectra reveal that the oligomer obtained by this free radical method is a poly(divinyl formal) with no ethylene incorporation (Figures 1b and 2b).[14] Additionally, the reaction of E and DVF was also performed in the presence of the cationic initiator $[Ph_3C][B(C_6F_5)_4]$ in toluene at 80 °C, affording a cross-linked material (Table 1, entries 11 vs 13). IR spectroscopy confirms that the polymer obtained by cationic polymerization is also a poly(divinyl formal) homopolymer with no substantial ethylene incorporation (Figure 2c).[14] The conversion of DVF in the cationic polymerization was ca. 50%. The material obtained is virtually insoluble in $C_2D_2Cl_4$ even at 130 °C. A small (ca. 1%) portion of soluble material amenable to high-resolution solution NMR spectroscopy also contains no polyethylene motifs (Figure 1a).

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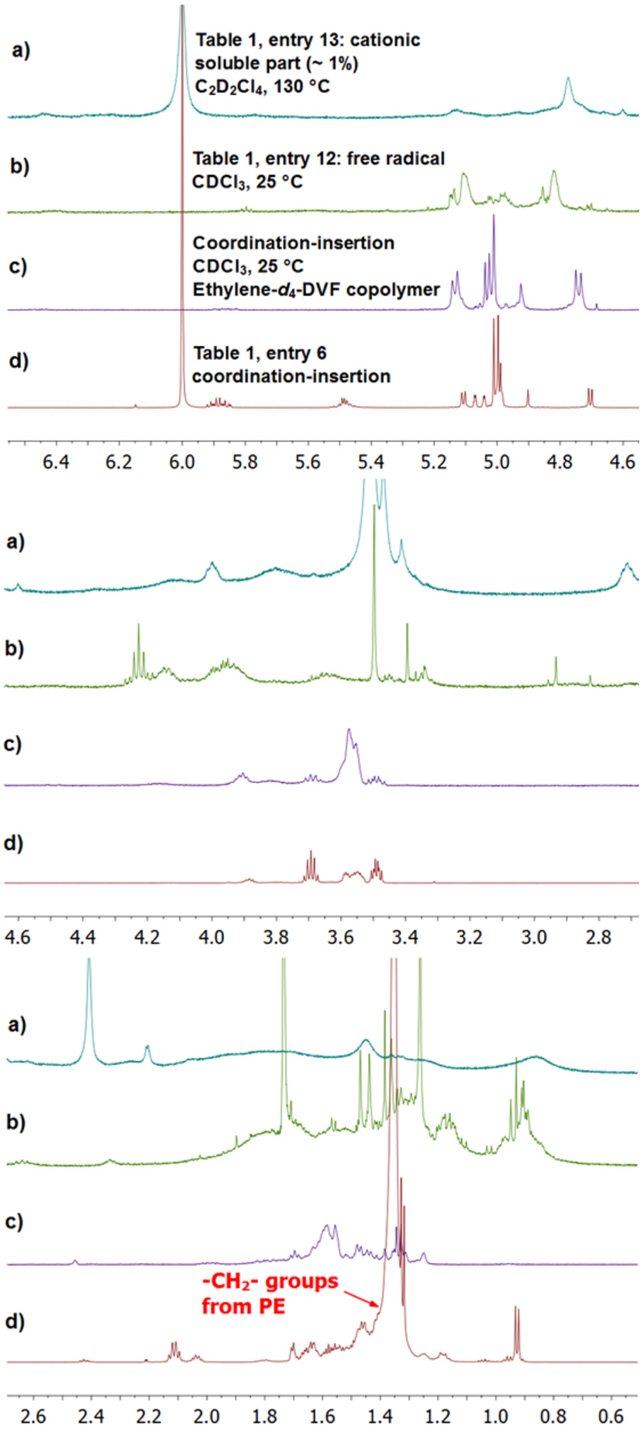


Figure 1. 1H NMR spectra of polymers from the copolymerization of E and DVF by different mechanisms (from top to bottom: 6.5−4.6, 4.6−2.7, and 2.6−0.5 ppm).

Microstructures of E−DVF copolymer were further analyzed. For the E−DVF copolymers, a richer variety of microstructure motifs results from the possible reaction pathways of the monomer's two vinylic double bonds. In principle, an incorporation of DVF can occur in a noncyclic fashion (repeat unit **I** from **2** and **5** in Scheme 2) or yield cyclic structures (**II** from **4**; **III** from **3**, **6**; or **IV** from **7**).

A representative E−DVF copolymer (Table 1, entry 8) features ^{1}H NMR resonances at δ = 5.01 (d, OCH_2O), 3.71 and 3.49 (m, CH), 1.64 and 1.58 (m, CH_2), 1.32 ppm (d, CH_3), arising from initiating chain-end ***trans*-II** units (Figure S7; for designation of microstructures cf. Figures 3 and 4). The resonances at δ = 4.99 (s, OCH_2O), 3.59 (m, CH) are attributed to the in-chain ***trans*-II** units. Another initiating chain-end in the form of ***cis*-III** units gives rise to weakly identifiable multiplets at δ = 3.81 and 3.59 (m, CH), 1.97 and 1.62 (m, cyclic CH_2), respectively. In-chain ***cis*-III** and ***trans*-III** units generate resonances at δ = 5.11 and 4.71 (d, OCH_2O), 3.55 (m, CH), 1.64 and 1.49 (m, CH_2), 1.54 and 1.36 (m, cyclic CH_2), 1.48 and 1.35 (m, CH_2); and 4.90 (s, OCH_2O), 3.89 (m, CH), 1.71 (m, cyclic CH_2), 1.81 and 1.51 ppm (m, CH_2), respectively. Note that seven-membered cycles (**IV**) were not detected by NMR and the noncyclic motif **I** gives rise to very weakly identifiable resonances at δ = 6.46 (dd, =CH), 4.48 and 4.15 (d, =CH_2), respectively. The regio- and stereochemistry of these E−DVF polymers was further illuminated by an analogous E-d_4−DVF copolymer (Figure 1c).[15] The NMR assignments of initiating chain ends ***trans*-II** and ***cis*-III** are also supported by analogous model compound reported previously.[16,17] Additionally, ATR-IR spectra of E−DVF copolymers feature characteristic bands at 1159, 1096, 1072, 1028, and 987 cm^{-1}, assigned to ν(C−O−C) of **II** and **III** units (Figures 2a and S17).

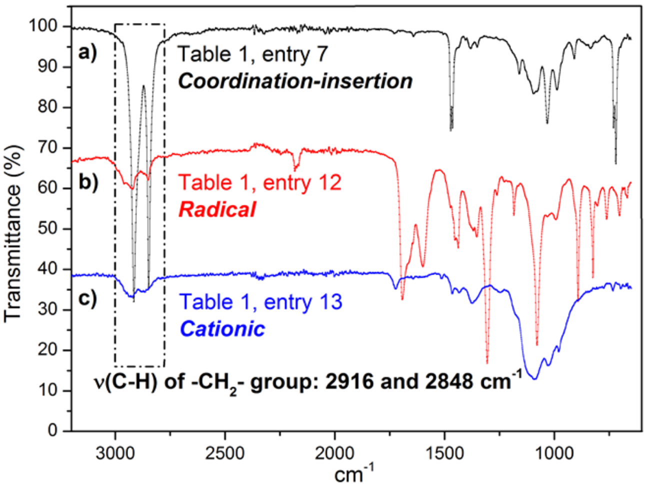
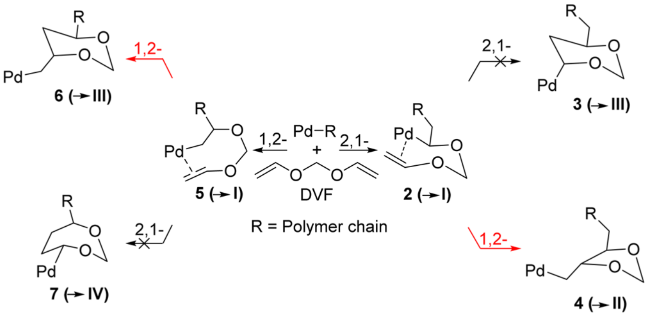


Figure 2. Comparative ATR-IR spectra of polymers formed from E/DVF reactions mixtures by different methods.

Scheme 2. Possible Microstructures from Insertion of DVF into Pd−R



Comprehensive 1D and 2D NMR analyses (Figures S4−S14) of all E−DVF copolymers reveal a highly linear microstructure (ca. 2−3 methyl branches/1000 C) with cyclic and noncyclic structures incorporated into both the main chain and the initiating chain-ends, but not into the terminating

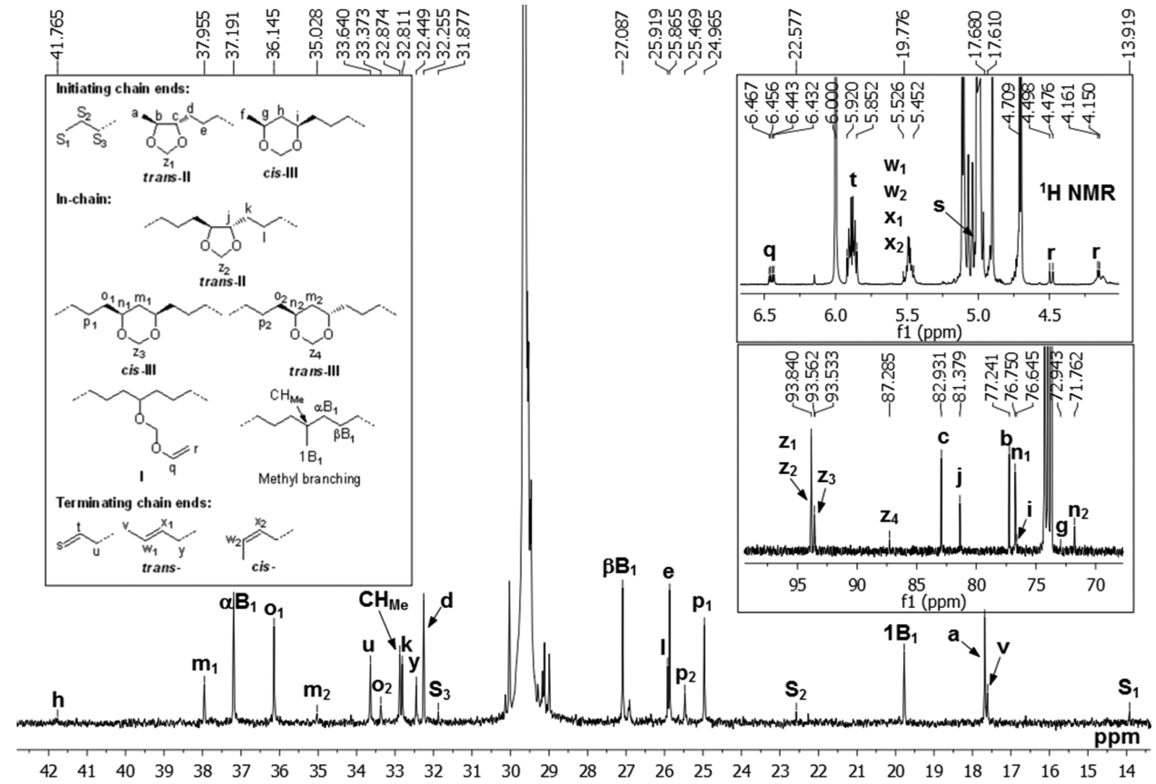


Figure 3. ^{1}H and ^{13}C{^{1}H} NMR spectra (110 °C, $C_2D_2Cl_4$) of an E−DVF copolymer (Table 1, entry 6).

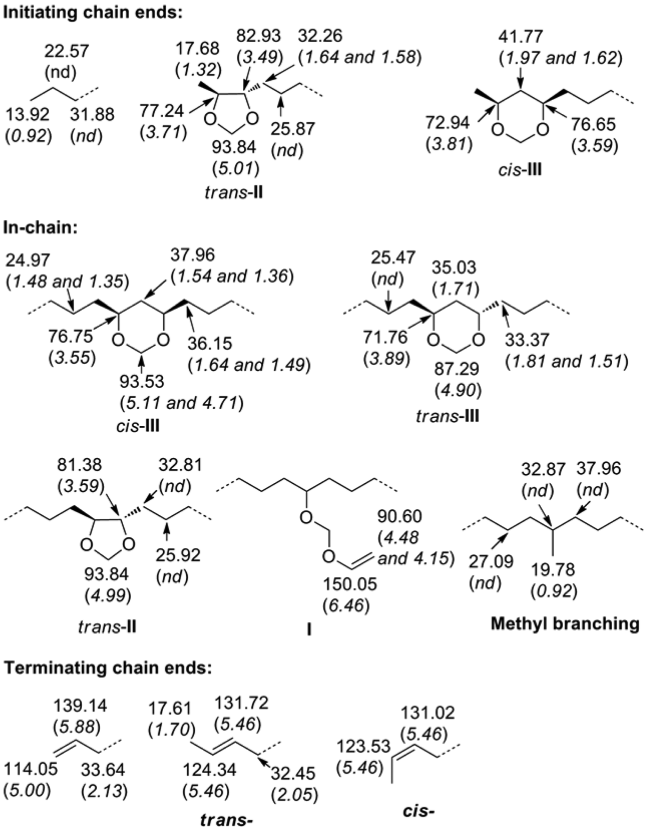


Figure 4. Comprehensive ^{1}H and ^{13}C{^{1}H} NMR spectroscopic data of the E−DVF copolymer (nd: not determined due to overlapping resonances).

chain-ends. This agrees with the results of the above monovinyl ether copolymerizations. Notably, E−DVF copolymers with virtually exclusively cyclic acetal units are accessible (>98%). That is, an initial insertion of DVF into the growing polymer chain is succeeded by an insertion of the monomer's second vinylic double bond (Scheme 2), rather than by an insertion of E. As a comparison, a similar scenario (>96% cyclic units) has been observed recently in the copolymerization of a difunctional acrylate or allyl ether by **1**.[12] ^{13}C NMR spectroscopy (Figure 3) confirms three observable initiating chain ends: *n*-alkyl (from the insertion of ethylene), ***trans*-II** (from consecutive 2,1−1,2-insertion of one DVF molecule into a Pd−H bond), and ***cis*-III** (from consecutive 1,2−1,2-insertion of one DVF molecule into a Pd−Me bond). Note that initiating chain-end ***trans*-II** predominates (>80%). For the terminating chain ends, only vinyl groups and internal isomers are detected, which are most likely formed via *β*-H elimination after ethylene insertion.[18] Full ^{1}H and ^{13}C NMR spectroscopic data based on multiple NMR techniques of E−DVF copolymers is given in Figure 4.

A further quantitative comparison of the comonomer-derived repeat units and end groups is instructive. First, as shown in Figure 5, with increasing DVF incorporation (as a result of an increased concentration in the reaction mixture), the ratio of in-chain ***trans*-II** repeat units to initiating chain-ends ***trans*-II** increases from less than unity to higher values. Second, the content of in-chain structures **III** (*cis*- and *trans*-) exceeds that of in-chain structure **II** (*trans*-), independent of the DVF incorporation (concentration) (Figure 5). Third, the ratio of total structure **II** (in-chain and initiating chain-end) to total structure **III** (in-chain and initiating chain-end) decreases with increasing DVF incorporation (concentration) (Figure 5, and Table 1, entries 6−9). Detailed analyses on all E−DVF copolymer microstructures reveal that, at the initiating chain

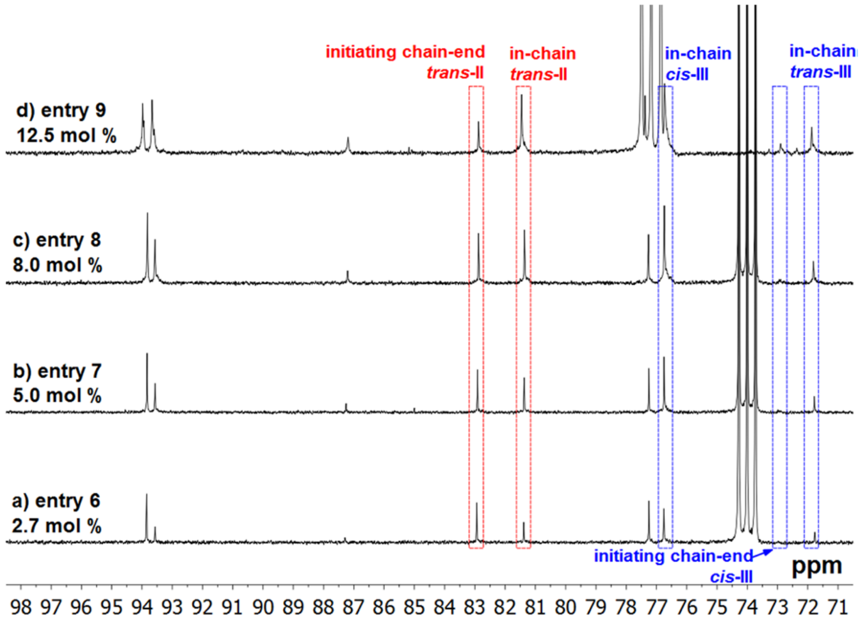


Figure 5. Comparative $^{13}C\{^1H\}$ NMR spectra (70−100 ppm) of E−DVF copolymers with different DVF incorporation (entries 6−8, $C_2D_2Cl_4$ at 110 °C; entry 9, $CDCl_3$ at 40 °C).

ends, the content of five-membered cyclic structure **II** is much higher than that of six-membered cyclic structure **III**. By contrast, for the in-chain structure, the content of six-membered cyclic structures **III** is higher than that of five-membered cyclic structure **II**. This suggests that, under polymerization conditions, 2,1−1,2-insertion of one molecule of DVF into a Pd−H bond is preferred (to form initiating chain-end **II**), but 1,2−1,2-insertion of one molecule of DVF into Pd−alkyls (growing polymer chain) is favored (to form in-chain **III**). Such an alteration of 1,2- and 2,1- regio-chemistry of insertion into Pd-species of variable steric bulk has also been found in other cases.[12b,19]

These findings also suggested the possibility of a homopolymerization of vinyl ether monomers. In the presence of catalyst precursor **1**, homopolymerization of monovinyl ether monomer BVE resulted in the formation of a lower molecular weight oligomer with degrees of polymerization of $DP_n \approx 5$ with a low productivity. This agrees with observations of three consecutive insertions or dimerization of monovinyl ether reported previously (Chart 1).[7,8] By contrast, under otherwise identical reaction conditions, DVF homopolymer was formed with a higher activity. The microstructure resembles those of the DVF repeat units in the aforementioned E−DVF copolymers (Figure S15). Degrees of polymerization amounted to $DP_n \approx 26$ (M_n = 2670 g mol^{-1}) (Figures S16). This compares to previous reports on the homopolymerization of a difunctional acrylate or allyl ether, where the degrees of polymerization also increase compared to the corresponding monofunctional monomers.[12]

■ CONCLUSIONS

In summary, the utilization of divinyl formal as a monomer allows for an enhanced incorporation and productivity of a vinyl ether-type monomer in coordination−insertion copolymerizations with ethylene. The resulting novel ethylene−divinyl formal copolymers, which have thus far been inaccessible by free radical or cationic polymerization techniques, possess exclusively five-membered dioxolane and six-membered dioxane cyclic acetal units. These are incorporated into the linear polyethylene main chain, and also into the initiating chain end of polyethylene. Even homopolymerization of divinyl formal is possible, which contrasts a few consecutive insertions for monovinyl ethers.

■ EXPERIMENTAL SECTION

General Procedures and Materials. Unless stated otherwise, all manipulations of air and moisture sensitive compounds were carried out under an inert gas atmosphere using standard glovebox and Schlenk techniques. Toluene was distilled from sodium, methylene chloride and pentane were distilled from CaH_2. Butyl vinyl ether (**BVE**, 98%) was obtained from Sigma-Aldrich, which was further dried over CaH_2 for 2 days and distilled. Ethylene (3.5 grade) was purchased from Praxair. Deuterated ethylene (99 atom % D) was purchased from Sigma-Aldrich. All deuterated solvents were supplied by Eurisotop. Palladium complex **1** was synthesized by reported procedures.[10q]

NMR spectra were recorded on a Varian Unity Inova 400, a Bruker Avance 400 or Bruker Avance 600 spectrometer, respectively. ^1H and ^{13}C chemical shifts were referenced to the solvent signals. Multiplicities are given as follows (or combinations thereof): s, singlet; d, doublet; t, triplet; quart,quartet; vt, virtual triplet; m, multiplet; br, broad. NMR assignments of complexes were confirmed by ^1H, ^{13}C, ^{31}P, ^1H,^1H-gCOSY, TOCSY2D, ^1H,^{13}C-gHSQC, and ^1H,^{13}C-gHMBC experiments. NMR assignments of polymers were confirmed by ^1H, ^{13}C, ^1H,^1H-gCOSY, TOCSY1D, TOCSY2D, ^{13}C DEPT-135, ^1H,^{13}C-gHSQC, and ^1H,^{13}C-gHMBC experiments. Room temperature measurements of polymers were performed in $CDCl_3$ at 25 °C (^1H NMR, 7.26 ppm; ^{13}C NMR, 77.00 ppm). High temperature measurements of polymers were performed in 1,1,2,2-tetrachlorethane-d_2 at 90−130 °C (^1H NMR: 6.00 ppm; ^{13}C NMR: 74.00 ppm).

For copolymers, GPC was carried out in 1,2,4-trichlorobenzene at 160 °C at a flow rate of 1 mL min^{-1} on a Polymer Laboratories 220 instrument equipped with Olexis columns with differential refractive index-, viscosity-, and light scattering- (15° and 90°) detectors. Data reported were determined directly against polyethylene standards. For homopolymers, molecular weights were determined by GPC on a polymer laboratories PL-GPC 50 instrument with two PLgel 5 μm MIXED-C columns and an RI-detector in THF against polystyrene standards.

Differential scanning calorimetry (DSC) was performed on a Netzsch DSC 204 F1 instrument at a heating and cooling rate of 10 K min^{-1}. DSC data reported were determined from the second heating scan.

IR spectra were acquired on a PerkinElmer Spectrum 100 instrument with an ATR unit.

Pressure Reactor Polymerization Procedure. Copolymerizations were carried out in a 250 mL stainless steel mechanically stirred (1000 rpm) pressure reactor equipped with a heating/cooling jacket supplied by a thermostat controlled by a thermocouple dipping into the polymerization mixture. A valve controlled by a pressure transducer allowed for applying and keeping up a constant ethylene pressure. The required flow of ethylene, corresponding to ethylene consumed by polymerization, was monitored by a mass flow meter and recorded digitally. Prior to polymerization experiments, the reactor was heated under vacuum to 90 °C for at least 60 min and then brought to the desired temperature and backfilled with argon.

A stock solution of the catalyst precursor **1** in methylene chloride was prepared daily and stored in the glovebox at −30 °C. The amount required was transferred into a syringe and transferred out of the box. 50 mL of toluene were transferred into the reactor via cannula in a slight argon stream, and then the catalyst precursor and the desired amount of comonomer were injected into the reactor sequentially. After the desired reaction time, the polymerization solution was poured into 500 mL of methanol to precipitate the copolymer. The obtained copolymer was filtered and dried at 50 °C under vacuum for at least 48 h.

Homopolymerization Procedure. In an 8 mL screw-cap vial under inert atmosphere, 36 mg (60 μmol) of catalyst precursor **1** was dissolved in a mixture (1:10) of dichloromethane and toluene, and then 225 equiv of divinyl formal was added to the mixture. The vial was transferred out of the glovebox, and the mixture was stirred at 80 °C for 4 h. The reaction mixture was filtered and unreacted monomer and solvent were removed under vacuum at 50 °C. The resulting yellow residues were washed with diethyl ether and dried under vacuum, yielding the divinyl formal homopolymer (110 mg, which contains decomposed catalyst).

The attempted homopolymerization of butyl vinyl ether was conducted analogously, yielding the butyl vinyl ether homopolymer (35 mg, which contains decomposed catalyst).

Synthesis of Divinyl Formal. At room temperature, 2 mL of 98% sulfuric acid were added to a flask containing a mixture of 21.2 g (0.70 mol) of $(CH_2O)_n$, 100 g of 4 Å molecular sieves and 124.0 g (1.54 mol, 2.2 equiv) of 2-chloroethanol. The reaction mixture was heated to 60 °C and stirred for 5 h. The resulting solution was cooled to room temperature and filtered and washed with dichloromethane. The filtrate was poured into 300 mL of water containing 10 g of Na_2CO_3. The organic layer was separated and dried with anhydrous magnesium sulfate. The solvent was removed and the remaining light yellow liquid was distilled under vacuum (60 °C/1.9 mbar) to afford bis(2-chloroethyl)formal as a colorless product (63.0 g, 52.0%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ = 4.77 ppm (s, 2H, OCH_2O), 3.85 (t, $^3J_{HH}$ = 5.6 Hz, 2H, OCH_2CH_2Cl), 3.66 (t, $^3J_{HH}$ = 5.6 Hz, 2H, OCH_2CH_2Cl).

At room temperature, 6 equiv of KOH were added to 34.6 g (0.20 mol) of bis(2-chloroethyl)formal in a flask. A Vigreux column was attached to the outlet of the reaction flask, and then the reaction mixture was heated to 190 °C and stirred. Divinyl formal, 2-chloroethyl vinyl formal, and water were distilled off spontaneously from the reaction mixture. The mixture of products was dried over KOH and redistilled from CaH_2 through a Vigreux column at 90 °C to afford pure colorless divinyl formal (9.0 g, 45.0%). ^{1}H NMR (400 MHz, 25 °C, CD_2Cl_2): δ = 6.40 ppm (dd, $^3J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 6.4 Hz, 2H, $CH_2{=}CHO$), 5.10 (s, 2H, OCH_2O), 4.50 (dd, $^3J_{HH}$ = 14.0 Hz, $^2J_{HH}$ = 1.6 Hz, 2H, $CH_2{=}CHO$), 4.19 (dd, $^3J_{HH}$ = 6.4 Hz, $^3J_{HH}$ = 2.0 Hz, 2H, $CH_2{=}CHO$). $^{13}C\{^1H\}$ NMR (100 MHz, 25 °C, CD_2Cl_2): δ = 149.84 ppm ($CH_2{=}CHO$), 92.93 (OCH_2O), 91.98 ($CH_2{=}CHO$).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.6b00983.

1D and 2D NMR spectra and detailed assignments of divinyl formal monomer, E−BVE copolymers and E−DVF copolymers. ATR-IR spectra, GPC traces and DSC traces of copolymers (PDF)

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Notes

The authors declare no competing financial interest.

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(14) In IR spectra of the copolymer (Figure 2a), very strong peaks at 2916 and 2848 cm^{-1} are mostly attributed to the C−H asymmetric and symmetric stretching vibrations of − CH_2− groups of the polyethylene backbone. Weak peaks in this frequency range are also found in the products of free-radical and cationic polymerizations (Figure 2, parts b and c), these are reasonably assigned to the C−H asymmetric and symmetric stretching vibrations of − CH_2− groups derived from poly(divinyl formal).

(15) The copolymerization of ethylene-d_4 and DVF was performed with catalyst precursor **1** under 2.5 bar of ethylene-d_4 pressure and 1.2 mol L^{-1} of DVF in 10 mL of toluene at 95 °C for 5 h in a 20 mL pressure reactor.

(16) As a model compound for the initiating chain end ***trans*-II** units, *trans*-4-butyl-2,2,5-trimethyl-1,3-dioxolane features the following key NMR resonances: $^1H(^{13}C)$ at δ = 3.70(76.7) and 3.50(82.4) (CH), 1.24(17.6) ppm (CH_3). Note that *cis*-4-butyl-2,2,5-trimethyl-1,3-dioxolane features distinctly different key resonances $^1H(^{13}C)$ at δ = 4.22(73.6) and 4.02(77.9) (CH), 1.14(15.5) ppm (CH_3). See: Vyvyan, J. R.; Meyer, J. A.; Meyer, K. D. Conversion of Epoxides to 1,3-Dioxolanes Catalyzed by Tin(II) Chloride. *J. Org. Chem.* **2003**, *68*, 9144.

(17) As a model for the initiating chain end ***cis*-III** units, *cis*-6-hexyl-4-methyl-2-(l-methylethyl)-1,3-dioxane features the following key NMR resonances: $^1H(^{13}C)$ at δ = 3.74−3.56(72.3) and 3.55−3.42(76.2) (CH), 1.85−1.68(39.1) (cyclic CH_2), 1.19(21.7) ppm (CH_3). Note that *trans*-6-hexyl-4-methyl-2-(l-methylethyl)-1,3-dioxane features distinctly different key resonances: $^1H(^{13}C)$ at δ = 4.25(67.6) and 3.75−3.63(71.2) (CH), 1.82−1.58(36.1) (cyclic CH_2), 1.29(17.1) ppm (CH_3). See: Rychnovsky, S. D.; Skalitzky, D. J. A Practical Preparation of.alpha.-Alkoxylithium Reagents: Synthesis of Syn or Anti 1,3-Diols. *J. Org. Chem.* **1992**, *57*, 4336.

(18) For the terminating chain ends: (1) the exocyclic double bond expected from β-H elimination after insertion of the second double bond of DVF monomer (Scheme 2, compounds **4** and **6**) is not observed by NMR; (2) vinyl groups are possibly to a minor extent formed via β-OR elimination after 1,2-insertion of the first double bond of DVF monomer (Scheme 2, compound **5**).

(19) We have found that 2,1-insertion of methyl acrylate into a Pd−H bond is preferred, but 1,2-insertion of methyl acrylate into a Pd−methyl bond is favored. Insertion occurs from different isomers with respect to the coordination site of the π-bound olefin relative to the P^O ligand. See: Wucher, P.; Roesle, P.; Falivene, L.; Cavallo, L.; Caporaso, L.; Göttker-Schnetmann, I.; Mecking, S. Controlled Acrylate Insertion Regioselectivity in Diazaphospholidine-Sulfonato Palladium(II) Complexes. *Organometallics* **2012**, *31*, 8505 In addition, 1,2-insertion of diallyl ether into the less bulky Pd−methyl bond is preferred, but 2,1-insertion of diallyl ether into more bulky Pd−polymeryls is favored. See ref 12b.