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Direct Synthesis of Telechelic Polyethylene by Selective Insertion Polymerization

Zhongbao Jian,^[a] Laura Falivene,^[b] Giusi Boffa,^[c] Sheila Ortega Sánchez,^[c] Lucia Caporaso,^{*[c]} Alfonso Grassi,^[c] and Stefan Mecking^{*[a]}

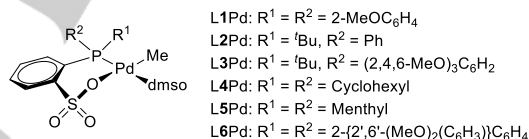
Abstract: A single-step route to telechelic polyethylene (PE) is enabled by selective insertion polymerization. Pd(II)-catalyzed copolymerization of ethylene and 2-vinylfuran (VF) generates α,ω -difuran telechelic polyethylene. Orthogonally reactive exclusively in-chain anhydride groups are formed by terpolymerization with carbic anhydride. Combined experimental and theoretical DFT studies reveal the key for this direct approach to telechelics to be a match of the comonomers' different electronics and bulk. Identified essential features of the comonomer are that it is an electron-rich olefin that forms insertion product stabilized by an additional interaction, namely a π - η^3 interaction for the case of VF.

Telechelic polymers, composed of chains with two distinctive endgroups, are of broad relevance. They are used, for example, as cross-linkers, chain extenders, and to form block copolymers and defined networks.^[1] Syntheses of telechelic polymers with well-defined structures from simple feedstocks such as ethylene are, however, rare. At the same time, telechelic polyethylenes (PEs) are finding increasing attention. They combine attractive properties such as crystallizability, chemical stability, a hydrophobic nature and compatibility with polyolefin materials.^[2]

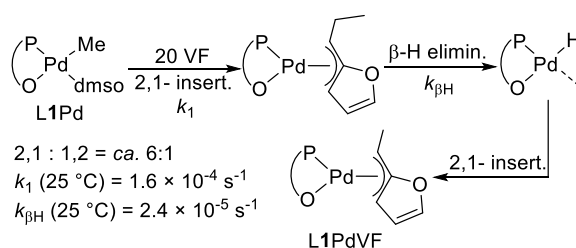
Existing approaches to produce telechelic PE comprise: 1) partial hydrogenation of polybutadiene followed by ethenolysis (metathesis degradation with ethylene);^[3] 2) ring-opening metathesis polymerization (ROMP) of cyclic olefin in the presence of a key chain transfer agent (CTA) containing reactive groups followed by functionalization and hydrogenation;^[4] 3) living coordinative polymerization of ethylene using functionalized initiators followed by chain-end-capping agent in the absence of ethylene;^[5] 4) catalyzed chain growth (CCG) polymerization^[6] of ethylene using the combination of a neodymium catalyst^[7] and a well-designed di(10-undecenyl)magnesium as a CTA followed by treatment with iodine and then ^tBuOK;^[8] 5) CCG polymerization of ethylene in the presence of a zirconium catalyst and a multinuclear alkylene zinc as a CTA.^[9] These various methods form linear or branched telechelic PEs with versatile functional

chain ends. However, they involve several steps. We now report on a preparation of telechelic polyethylene by direct selective generation of furan endgroups during ethylene chain growth.

While traditional catalysts for ethylene polymerization are not compatible with polar reagents or even solvents, significant progress has been made to this end with late transition metal catalysts.^[10,11] Particularly phosphinesulfonato-coordinated Pd(II) complexes have proven to be tolerant towards a large scope of polar vinyl monomers in ethylene copolymerizations.^[11d,12] Distinct features of the formed polymers are: 1) functional groups are predominantly incorporated into the PE backbone; 2) a random coexistence of initiating (α -) chain ends derived from ethylene and polar vinyl monomer; and 3) a random coexistence of terminating (ω -) chain ends derived from chain transfer after insertion of ethylene and polar vinyl monomer. These features are prohibitive for a selective synthesis of telechelics. However, we observed a very different reactivity for 2-vinylfuran (VF), a monomer that to our knowledge has not been studied in insertion polymerizations.



Scheme 1. Catalyst precursors L1Pd–L6Pd studied.



Scheme 2. Stoichiometric insertion of 2-vinylfuran into L1Pd.

The insertion reactivity of VF towards catalyst precursor L1Pd^[12g] (Scheme 1) was monitored by ¹H NMR spectroscopy (Figures S1–S3). Under pseudo-first-order conditions (excess VF, ca. 20 equiv.), the insertion of VF into the Pd–Me bond at 25 °C predominantly yields the 2,1- insertion product (2,1-:1,2- = ca. 6:1) with an observed rate constant (k_1) of $1.6 \times 10^{-4} \text{ s}^{-1}$ (Scheme 2). Note that, with prolonged reaction time, no second insertion of VF is detected, but rapid β -H elimination reaction ($k_{\beta\text{H}} = 2.4 \times 10^{-5} \text{ s}^{-1}$) of the VF 2,1- insertion product is observed to generate the Pd hydride that further reacts with another molecule of VF. Based on these kinetic results, the key 2,1- insertion product L1PdVF from the reaction of VF with L1Pd for 30 h at 25 °C could be isolated

[a] Dr. Z. Jian, Prof. Dr. S. Mecking
Chair of Chemical Materials Science, Department of Chemistry
University of Konstanz
Universitätsstrasse 10, 78457 Konstanz, Germany
E-mail: stefan.mecking@uni-konstanz.de

[b] Dr. L. Falivene
Physical Sciences and Engineering, Kaust Catalysis Center
King Abdullah University of Science and Technology (KAUST)
Thuwal 23955-6900 (Saudi Arabia)

[c] G. Boffa, S. O. Sánchez, Prof. Dr. L. Caporaso, Prof. Dr. A. Grassi
Department of Chemistry and Biology
University of Salerno
Via Giovanni Paolo II, 132 - 84084 - Fisciano (SA) (Italy)
E-mail: lcaporaso@unisa.it

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(Scheme 2), and fully characterized by comprehensive NMR spectroscopy (Figures S4–S8). The solid-state structure of L1PdVF was further determined by single crystal X-ray diffraction, indicating that incorporated VF coordinates to the metal center in a π - η^3 mode (Figure 1).^[13] Note that the pyridine adduct of L1PdVF is unstable and decomposes to give a bis(phosphinesulfonato) palladium complex (L1)₂Pd (Figure S42). All these findings underline the propensity of the insertion products of VF for β -H elimination, which is a chain transfer reaction in polymerization.

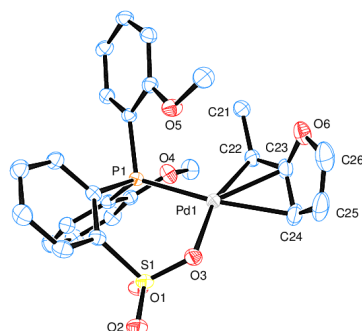
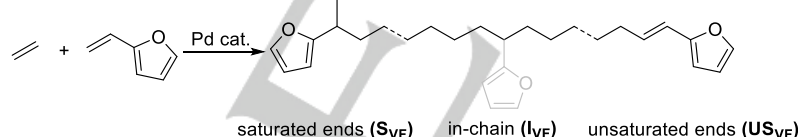


Figure 1. ORTEP plot of L1PdVF drawn with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Copolymerizations of VF and ethylene (E) were investigated using the benchmark Pd catalyst precursor L1Pd (Scheme 1). Under pressure-reactor conditions, exposure of L1Pd to 5 bar of

E and 0.075 M of VF at 95 °C resulted in the formation of a copolymer with a low VF incorporation of 0.4 mol % (Table 1, entry 1). Preliminary ¹H and ¹³C NMR spectra of this E–VF copolymer indicated that incorporated VF is overwhelmingly (95%) located in both saturated (S) chain ends and unsaturated (US) chain ends, in a ratio of ca. 1:1 ($S_{VF}:US_{VF} = 44\%:51\%$). Only 5% of incorporated VF is located in the backbone. This selectivity for incorporation of VF in endgroups is all the more remarkable given the much large number of chain growth insertion events vs. endgroups in the formation of a polymer chain. Note that this formation of VF-based unsaturated endgroups rather than main chain incorporation of isolated or consecutive VF units under pressure reactor conditions agrees with the above NMR studies, where insertion of VF into a Pd-alkyl is followed by a rapid β -H elimination, not insertion of further monomer. Due to the low concentration of VF in the reaction mixture of this copolymerization experiment, the larger part of both saturated and unsaturated ends is still ethylene-based ($S_{VF}/S_{E+VF} = 33\%$ and $US_{VF}/US_{E+VF} = 31\%$). However, increasing the VF concentration, a majority of VF-based endgroups at both chain ends could be achieved, 67 and 75 %, respectively (Table 1, entries 2–5). These promising results encouraged us to screen further catalyst precursors L2Pd–L6Pd^[12f,m,14] (Scheme 1). At a concentration [VF] = 0.6 mol L⁻¹, copolymerizations of E and VF using L2Pd–L6Pd gave E–VF copolymers with variable location of the incorporated VF (Table 1, entries 6–10). Excitingly, in the E–VF copolymer obtained with L3Pd (Table 1, entry 7), nearly exclusively VF-based endgroups are located at both chain ends:

Table 1. Copolymerization of 2-Vinylfuran with Ethylene.^[a]



Entry	Cat.	Conc. [mol L ⁻¹]	<i>t</i> [h]	Yield [mg]	Act. ^[b]	Incorp. ^[c] [mol %]	Chain ends ^[d] (%)			Incorporated VF ^[c]			<i>M_n</i> ^[e] [g mol ⁻¹]	<i>M_w</i> / <i>M_n</i> ^[e]	<i>T_m</i> ^[f] [°C]
							<i>S_{VF}</i> / <i>S_{E+VF}</i>	<i>US_{VF}</i> / <i>US_{E+VF}</i>	<i>S_{VF}</i> (%)	<i>I_{VF}</i> (%)	<i>US_{VF}</i> (%)				
1	L1Pd	0.075	2	420	10.5	0.4	33	31	44	5	51	3400	2.0	127	
2	L1Pd	0.15	3	400	6.7	0.6	43	45	45	6	49	3000	2.0	127	
3	L1Pd	0.3	4	200	2.5	1.1	55	63	45	6	49	2000	1.9	124	
4	L1Pd	0.6	7	190	1.4	2.1	66	74	43	9	48	1200	2.1	120	
5 ^[g]	L1Pd	1.2	8	200	0.3	3.7	67	75	41	14	45	1100	1.7	112	
6	L2Pd	0.6	7	450	3.2	2.5	79	77	46	11	43	1900	1.9	122	
7	L3Pd	0.6	7	310	2.2	4.4	90	97	47	7	46	1900	2.0	121	
8	L4Pd	0.6	7	670	4.8	2.2	79	62	51	13	36	2500	1.9	126	
9	L5Pd	0.6	5	1700	17	1.0	84	84	28	48	24	8700	2.2	129	
10	L6Pd	0.6	3	2700	45	0.3	38	25	38	38	24	16000	2.0	134	

[a] Conditions: toluene + monomer: 50 mL; 95 °C; catalyst precursor: 20 μmol; ethylene: 5 bar; 1000 rpm; unless stated otherwise. [b] Units: kg mol_{Pd}⁻¹ h⁻¹. [c] Determined by ¹H NMR in C₂D₂Cl₄ at 100–130 °C. [d] Determined by ¹H NMR, *S_{VF}*/*S_{E+VF}*: saturated chain ends from VF/saturated chain ends from both VF and E, *US_{VF}*/*US_{E+VF}*: unsaturated chain ends from VF/unsaturated chain ends from both VF and E. [e] Determined by GPC in 1,2,4-trichlorobenzene at 160 °C vs linear polyethylene. [f] Determined by DSC. [g] catalyst L1Pd: 100 μmol. [h] 150 mg butylated hydroxytoluene (BHT) was added.

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9 out of 10 chains are initiated by insertion of VF into a Pd-H species ($S_{VF}/S_{E+VF} = 90\%$), and chain **termini** are formed exclusively by β -H elimination after an insertion of VF into the growing chain ($US_{VF}/US_{E+VF} = 97\%$). At the same time, the main chain is composed virtually exclusively ($> 99\%$) of polyethylene.

The microstructures of all E-VF copolymers were confirmed by comprehensive 1D and 2D NMR spectroscopic data (Figures S10–S14). As shown in Figure 2 for a representative sample (Table 1, entry 7), the characteristic resonances for saturated endgroups S_{VF} at $\delta = 19.09$ (a), 33.22 (b), 35.91 (c), and 27.13 ppm (d) overwhelmingly predominate for the initiating chain ends, and likewise for unsaturated terminating chain ends resonances of US_{VF} at $\delta = 118.69$ (p), 130.63 (q), and 32.68 ppm (r) are detected exclusively. By contrast, the in-chain structure (I_{VF}) only showed some weak signals such as at $\delta = 39.13$ ppm (e).

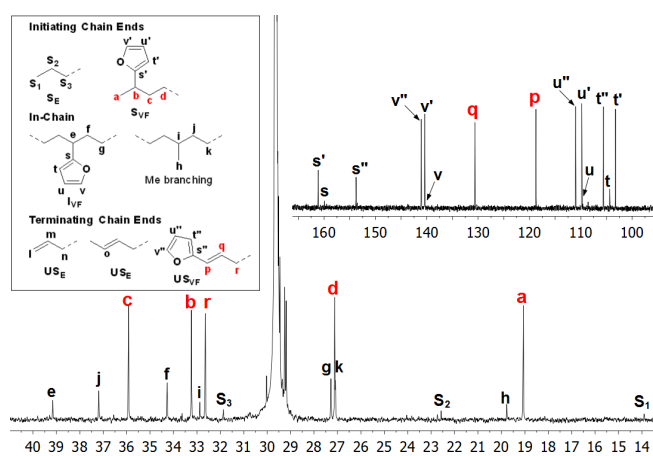


Figure 2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (400 MHz, 100°C , $\text{C}_2\text{D}_2\text{Cl}_4$) of α,ω -di-furan telechelic PE (furan-PE-furan) (Table 1, entry 7).

To further explore the scope of this novel route to telechelics, incorporation of a second functional monomer with an orthogonal reactivity to VF concerning insertion chain growth as well as its functional group was studied. Carbic anhydride (CA) can introduce a reactive anhydride functionality, and in insertion copolymerization with ethylene preferentially incorporates into the PE backbone.^[15] Under pressure-reactor conditions, exposure of

L1Pd to 5 bar of E and 0.6 M of VF and 0.1 M of VF at 95°C resulted in the formation of a novel hetero-functionalized PE with furan groups exclusively at both (α,ω -) chain ends (S_{VF} and US_{VF} : 88%) and anhydride groups incorporated into the backbone (I_{CA} : 96%) (Table 2, entry 1). As anticipated, by using L3Pd, both ratios of $S_{VF}/S_{E+VF+CA}$ and $US_{VF}/US_{E+VF+CA}$ increased to reach 72% and 95%, respectively. While α,ω -di-furan chain ends are predominant (88%), in the backbone PE chain anhydride groups are incorporated exclusively (I_{CA} : 94%; Table 2, entry 3. Cf. Figures S15–S16 in the SI for a full microstructure analysis). Likewise, a hetero-functionalized PE with α,ω -furan endgroups (S_{VF} and US_{VF} : 90%) and ester group incorporated into the backbone (I_{MA} : 88%) was synthesized by terpolymerization of E, VF, and methyl acrylate (MA) (Table 2, entry 5, Figure S17–S18).

Computational Studies. To rationalize the unusual selectivity of VF in the copolymerizations, we studied chain propagation and transfer by DFT methods (Schemes 3 and 4). Only relevant species along the lowest energy pathways are shown, for other geometries, cf. SI Schemes S1–S10).

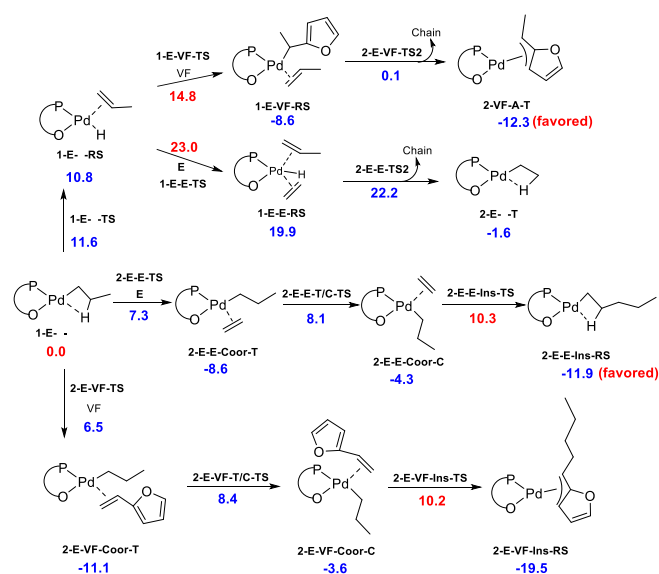
Starting from **1-E- β -T** as a model of the growing polyethenyl chain, the insertion reaction proceeds through the concerted breaking of the β -agostic interaction and monomer coordination to the metal *cis* to the P,O oxygen atom (cf. L1Pd) with a barrier of ca. 7 kcal/mol for either monomer. This olefin coordination is favorable in both cases and, as expected, coordination of the electron-rich VF is favored over ethylene (by 2.5 kcal/mol), despite its greater steric demand. The system isomerizes via a penta-coordinated Berry's pseudo-rotation $\text{TS}^{[16]}$ to reach the less stable coordination product with the monomer *trans* to the O atom. The following insertion of the monomers into the Pd-C bond affords the products, stabilized by a β -agostic interaction in case of ethylene (**2-E-E-Ins-RS**) and by a more favored π - η^3 interaction in the case of VF (**2-E-VF-Ins-RS**). However, although the final insertion product **2-E-VF-Ins-RS** is thermodynamically favored over **2-E-E-Ins-RS** by ca. 8 kcal/mol, the energy barrier to the insertion (the rate determining step (rds) of both insertion pathways) is 2.4 (2.8?) kcal/mol higher for VF than for E, as result of the higher steric demand and, above all, the stronger coordination of the VF. Note that this picture connects well to the experimentally found preference for E incorporation in the chain.

Table 2. Terpolymerization of Ethylene with 2-Vinylfuran and Carbic Anhydride or Methyl Acrylate.^[a]

Entry	Cat.	Conc. [VF/CA] [mol L ⁻¹]	Act. ^[b]	Incorp. ^[c] [VF/CA] [mol %]	Chain ends ^[d] (%)		Incorporated VF ^[c]			Incorporated CA ^[c]			M_n ^[e] [g mol ⁻¹]	M_w/M_n ^[e]	T_m ^[f] [°C]
					$S_{VF}/S_{E+VF+CA}$	$US_{VF}/US_{E+VF+CA}$	S_{VF} (%)	I_{VF} (%)	US_{VF} (%)	S_{CA} (%)	I_{CA} (%)	US_{CA} (%)			
1	L1Pd	0.6/0.1	1.3	1.5/4.6	50	67	43	12	45	3	96	< 1	1700	1.6	95
2	L1Pd	0.6/0.25	1.0	1.1/9.1	60	71	43	11	46	1	99	< 0.2	2500	1.3	77
3	L3Pd	0.6/0.25	0.8	2.0/1.8	72	95	42	12	46	5	94	< 1	1800	1.9	114
4	L3Pd	0.3/0.5	1.3	1.0/3.0	51	92	40	14	46	6	93	< 1	3100	1.8	110
5 ^[g]	L1Pd	0.6/0.1	0.8	2.4/3.3	65	56	50	10	40	4	88	8	1500	1.4	106

[a] Conditions: toluene + monomer: 50 mL; 95°C ; 6 h; catalyst precursor: 40 μmol ; ethylene: 5 bar; 1000 rpm; unless stated otherwise. [b] Units: $\text{kg mol}^{-1} \text{h}^{-1}$. [c] Determined by ^1H NMR in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100 – 130°C . [d] Determined by ^1H NMR, $S_{VF}/S_{E+VF+CA}$: saturated chain ends from VF/saturated chain ends from both VF and E and CA, $US_{VF}/US_{E+VF+CA}$: unsaturated chain ends from VF/unsaturated chain ends from both VF and E and CA. [e] Determined by GPC in 1,2,4-trichlorobenzene at 160°C vs linear polyethylene. [f] Determined by DSC. [g] Methyl acrylate instead of carbic anhydride and 150 mg of BHT.

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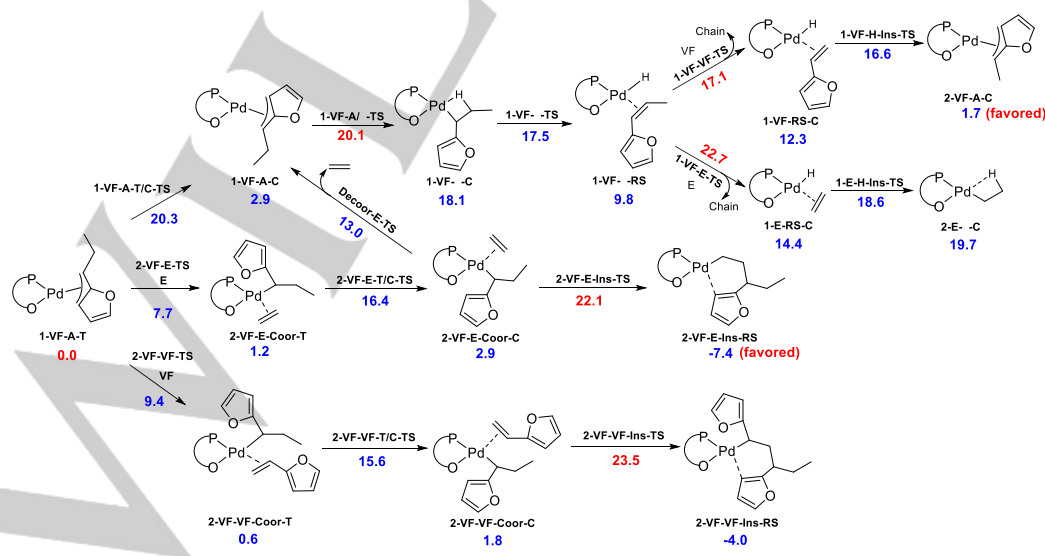
Scheme 3. The reaction mechanisms of the competitive pathways for the E insertion, the VF insertion, and the chain transfer reaction to E and VF from Pd-CH₂-CH₂-CH₃ species (Free energies in toluene in kcal/mol)

The chain transfer pathways from **1-E-β-T** are instructive for comparison with the actually preferred pathways (*vide infra*). Through a β-H elimination TS (**1-E-β-TS**) of 11.6 kcal/mol, a reactive (10.8 kcal/mol) hydride species **1-E-β-RS** forms. In the case of E, **1-E-β-RS** proceeds by an associative TS at 23.0 kcal/mol where the ethylene coordinates to the Pd-H-propene species (**1-E-E-TS**) to produce the five coordinated **1-E-E-RS** intermediate at 19.9 kcal/mol with the propene still coordinated. The Pd-ethyl β-agostic product (**2-E-β-T**) at -1.6 kcal/mol is reached through the **2-E-E-TS2** (at 22.2 kcal/mol) involving the simultaneous release of propene and insertion of the ethylene into the Pd-H bond. In the case of the electron-rich VF, the easier insertion into the Pd-H bond occurs directly from **1-E-β-RS**

through a TS at 14.8 kcal/mol (**1-E-VF-TS**), leading to **1-E-VF-RS** product (at -8.6 kcal/mol) with the new chain located at the electronically favored position *trans* to the O atom. Finally, the release of propene is easily reached through the **2-E-VF-TS2**, with a barrier of 8.7 kcal/mol, leading to **2-VF-A-T** (at -12.3 kcal/mol) stabilized by a π-η³ interaction with the Pd center. By comparing the energies involved in the rate determining step of the chain transfer pathways for E and VF (**1-E-E-TS** and **1-E-VF-TS** in Scheme 3), it clearly emerges that, once the β-H elimination occurs, the chain transfer involves prevalently the VF monomer ($\Delta G_{E-VF}^{\ddagger}$ is about 8 kcal/mol) so that the new chain is initiated by VF, as found experimentally.

Concerning the reactivity of a chain with a last incorporated VF unit (**1-VF-A-T** in Scheme 4), the insertion reaction pathways show that the coordination products (**2-VF-E-Coor-T** and **2-VF-VF-Coor-T**) are similar in energy to the starting species **1-VF-A-T** for both monomers, which differs from the polyethylenyl chain (cf. **1-E-β-T**, Scheme 3). This not only results from the greater stability of the π-η³ interaction with the Pd in **1-VF-A-T** compared to the β-agostic interaction in **1-E-β-T**, but from the greater steric demand of the 2,1-VF chain unit. The different size of the E and VF monomers plays a main role also in the key steps of the insertion pathway and in the corresponding products. As shown in Scheme 4, the insertion of E is more favored than the insertion of VF from both a kinetic and a thermodynamic point of view. In fact, the E insertion energy barrier is 1.4 kcal/mol lower than the VF insertion energy barrier and the insertion product is 3.4 kcal/mol more stable for E than for VF (compare **2-VF-E-Ins-TS** with **2-VF-VF-Ins-TS** for the ΔG^{\ddagger} , and **2-VF-E-Ins-RS** with **2-VF-VF-Ins-RS** for the ΔG of the insertions). In conclusion, also after a VF insertion, propagation via an insertion of E is much favored over a consecutive VF insertion, as found experimentally.

Rather, starting from **1-VF-A-T**, a relevant competitive reaction to ethylene insertion is chain transfer. The lowest energy chain transfer path involves a β-H elimination TS starting from a **1-VF-A-C** species with the chain located *cis* to the O atom (the chain transfer reaction from **1-VF-A-T** is about 7 kcal/mol higher in energy, cf. SI).



Scheme 4. The reaction mechanisms of the competitive pathways for the E insertion, the VF insertion, and the chain transfer reaction to E and VF from Pd-CH(CH₂-CH₃)(C₄H₉O) species. (Free energies in toluene in kcal/mol)

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There are two possible ways to reach **1-VF-A-C** from **1-VF-A-T**: the direct **1-VF-A-T/C-TS** isomerization from **1-VF-A-T** and the de-coordination of the ethylene from **2-VF-E-Coor-C** (Scheme 4). That is, along the E coordination/insertion path, once **2-VF-E-Coor-C** is reached, the coordinated ethylene either could insert to form **2-VF-E-Ins-RS** through a TS at 22.1 kcal/mol or be released through a more favored TS **Decoor-E-TS** at 13.0 kcal/mol to form **1-VF-A-C**. The further chain transfer reaction proceeds through an isomerization TS (at 20.1 kcal/mol) where the π - η^3 coordination of the chain evolves to a β -agostic interaction. The following β -H elimination through the **1-VF- β -TS** leads to **1-VF- β -RS**, in which the unsaturated chain is bound to Pd *cis* to the O atom. Due to the greater steric demand of a chain with a last incorporated VF unit compared with an E derived unit (cf. reactions of **1-E- β -RS** in Scheme 3), in this case with both monomers the favored chain transfer pathway proceeds through a dissociative TS where the incoming monomer replaces the unsaturated chain.

For electronic reasons chain transfer to VF is favored by 5.6 kcal/mol over chain transfer to E (cf. the charge of -0.50e on atom **3** of the incoming VF in **1-VF-VF-TS** vs. -0.46e of the incoming E in **1-VF-E-TS** in Figure 3). Interestingly, after the monomer insertion into Pd-H, the chain is already *cis* to the O atom and, as a consequence, in the favored position for the next monomer insertion, i.e. the first step of chain growth.

Comparing the energetics of the competitive pathways in Scheme 4 shows that when a VF insertion occurs into the chain, a subsequent chain transfer reaction preferentially involves VF monomer **too** so that the resulting chain is terminated with an unsaturated VF-based unit and, at the same time, the new chain is again initiated by VF, as experimentally observed.

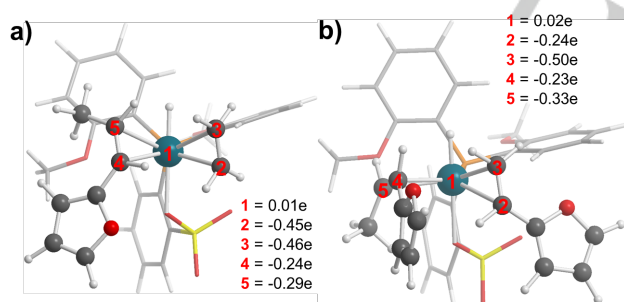


Figure 3. Transition states for the chain transfer reaction to ethylene **1-VF-E-TS** (a) and to vinylfuran **1-VF-VF-TS** (b). The NPA charge analysis on the atoms numbered in red is also reported.

In summary, this direct synthesis of α,ω -di-furan end group functionalized telechelic polyethylene is the result of matched steric and electronic differences between the two monomers. In the chain transfer reactions, the electronic differences predominate so that the insertion of the electron-rich vinylfuran monomer into Pd-H selectively occurs. *Vice versa*, in the chain propagation steps, sterics prevails over electronics so that the insertion of the less bulky ethylene monomer is always favored. However, when a VF insertion occurs, once the chain is in the position *cis* to the phosphinesulfonato O atom, the following monomer insertion is prevented by a strong π - η^3 coordination of the chain to the Pd center that allows an easier β -H elimination, so that chain transfer is preferred to chain propagation.

As an insight from the combination of the experimental and theoretical findings, a generic feature of vinylfuran that enables the selective incorporation into both saturated and unsaturated end groups of polyethylene but not into the chain is that it is an electron-rich monomer and that it forms relatively stable insertion products by a secondary interaction, in this case a π - η^3 -allyl interaction. Additionally, it is relevant that VF is bulkier than ethylene, which however applies to any co-monomer to some extent. This can also serve as a guideline for the design of other selective copolymerizations to telechelics.

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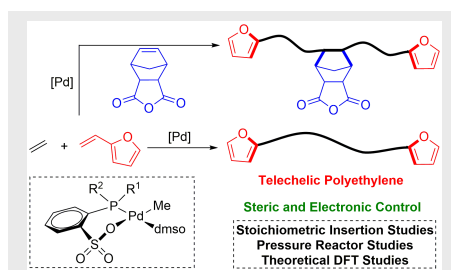
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Layout 1:

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Telechelic Polyethylene:

Using an insertion polymerization method, α,ω -di-furan telechelic PE has been selectively and directly synthesized by a single step. This method can be extended to produce a novel hetero-functionalized PE with furan groups at α,ω - chain ends and anhydride group in the backbone. Combined experimental and theoretical DFT studies reveal the key for this direct approach to telechelics.



Zhongbao Jian, Laura Falivene, Giusi Boffa, Sheila Ortega Sánchez, Lucia Caporaso,* Alfonso Grassi, and Stefan Mecking*

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Direct Synthesis of Telechelic Polyethylene by Selective Insertion Polymerization

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