

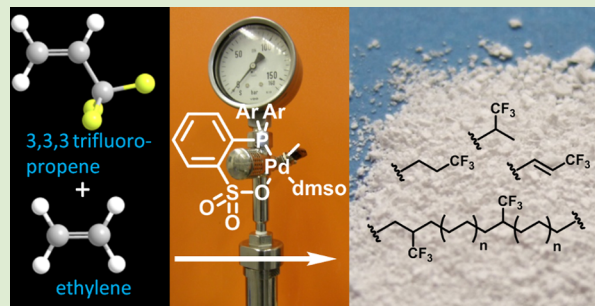
Copolymerization of Ethylene and 3,3,3-Trifluoropropene Using (Phosphine-sulfonate)Pd(Me)(DMSO) as Catalyst

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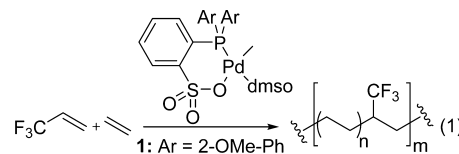
Supporting Information

ABSTRACT: (Phosphine-sulfonate)Pd(Me)(DMSO) catalyzed copolymerization of ethylene and 3,3,3-trifluoropropene (TFP) allows the synthesis of linear copolymers with high fluorine contents of up to 15 wt % (8.9 mol % TFP). ^{13}C and ^{19}F NMR analyses of the copolymers were performed, showing that most of the incorporated TFP is located in the polymer backbone. Copolymerization of ethylene- d_4 with TFP revealed that TFP is inserted into Pd-D bonds in 1,2- as well as in 2,1-mode, although 1,2-insertion is slightly preferred. Chain transfer after TFP insertion is exclusively observed following 2,1-insertion. With higher TFP incorporation, an increase in the ratio of internal to terminal double bonds was detected in the ^1H NMR spectra. This indicates that, in the case of 2,1-insertion of TFP, chain walking is facilitated relative to direct chain release after β -H transfer to the palladium center.



Fully, as well as partially, fluorinated polyolefins, such as polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP), and polyvinylidene difluoride (PVDF) are known to exhibit extraordinary chemical, physical, electrical, and mechanical properties that are mostly based on the high polarity and strength of C–F bonds.^{1–3} These fluorinated polyolefins are usually synthesized via radical polymerization reactions.¹ Nevertheless, partially fluorinated polyolefins can also be obtained by various other synthetic strategies, such as postpolymerization fluorination or defluorination, ring opening polymerization, and acyclic diene metathesis polymerization reactions.^{4–10} Formation of CF_3 side groups was achieved by postpolymerization fluorination of poly(acrylic acid), or esters thereof, with SF_4 and HF .⁶ Neutral (phosphine-sulfonate)Pd-based catalysts are known for their excellent functional group tolerance in ethylene (C_2H_4) copolymerization reactions and yield linear copolymers with low amounts of CH_3 branches ($<10 \text{ CH}_3/10^3 \text{ C}$).^{11–20} Jordan et al. used these systems for the copolymerization of vinyl fluoride (VF) and C_2H_4 , thus, presenting the first coordination–insertion copolymerization of a fluorinated olefin with C_2H_4 .⁴ VF contents of up to 0.45 mol % were obtained with molecular weights (M_n) of up to 2×10^4 g/mol. Tetrameric (phosphine-sulfonate)Pd catalysts linked by a $\text{Li}_4\text{S}_4\text{O}_{12}$ unit allow the incorporation of up to 3.6 mol % of VF with $M_n < 1 \times 10^4$ g/mol and broad molecular weight distributions.²¹ Along with VF, 4-fluorostyrene and fluorinated acrylates were used as fluorinated comonomers for C_2H_4 insertion copolymerization.^{22,23} Radical copolymerization of C_2H_4 was performed with commercially available 3,3,3-trifluoropropene (TFP) as early as 1949.²⁴ TFP appears to be an ideal comonomer for C_2H_4 coordination–

insertion copolymerization in order to get access to highly fluorinated, well-defined, linear polyolefins, which cannot be synthesized by radical polymerization.



Complex 1 was chosen as catalyst as it is a highly active, well-studied (phosphine-sulfonate)Pd(Me) catalyst that is known to allow high insertion ratios of polar comonomers.^{11,15}

Copolymerizations of C_2H_4 and TFP in the presence of 1 were performed at various reaction conditions (Table 1). Fluorine contents of up to 15 wt % could be obtained when high amounts of TFP (8.70 g) and low C_2H_4 partial pressures ($p_{\text{C}_2\text{H}_4} = 2.5$ bar) were applied. Reduced amounts of TFP and increased $p_{\text{C}_2\text{H}_4}$ both led to decreased TFP incorporations, higher molecular weights, and increased polymer yields (Figure 1).

In order to verify that a coordination–insertion-type polymerization takes place, reactions were performed with and without addition of excess 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT) as radical scavenger.^{17,21} No significant

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Table 1. Copolymerization of Ethylene and 3,3,3-Trifluoropropene^a

entry	TFP (g)	$p_{C_2H_4}^c$	yield (g)	% F ^d	TFP ^e (mol %)	M_n^f
1 ^b	0.00	5.0	0.85	0.0	0.0	7.5
2	0.00	5.0	0.78	0.0	0.0	9.9
3	4.35	2.5	0.18	6.6	3.5	5.2
4	4.35	5.0	0.79	3.9	2.0	5.2
5	4.35	15	1.61	1.2	0.6	10
6	4.35	30	3.02	0.6	0.3	15
7	8.70	5.0	0.16	6.8	3.6	6.1
8	8.70	2.5	0.11	15	8.9	5.1
9 ^b	4.35	5.0	0.60	4.6	2.4	8.0

^aConditions: 3 μ mol of complex **1**, 30 mL of toluene, 0.9 mL of methylene chloride, 150 μ mol 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT), 95 °C, 30 min, in a 50 mL autoclave. ^bExperiments were conducted without BHT. ^cEthylene partial pressure in bar. ^dFluorine content in wt %, determined by elemental analysis. ^eTFP content in mol % calculated from the fluorine content (elemental analysis). ^fMolecular weight M_n in 10³ g/mol, determined by size exclusion chromatography (see Supporting Information for details).

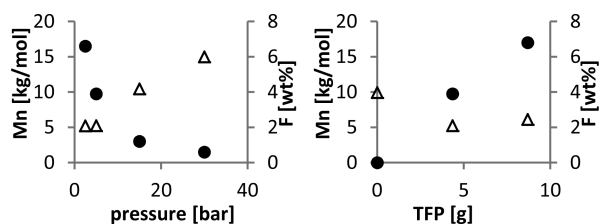


Figure 1. Plots of molecular weight M_n in kg/mol (Δ) and fluorine content in wt % (\bullet) vs ethylene partial pressure $p_{C_2H_4}$ in bar (left) and amount of TFP in gram (right).

effect on the copolymerization reaction and the properties of the obtained polymers were observed.

Extensive NMR spectroscopic analyses of the polymers were performed including ¹H-, ¹³C-, ¹⁹F-, ¹H-COSY, and ¹H-¹³C-HSQC NMR experiments. Low amounts of CH₃ branches (B, Figure 2) of less than 10 CH₃/10³ C could be quantified from ¹³C NMR spectra, which is in accordance to literature reports for C₂H₄ polymers with other comonomers under similar conditions.¹¹ In addition, for TFP-rich copolymers, CF₃ branches (A, Figure 2) could also be quantified. The resulting fluorine contents fit well to the respective values from elemental analyses (see Supporting Information, Table S1). In the ¹³C NMR spectra, next to the signal corresponding to the tertiary carbon atom A_{br} (43.3 ppm, $q^2J(CF) = 24$ Hz), there are three more signals of neighboring CH₂ groups A_w, A _{β} , and A _{γ} . These are clearly separated from the signal of the CH₂ backbone at 30.7 ppm. Due to its low intensity and signal splitting by ¹J-CF coupling (ca. 280 Hz), no signal could be detected for the CF₃ carbon atom A _{γ} , which would be expected at approximately 125 ppm.²⁵

In ¹⁹F NMR spectra, three signal sets corresponding to CF₃ groups could be detected, which are bound to sp³ C atoms (A_F, C_F, and D_F, Figure 3). The main signal A_F is assigned to CF₃ branches in the polymer backbone from TFP incorporation. A_F is accompanied by several smaller signals in the region of -71.5 to -72.3 ppm. We assume these signals to be caused by CF₃ groups in proximity to functionalities besides CH₂ groups from the linear backbone, for example, CF₃-, CH₃-, or olefinic groups. The fact that A_F is by far the dominant signal in ¹⁹F

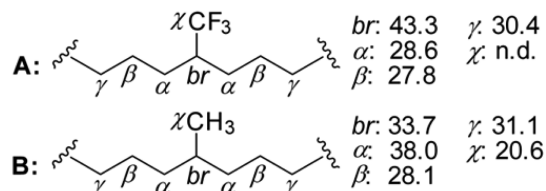
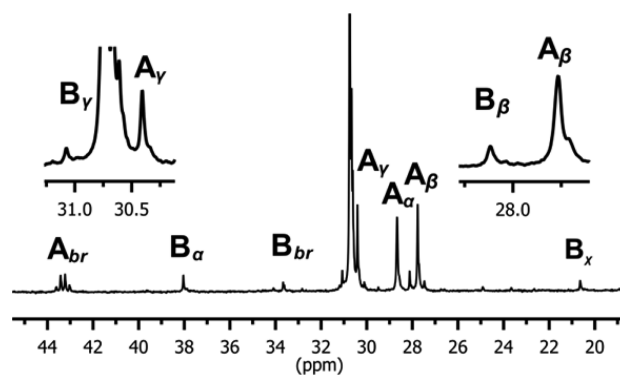


Figure 2. Aliphatic region of the ¹³C NMR spectrum (C₆D₅Br, 20 °C) of entry 8 (top) with peak assignments (chemical shifts in ppm) to CH₃ and CF₃ branches and neighboring CH₂ groups (bottom).

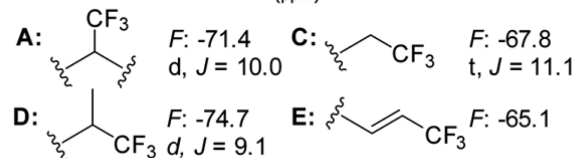
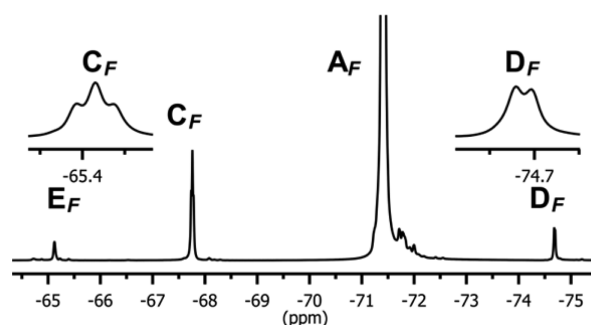
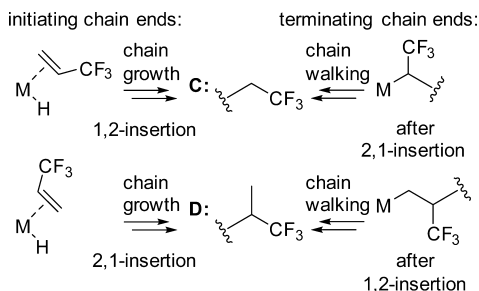


Figure 3. ¹⁹F NMR spectrum (C₆D₅Br, 25 °C) of entry 8 (top) with peak assignments (chemical shifts in ppm, coupling constants in Hz) of relevant groups (bottom).

NMR spectra shows that TFP is mainly incorporated into the polymer backbone, instead of being mostly located at the chain ends.

Singlet E_F is assigned to CF₃ groups that are attached to sp² C atoms (E, Figure 3).²⁶ Terminating chain end E is exclusively formed by chain release after β -H transfer to palladium following a 2,1-insertion of TFP.¹³ Signals C_F and D_F (Figure 3) are assigned to groups C and D (Scheme 1), respectively, due to their multiplicities and chemical shifts.²⁷ Both groups, C and D, can be initiating chain ends caused by 1,2-insertion or 2,1-insertion of TFP into a Pd-H bond, respectively. In theory, D could also be caused by 1,2-insertion of TFP into a Pd-Me bond, but as those only exist before the first insertion of monomer takes place, this pathway is neglected. Furthermore, C and D can be terminating chain ends that are formed via the well-known chain walking mechanism (Scheme 1, Supporting Information, Scheme S1).¹³ Within chain walking, repetitive β -H transfers to the palladium center, each followed by rotation

Scheme 1. Pathways Towards Groups C and D



and reinsertion, lead to a migration of the metal center into the polymer chain. Upon chain release, a polymeric olefin with an internal double bond is formed. If TFP is the last inserted monomer, chain walking leads to saturated terminating end groups C and D.

In ^{19}F NMR spectra (see Supporting Information, Figure S10 and Scheme S2) of a copolymer of deuterated ethylene (C_2D_4) and TFP, the signals which correspond to groups $\text{C}_{\text{initiating}}$ and $\text{C}_{\text{terminating}}$ can be distinguished due to slightly different chemical shifts and characteristic signal splitting ($\text{C}_{\text{initiating}}$: -67.84 ppm, doublet, $^3J_{\text{F-H}} = 11.1$ Hz and $\text{C}_{\text{terminating}}$: -67.76 ppm, triplet, $^3J_{\text{F-H}} = 11.1$ Hz). Furthermore, $\text{D}_{\text{initiating}}$ and $\text{D}_{\text{terminating}}$ should give different coupling patterns, but only the doublet caused by $\text{D}_{\text{initiating}}$ was observed ($\text{D}_{\text{initiating}}$: -74.60 ppm, doublet, $^3J_{\text{F-H}} = 9.2$ Hz). The insertion of TFP into a Pd–D bond is therefore found not to be regioselective, but only slightly regioselective toward 1,2-insertion. We assume that insertion of TFP into a Pd–H bond in case of C_2H_4 copolymerization takes place accordingly.

Besides the olefinic terminating end group E, only terminating chain end group $\text{C}_{\text{terminating}}$ could be detected. $\text{C}_{\text{terminating}}$ arises from chain walking following 2,1-insertion of TFP (see Supporting Information, Figure S10 and Scheme S2). For this finding there are two possible explanations: Either the insertion into a Pd–C bond is highly selective toward 2,1-insertion, or the ratio of chain propagation to chain termination is much lower following 2,1-insertion compared to 1,2-insertion.

A high selectivity toward 2,1-insertion into a Pd–C bond would be in contrast to the finding that insertion into a Pd–H bond is slightly selective toward 1,2-insertion. Anyhow, it is known from literature, that insertion into Pd–H and Pd–C bonds take place from different isomers with the olefin being either *trans* or *cis* to the phosphorus atom of the ligand, respectively.^{13,28} Therefore, a significant difference in the regioselectivity for the insertion of TFP into Pd–H and Pd–C bonds is well possible.

Electron-deficient olefins such as acrylonitrile (AN) and methyl acrylate (MA) are known to selectively insert in a 2,1-fashion, while electron-rich olefins, such as vinyl ethers, prefer 1,2-insertion.^{4,12,16,29,30} Theoretical investigations on the insertion regiochemistry of various alkenes to cationic (σ -Me)diimine)palladium(II) revealed that for TFP the difference between the activation energies for 2,1- and 1,2-insertion is only slightly smaller than in case of MA and AN ($\Delta\Delta E = -4.8$, -6.4 , and -5.4 kcal/mol, respectively).³¹ Nevertheless, regioselectivity can not only be governed by electronic but also by steric effects. Experimental and theoretical investigations on the insertion of MA into Pd–Me bonds of highly sterically demanding phosphine sulfonate palladium complexes

showed that steric interactions between the ligand and the monomer can lead to a complete inversion of the regioselectivity leading to 1,2-insertion.^{28,32}

In contrast to 1,2-insertion, 2,1-insertion of TFP leads to the CF_3 group being in α -position of the Pd center. Literature reports state that electron withdrawing substituents in α -position of the growing polymer chain hinder the subsequent insertion of C_2H_4 .^{21,29,30} This might lead to a much lower ratio of chain propagation to chain termination in the case of 2,1-insertion.

In ^1H NMR spectra, all signals for olefinic groups E, F, and G could be identified (Figure 4). The comparison of the ratio of

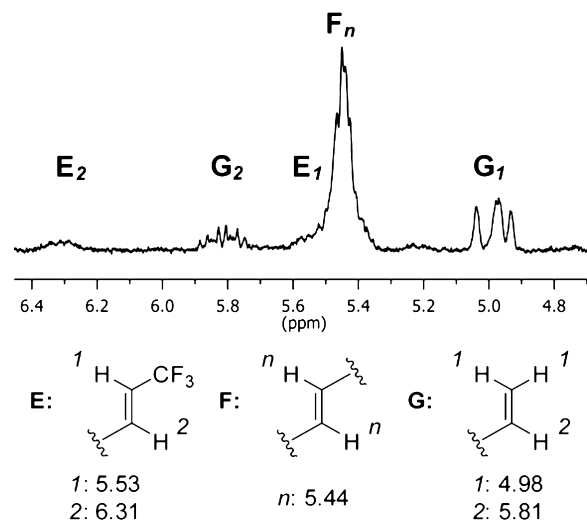


Figure 4. Olefinic region of the ^1H NMR spectrum ($\text{C}_6\text{D}_5\text{Br}$, 130 °C) of entry 8 (top) with peak assignments (chemical shifts in ppm) to olefinic groups (bottom).

internal olefinic groups F to terminal olefinic end groups E and G [$\text{F}/(\text{E} + \text{G})$] (see Supporting Information, Table S1) for C_2H_4 homopolymer (entry 2: $(\text{F}/(\text{E} + \text{G})) = 0.75$) and TFP rich copolymer (entry 7: $(\text{F}/(\text{E} + \text{G})) = 3.8$) indicates that following the 2,1-insertion of TFP, chain walking (leading to group $\text{C}_{\text{terminating}}$ and internal double bond F) is facilitated relative to chain release after β -H transfer to the metal center (yielding group E). Additionally, this is supported by a ratio of 0.85/1 for $\text{E}/\text{C}_{\text{terminating}}$ found in the ^{19}F NMR spectra of the C_2D_4 /TFP copolymer (see Supporting Information, Figure S10 and Scheme S2).

In summary, we could show that (phosphine-sulfonate)Pd-(Me)(DMSO) catalyzed insertion-copolymerization of C_2H_4 and TFP yields linear, well-defined copolymers with high fluorine contents of up to 15 wt %. ^{19}F and ^{13}C NMR analyses reveal that TFP is mainly incorporated into the polymer backbone. ^{19}F NMR analysis of a copolymer of C_2D_4 and TFP revealed that the insertion of TFP into Pd–D bonds preferably takes place in 1,2-regiochemistry, while chain transfer seems to occur mainly following 2,1-insertion of TFP. Reduced catalyst activities and molecular weights at elevated TFP concentrations indicate that following the incorporation of TFP, the subsequent insertion of another monomer is hindered. Furthermore, ^1H NMR analyses imply that TFP insertion leads to facilitated chain walking relative to direct chain release after β -H transfer to the metal center.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental procedures and further analytical and characterization data for polymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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