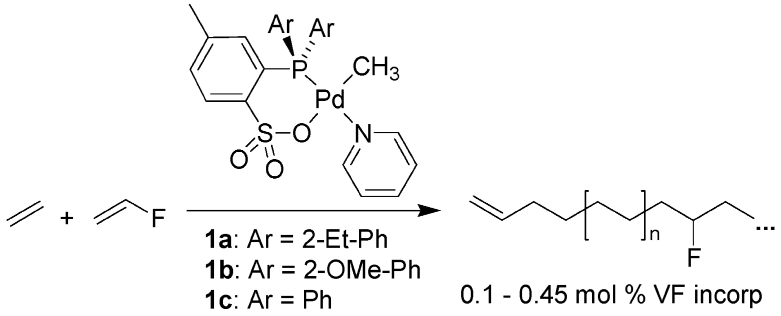
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

Copolymerization of Ethylene and Vinyl Fluoride by (Phosphine-Sulfonate)Pd(Me)(py) Catalysts

Wei Weng, Zhongliang Shen, and Richard F. Jordan

J. Am. Chem. Soc., **2007**, 129 (50), 15450-15451 • DOI: 10.1021/ja0774717



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Copolymerization of Ethylene and Vinyl Fluoride by (Phosphine-Sulfonate)Pd(Me)(py) Catalysts

Wei Weng, Zhongliang Shen, and Richard F. Jordan*

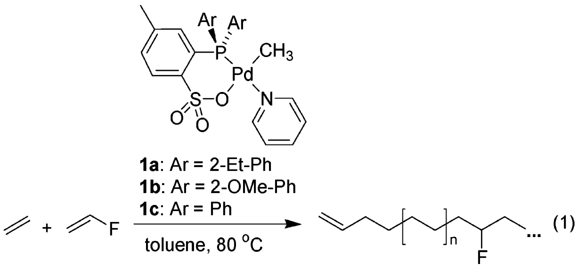
Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

Received September 27, 2007; E-mail: rfjordan@uchicago.edu

The incorporation of halogens into polyolefins influences many key polymer properties, including solvent resistance, barrier properties, gas permeability, adhesion, flammability, toughness, and thermal properties.[1−3] Halogenated polyolefins can be prepared by (i) radical copolymerization of ethylene and vinyl halides, which requires high pressure and produces branched LDPE-type materials;[4] (ii) halogenation of polyolefins, which generally gives a nonuniform distribution of halogens;[2,5] (iii) partial reduction of poly(vinyl halide)s using Bu$_3$SnH or other reagents;[6] and (iv) ROMP of halogen-substituted cyclooctenes or ADMET of halogen-substituted dienes followed by hydrogenation,[3,7] which provide exquisite control over polymer composition and structure but require special monomers and, in the latter case, feature poor atom economy. The direct copolymerization of olefins and vinyl halides to halogenated linear polyolefins by insertion chemistry would provide an attractive and long-sought alternative to these routes.[1] Here we report that (phosphine-sulfonate)Pd(Me)(pyridine) catalysts[8] incorporate low levels of vinyl fluoride in ethylene polymerization.

Previous studies identified several key obstacles to insertion copolymerization of vinyl halides with olefins, including (i) competing radical polymerization of the vinyl halide initiated by catalyst-derived radicals,[9] (ii) low insertion reactivity of L$_n$-MCHXCH$_2$R species generated by 2,1 insertion of vinyl halide into active L$_n$MR species, due to the electron-withdrawing effect of the halogen,[10] and (iii) β-halogen elimination of L$_n$MCH$_2$CHRX species formed by 1,2-insertion (or L$_n$MCHRCH$_2$X from 2,1 insertion and chain-walking), which yields inactive L$_n$MX species and terminates polymerization.[9,11]

To avoid these issues, we studied the copolymerization of ethylene and vinyl fluoride (VF) by the [PO]PdMe(py) catalysts **1a**−**c** in eq 1. VF is a promising potential comonomer because it is less susceptible to free radical polymerization than the other vinyl halides.[4b,c] Also, while β-F elimination is known,[11b,e] this process may be less favorable than other β-halogen eliminations because of the high C−F bond strength.[12] [PO]PdR catalysts are promising candidates for ethylene/VF copolymerization because they produce linear polyethylene as well as linear vinyl-acetate/CO and ethylene/vinyl-ether copolymers suggesting that β-H, β-OAc, and β-OR eliminations are slow relative to chain growth.[13] Also, [PO]PdR catalysts copolymerize ethylene and acrylonitrile (AN);[14] since AN likely undergoes 2,1 insertion,[15] this result suggests that [PO]-PdCHXR species with electron-withdrawing X groups may be reactive for ethylene insertion.



(1)

Complexes **1a**−**c** catalyze ethylene/VF copolymerization to linear fluorinated polyethylene in toluene at 80 °C, as shown in eq 1. Representative results are summarized and compared to an ethylene homopolymerization in Table 1. Low levels (0.1−0.5 mol %) of VF incorporation are observed under these conditions. At a total pressure of 300 psi, increasing the proportion of VF in the feed results in an increase in the VF incorporation level and a decrease in copolymer yield and molecular weight. While **1a** is more reactive and produces higher molecular weight copolymer than **1b**,**c**, all three catalysts incorporate similar levels of VF.

The NMR spectra of the ethylene/VF copolymers produced by **1a**−**c** are identical (except for resonances due to C═C units) to those of "precision" fluorinated polyethylene synthesized by Wagener et al. by ADMET/hydrogenation of a fluorinated diene.[3c] The ^{1}H spectrum contains a doublet at δ 4.49 ($^2J_{\mathrm{H-F}} = 48$ Hz) for the $-\mathrm{CH_2C}H\mathrm{FCH_2}-$ hydrogen (Figure 1) and vinyl and internal olefin (likely to be mostly 2-olefin)[13b] resonances resulting from chain transfer by β-H transfer. A ^{1}H resonance at δ 1.7 for the $-\mathrm{C}H_2\mathrm{CHF}-$ hydrogens is partially masked by the allylic CH$_2$ and CH$_3$ resonances associated with the C═C units. The ^{19}F{^{1}H} spectrum (Figure 2, top) contains a sharp signal at δ −179.4 for the $-\mathrm{CH_2CH}F\mathrm{CH_2}-$ unit and a weak resonance at δ −171.8 for $-\mathrm{CH_2CH}F\mathrm{CH_3}$ chain end units.[16] The ^{13}C{^{1}H} spectrum contains doublets at δ 94.6 ($^1J_{\mathrm{C-F}} = 168$), 35.6 ($^2J_{\mathrm{C-F}} = 36$), and 25.5 ($^3J_{\mathrm{C-F}} = 5$) for the $-\mathrm{CH_2CH_2CHF}-$ units.

The NMR spectra of the ethylene/VF copolymer do not contain resonances for poly(VF) homopolymer (^{19}F: δ −179 to −183, $-\mathrm{CH_2CH}F\mathrm{CH_2}-$); −189 to −199, $-\mathrm{CH_2CH}F\mathrm{CH}F-$).[17] Also, neither removal of the volatiles under vacuum, nor repetitive recrystallization of the copolymer from CHCl$_2$CHCl$_2$ results in changes in the NMR spectra, which shows that the −CHF− resonances are not associated with a small molecule contaminant. These results support the assignment of a copolymer structure.

Several lines of evidence rule out a radical mechanism for eq 1. First, while AIBN initiates radical ethylene/VF copolymerization under the conditions of entry 3 in Table 1, only low yields (∼20 mg) of copolymer are formed. The radical copolymer is more highly branched (70 Me/10^3 C) and has a lower M_w (19 × 10^3) and T_m (116.5 °C) than the copolymers from **1a**−**c**. The radical copolymer is moderately soluble in *o*-dichlorobenzene at 25 °C, while the **1a**−**c** copolymers are not. The ^{19}F NMR spectrum of the radical copolymer (Figure 2, bottom) contains a singlet at δ −179.4, which is broader than that for the **1a**−**c**-produced copolymers, and resonances at δ −178 to −182 that are absent from the spectrum of the **1a**−**c**-produced copolymers. These differences result from the presence of multiple F environments in the radical copolymer due to the branching. It is clear from Figure 2 that the Pd-produced copolymers do not contain significant amounts of radical copolymer.

10.1021/ja0774717 CCC: $37.00 © 2007 American Chemical Society

Table 1. Copolymerization of Ethylene and Vinyl Fluoride[a]

entry	1	2	3	4	5	6	7
catalyst	**1a**	**1a**	**1a**	**1a**	**1a**	**1b**	**1c**
P_{VF} (psi)[b]	0	40	80	160	240	80	80
P_{C2H4} (psi)[b]	300	260	220	140	60	220	220
yield (g)	5.93	0.77	0.44	0.17	0.10	0.22	0.41
M_w (10^3)[c]	56.3	43.6	35.4	23.8	17.7	17.0	11.2
M_w/M_n[c]	3.4	3.0	2.9	2.7	2.6	2.7	2.5
Me/10^3 C	0.3	1.3	0.9	1.1	2.4	2.7	4.7
VF (mol %)[d]	-	0.09	0.17	0.37	0.45	0.15	0.14
VF/chain	-	0.9	1.2	2.2	1.3	0.4	0.4
T_m[e]	133.6	132.6	132.6	131.7	130.7	130.2	129.6

[a] Conditions: toluene, 50 mL, [cat] = 0.2 mM, 80 °C, 2 h, total pressure 300 psi. [b] The reactor was charged with the given pressure of VF at 25 °C, pressurized with ethylene (on demand) to achieve a total pressure of 300 psi, and then heated to 80 °C. [c] GPC. [d] The mol % VF incorporation in copolymer was determined by ^{1}H NMR. [e] DSC.

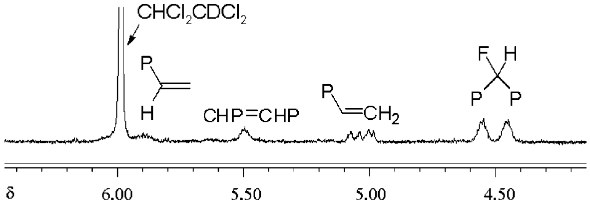


Figure 1. ^{1}H NMR spectrum ($CDCl_2CDCl_2$, 120 °C) of ethylene/vinylfluoride copolymer produced by **1a** (Table 1, entry 4) (P = polymeryl).

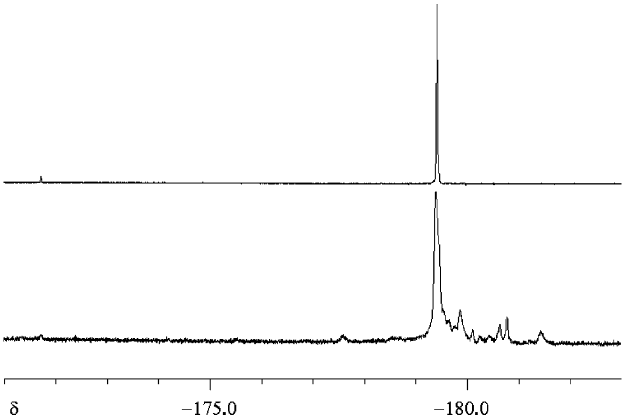


Figure 2. ^{19}F{^{1}H} NMR spectra (*o*-DCB-d_4, 110 °C) of ethylene/vinylfluoride copolymer produced by **1a** (top; Table 1, entry 3) and AIBN (bottom; same conditions as Table 1, entry 3).

Second, galvinoxyl (5 equiv vs **1a**) does not inhibit or influence the VF incorporation level in **1a**-catalyzed ethylene/VF copolymerization. GC−MS established that ≥93% of the galvinoxyl was present at the end of the copolymerization, showing that the lack of inhibition is not due to decomposition of galvinoxyl. In contrast, galvinoxyl completely quenches the AIBN-initiated copolymerization. Third, recrystallization of an intimate mixture of AIBN- and **1a**-produced copolymers removes the AIBN-produced component. However, no ^{19}F-containing species were detected in the mother liquor from recrystallization of **1a**-produced copolymer. Therefore, we propose that eq 1 proceeds by an insertion mechanism.

The low VF incorporation levels in eq 1 imply that VF competes poorly with ethylene for insertion into [PO]Pd(R) species. VF is a poor σ-donor and is expected to coordinate more weakly than ethylene to Pd^{II} species in which backbonding is weak.[11a,18] Also, DFT studies predict that the barriers to 1,2 and 2,1 insertion of $(HN{=}CHCH{=}NH)Pd(Me)(VF)^+$ are similar and ca. 2 kcal/mol higher than that for the analogous ethylene complex.[19] The reduction in polymer M_w and yield caused by VF may result from inhibition of growth by slow insertion of $[PO]Pd(CHFCH_2R)$ species formed by 2,1-VF insertion or dative fluorine coordination in $[PO]Pd(CH_2\text{-}CHFR)$ species formed by 1,2-VF insertion. Catalyst deactivation by β-F elimination is also possible. We are studying the reactions of base-free [PO]PdR complexes[13b] with VF to address these issues.

This work shows that [PO]Pd(Me)(py) catalysts[8] incorporate low levels of VF in ethylene polymerization to produce fluorinated HDPE. It may be possible to enhance the polymerization rate and VF incorporation level by modification of the catalyst.

Acknowledgment. This work was supported by the U.S. Department of Energy (Grant DE-FG-02-00ER15036). We thank Professor Kenneth Wagener and Emine Boz (University of Florida) for providing a sample of ADMET fluorinated polyethylene.

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.

References

(1) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479.
(2) (a) Kharitonov, A. P.; Taege, R.; Ferrier, G.; Teplyakov, V. V.; Syrtsova, D. A.; Koops, G.-H. *J. Fluorine Chem.* **2005**, *126*, 251. (b) Andrews, G.; Dawson, L. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Klingsberg, A., Muldoon, A., Eds.; Wiley: New York, 1986; Vol. 6, p 495.
(3) (a) Boz, E.; Nemeth, A. J.; Ghiviriga, I.; Jeon, K.; Alamo, R. G.; Wagener, K. B. *Macromolecules* **2007**, *40*, 6545. (b) Boz, E.; Nemeth, A. J.; Alamo, R. G.; Wagener, K. B. *Adv. Synth. Catal.* **2007**, *349*, 137. (c) Boz, E.; Wagener, K. B.; Ghosal, A.; Fu, R.; Alamo, R. G. *Macromolecules* **2006**, *39*, 4437.
(4) (a) Doak, K. W. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Klingsberg, A., Muldoon, A., Eds.; Wiley: New York, 1986; Vol. 6, p 383. (b) Sianesi, D.; Caporiccio, G. *J. Polym. Sci., Part A-1* **1968**, *6*, 335. (c) Burkhart, R. D.; Zutty, N. L. *J. Polym. Sci., Part A* **1963**, *1*, 1137.
(5) Chang, B. H.; Zeigler, R.; Hiltner, A. *Polym. Eng. Sci.* **1988**, *28*, 1167.
(6) Schilling, F. C.; Tonelli, A. E.; Valenciano, M. *Macromolecules* **1985**, *18*, 356.
(7) (a) Hillmyer, M. A.; Laredo, W. R.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 6311. (b) Yang, H.; Islam, M.; Budde, C.; Rowan, S. J. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2107.
(8) (a) Drent, E.; van Dijk R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 744. (b) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 964.
(9) (a) Stockland, R. A., Jr.; Foley, S. R.; Jordan, R. F. *J. Am. Chem. Soc.* **2003**, *125*, 796. (b) Boone, H. W.; Athey, P. S.; Mullins, M. J.; Philipp, D.; Muller, R.; Goddard, W. A. *J. Am. Chem. Soc.* **2002**, *124*, 8790.
(10) Foley, S. R.; Shen, H.; Qadeer, U. A.; Jordan, R. F. *Organometallics* **2004**, *23*, 600.
(11) (a) Foley, S. R.; Stockland, R. A., Jr.; Shen, H.; Jordan, R. F. *J. Am. Chem. Soc.* **2003**, *125*, 4350. (b) Strazisar, S. A.; Wolczanski, P. T. *J. Am. Chem. Soc.* **2001**, *123*, 4728. (c) Kang, M.; Sen, A.; Zakharov, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **2002**, *124*, 12080. (d) Gaynor, S. G. *Macromolecules* **2003**, *36*, 4692. (e) Watson, L. A.; Yandulov, D. V.; Caulton, K. G. *J. Am. Chem. Soc.* **2001**, *123*, 603.
(12) Zhao, H.; Ariafard, A.; Lin, Z. *Organometallics*, **2006**, *25*, 812.
(13) (a) Newsham, D. K.; Borkar, S.; Sen, A.; Conner, D. M.; Goodall, B. L. *Organometallics* **2007**, *26*, 3636. (b) Vela, J.; Lief, G. R.; Shen, Z.; Jordan, R. F. *Organometallics*, in press. (c) Kochi, T.; Nakamura, A.; Ida, H.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 7770. (d) Luo, S.; Vela, J.; Lief, G. R.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 8946.
(14) Kochi, T.; Noda, S.; Yoshimura, K.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 8948.
(15) (a) Wu, F.; Foley, S. R.; Burns, C. T.; Jordan, R. F. *J. Am. Chem. Soc.* **2005**, *127*, 1841. (b) Groux, L. F.; Weiss, T.; Reddy, D. N.; Chase, P. A.; Piers, W. E.; Ziegler, T.; Parvez, M.; Benet-Buchholz, J. *J. Am. Chem. Soc.* **2005**, *127*, 1854.
(16) The $-CHFCH_3$ ^{1}H NMR resonance (δ 4.69, d, J_{H-F} = 49) was detected in copolymers made at high temperature and low pressure.
(17) (a) Ovenall, D. W.; Uschold, R. E. *Macromolecules* **1991**, *24*, 3235. (b) Bruch, M. D. *Macromolecules* **1989**, *22*, 151.
(18) Quinn, H. W.; Van Gilder, R. L. *Can. J. Chem.* **1971**, *49*, 1323.
(19) von Schenck, H.; Strömberg, S.; Zetterberg, K.; Ludwig, M.; Akermark, B.; Svensson, M. *Organometallics* **2001**, *20*, 2813.

JA0774717