J|A|C|S
COMMUNICATIONS

Published on Web 09/28/2009

Copolymerization of Vinyl Acetate with Ethylene by Palladium/Alkylphosphine−Sulfonate Catalysts

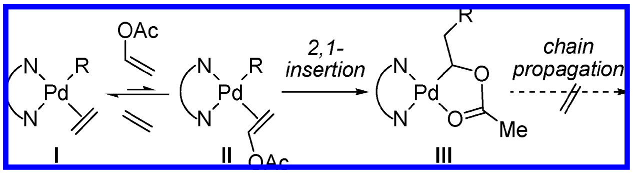
Shingo Ito, Kagehiro Munakata, Akifumi Nakamura, and Kyoko Nozaki*

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku 113-8656, Japan

Received June 20, 2009; E-mail: nozaki@chembio.t.u-tokyo.ac.jp

Vinyl acetate (VAc) is an industrially important monomer for the production of poly(VAc)s and ethylene/VAc copolymers, which are used directly or after hydrolysis in a wide range of applications including paints and adhesives.[1] The polymers have been conventionally produced by radical polymerization; however, it generally does not give well-defined polymer structures because of the high chain-transfer constants of VAc and VAc polymers.[1d] During the past decade, the coordination polymerization of polar vinyl monomers by late transition metals has been extensively investigated, since it allows more precise control over the microstructures of polymers.[2] Nonetheless, VAc has been among the most challenging monomers for metal-catalyzed coordination polymerization and copolymerization.[3] For example, Brookhart et al. thoroughly studied the reactions of VAc with Pd and Ni α-diimine complexes to provide significant insights into the difficulty in the coordination copolymerization of VAc with ethylene.[3d] The problems could be attributed mainly to (i) weaker π-coordination ability of VAc than ethylene to shift the equilibrium between I and II to the left (Scheme 1) and (ii) low reactivity of $L_nMCH(OAc)CH_2R$ species (III), formed by 2,1-insertion of VAc from II, toward the coordination and insertion of the next monomer. The low activity arises from the formation of a relatively stable five-membered chelate structure and the presence of an electron-withdrawing acetoxy group at C_α.[3d] In addition, β-acetoxy elimination after the 1,2-insertion of VAc might also retard the polymerization of VAc.

Scheme 1



Recent developments of Pd/phosphine−sulfonate catalysts[2,4] have enabled the main-chain incorporation of polar vinyl monomers including methyl acrylate,[4a−c,i] vinyl ethers,[4d] acrylonitrile,[4e] vinyl fluoride,[4f] and other important comonomers[4g,h] into linear polyethylenes. In this regard, we have succeeded in the copolymerization of VAc with carbon monoxide as the first example of coordination polymerization of VAc.[5] This success motivated us to investigate the copolymerization of VAc with ethylene.[6] Herein, we report the synthesis of novel palladium complexes bearing alkylphosphine−sulfonate ligands[7] and their successful use in the coordination copolymerization of VAc with ethylene, leading to linear copolymers that possess in-chain $-CH_2CH(OAc)-$ units.

Pd/alkylphosphine−sulfonate complexes **3a**[4e] and **3b**[4i] were synthesized from dicyclohexylphosphonium−sulfonate **1**. The structure of **3a** was unequivocally determined by X-ray crystallographic analysis: **3a** possesses a distorted square-planar geometry around the Pd center, which is similar to that of the Pd/arylphosphine−sulfonate complex **4**.[8]

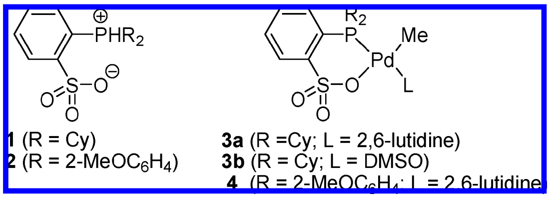
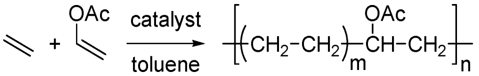


Figure 1. Catalysts and ligands examined in the copolymerization of vinyl acetate with ethylene. Cy = cyclohexyl.

Initially, the homopolymerization of ethylene was investigated. The palladium catalysts *in situ* generated from $Pd(dba)_2$ and **1** produced completely linear polyethylenes with less than 1 branch/10^3 C (activity = 6.0 $g\cdot mmol^{-1}\cdot h^{-1}$; $M_n = 2.9 \times 10^4$; $M_w/M_n = 1.9$; at 3.0 MPa of ethylene pressure in toluene at 80 °C).[9] The catalytic activity and molecular weight were lower than those obtained by the corresponding arylphosphine ligand **2**.[4d]

Table 1. Copolymerization of Vinyl Acetate with Ethylene[a]



$$CH_2{=}CH_2 + CH_2{=}CH(OAc) \xrightarrow[\text{toluene}]{\text{catalyst}} \left[(CH_2-CH_2)_m - \overset{OAc}{CH} - CH_2 \right]_n$$

entry	catalyst	VAc (mL)	activity ($g\cdot mmol^{-1}\cdot h^{-1}$)	M_n (10^3)	M_w/M_n	VAc[b] (%)
1	**2**, $Pd(dba)_2$	7.5	0.22	7.6	2.1	0.5
2	**1**, $Pd(dba)_2$	7.5	0.66	9.9	2.3	0.6
3	**1**, $Pd(dba)_2$	12	0.30	6.1	2.0	1.2
4	**1**, $Pd(dba)_2$	15	0.17	4.7	2.0	1.5
5	**3a**	12	0.67	5.8	2.3	1.9
6	**3b**	12	0.97	5.0	2.3	1.7
7	**4**	12	0.44	5.8	2.1	1.6

[a] Conditions: 0.10 mmol of $Pd(dba)_2$ and 0.12 mmol of **1** or **2** (or 0.10 mmol of **3** or **4**), 3.0 MPa of ethylene pressure, 15 mL of total volume (VAc and toluene), 80 °C, 15 h, in a 50 mL autoclave. [b] The molar ratio of incorporated VAc.

As demonstrated in Table 1, VAc and ethylene were successfully copolymerized by Pd/phosphine−sulfonate catalysts. The copolymerization was carried out by exposing a mixture of $Pd(dba)_2$ and ligand precursors **1** or **2**, or preformed complexes **3** or **4**, to VAc and ethylene in toluene at 80 °C. The polymers were isolated by precipitation with MeOH and purified by reprecipitation from hot 1,2-dichlorobenzene/CH_2Cl_2 to remove any traces of catalyst residues.[10] Alkylphosphine ligand **1** exhibited higher catalytic activity than arylphosphine ligand **2** (entries 1 and 2). The increase of the amount of VAc enhanced the incorporation efficiency at the expense of catalytic activity and molecular weight (entries 2−4). Preformed complexes **3** exhibited higher catalytic activity as

10.1021/ja9050839 CCC: $40.75 © 2009 American Chemical Society

compared to the *in situ* generated catalysts (compare entry 3 with entries 5 and 6), providing the copolymers with a VAc ratio of up to *ca.* 2%.[11] The activity of alkylphosphine complexes **3** was higher than that of arylphosphine complex **4** (compare entries 5 and 6 with entry 7).

The characterization of the products revealed that the polymers obtained are undoubtedly copolymers rather than a mixture of homopolymers. According to the ^{13}C NMR spectrum (Figure 2), the copolymers possess highly linear polyethylene backbones without a detectable branching unit (<1 branch/10^3 C). The acetoxy groups were linked to the main chain as well as to initiating and terminating chain ends. The comparison of the ^{13}C NMR data with those of some model compounds also supports the NMR assignments.[9]

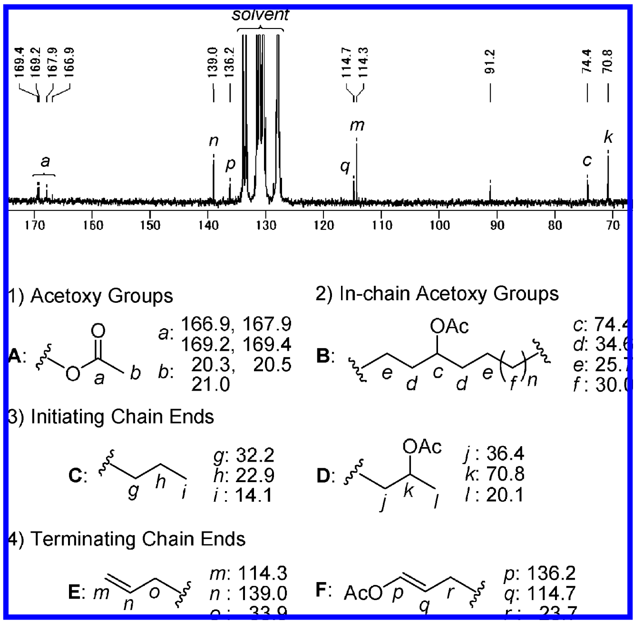


Figure 2. ^{13}C NMR spectrum (1,2,4-trichlorobenzene, 120 °C) and the assignments for the vinyl acetate/ethylene copolymers obtained in entry 5, Table 1. Further assignments for other minor signals are shown in the Supporting Information.

Chain-end analysis revealed the presence of two major initiating chain ends, *n*-alkyl (**C**) and 2-acetoxypropyl (**D**) groups (**C**:**D** = *ca.* 2:3). The copolymerization initiated by **3a** would begin with the insertion of either ethylene or VAc into the Pd−Me bond. In fact, however, only group **C** was detected when the copolymerization was quenched at a shorter reaction time.[9] This corresponds with the fact that ethylene insertion into the Pd−Me bond was the only pathway to initiate the copolymerization. Initiating chain ends **D** gradually appeared with a longer reaction time, which can be attributed to the initiation by the 2,1-insertion of VAc into a Pd−H bond. There were two types of terminating chain ends, vinyl (**E**) and (*E*)-2-acetoxyethenyl (**F**) groups (**E**:**F** = *ca.* 3:1). Group **E** is formed via β-H elimination after ethylene insertion or via β-OAc elimination after 1,2-insertion of VAc, and group **F** is formed via β-H elimination after 2,1-insertion of VAc. The resulting Pd−H species can initiate the copolymerization to form initiating groups **C** and **D**.

Control experiments clearly exclude the possibility of radical polymerization:[9] (i) A radical inhibitor, galvinoxyl, did not affect the copolymerization of VAc with ethylene by **3a**. (ii) The AIBN-initiated radical polymerization afforded only VAc homopolymers. These results suggest that the copolymerization of VAc with ethylene by Pd/phosphine−sulfonate catalysts proceeds via the coordination−insertion mechanism.

In summary, we have developed the copolymerization of vinyl acetate with ethylene by Pd/alkylphosphine−sulfonate catalysts, leading to highly linear copolymers possessing in-chain and chain-end VAc units. The present study provides the first example of the coordination copolymerization of VAc with ethylene. Further investigations to enhance the catalytic activity and VAc incorporation ratio as well as mechanistic studies are currently underway in our group.

Acknowledgment. This work was supported by Grant-in-Aid for Scientific Research on Priority Areas “Advanced Molecular Transformations of Carbon Resources” and the Global COE Program “Chemistry Innovation through Cooperation of Science and Engineering” from MEXT, Japan. A.N. is grateful for a Research Fellowship for Young Scientists from JSPS.

Supporting Information Available: Experimental procedures and product characterization (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Doak, K. W. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1986; Vol. 6, pp 386−429. (b) Daniels, W. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1989; Vol. *17*, pp 393−455. (c) Whiteley, K. S.; Heggs, T. G.; Koch, K.; Mawer, R. L.; Immel, W. *Ullmann’s Encyclopedia of Industrial Chemistry*, 6th ed.; Wiley-VCH: Weinheim, 2003; Vol. 28, pp 393−495. (d) Rinno, H. *Ullmann’s Encyclopedia of Industrial Chemistry*, 6th ed.; Wiley-VCH: Weinheim, 2003; Vol. 29, pp 49−59.

(2) (a) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479–1493. (b) Sen, A.; Borkar, S. *J. Organomet. Chem.* **2007**, *692*, 3291–3299. (c) Berkefeld, A.; Mecking, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 2538–2542. (d) Nakamura, A.; Ito, S.; Nozaki, K. *Chem. Rev.* **2009**, in press (DOI: 10.121/cr900079r).

(3) (a) Klabunde, U.; Ittel, S. D. *J. Mol. Catal.* **1987**, *41*, 123–134. (b) Boone, H. W.; Athey, P. S.; Mullins, M. J.; Philipp, D.; Muller, R.; Goddard, W. A. *J. Am. Chem. Soc.* **2002**, *124*, 8790–8791. (c) Conner, E. F.; Younkin, T. R.; Henderson, J. I.; Hwang, S.; Grubbs, R. H.; Roberts, W. P.; Litzau, J. I. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2842–2854. (d) Williams, B. S.; Leatherman, M. D.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2005**, *127*, 5132–5146.

(4) (a) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 744–745. (b) Kochi, T.; Yoshimura, K.; Nozaki, K. *Dalton Trans.* **2006**, 25–27. (c) Skupov, K. M.; Marella, P. R.; Simard, M.; Yap, G. P. A.; Allen, N.; Conner, D.; Goodall, B. L.; Claverie, J. P. *Macromol. Rapid Commun.* **2007**, *28*, 2033–2038. (d) Luo, S.; Vela, J.; Lief, G. R.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 8946–8947. (e) Kochi, T.; Noda, S.; Yoshimura, K.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 8948–8949. (f) Weng, W.; Shen, Z.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 15450–15451. (g) Skupov, K. M.; Piche, L.; Claverie, J. P. *Macromolecules* **2008**, *41*, 2309–2310. (h) Borkar, S.; Newsham, D. K.; Sen, A. *Organometallics* **2008**, *27*, 3331–3334. (i) Guironnet, D.; Roesle, P.; Rünzi, T.; Göttker-Schnetmann, I.; Mecking, S. *J. Am. Chem. Soc.* **2009**, *131*, 422–423.

(5) (a) Kochi, T.; Nakamura, A.; Ida, H.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 7770–7771. See also: (b) Nakamura, A.; Munakata, K.; Kochi, T.; Nozaki, K. *J. Am. Chem. Soc.* **2008**, *130*, 8128–8129.

(6) In a patent literature, Drent reported that Pd/arylphosphine-sulfonate catalysts copolymerized ethylene and VAc with a trace amount of VAc incorporation, but no detailed product characterization was described. Drent, E.; Pello, D. H. L.; Jager, W. W. Eur. Pat. Appl. 1994, 589527.

(7) Compared with *aryl*phosphine-sulfonate ligands, *alkyl*phosphine-sulfonate ligands have been less investigated. For a report on the synthesis of an alkylphosphine-sulfonate ligand and its nickel complex, see: Zhou, X.; Bontemps, S.; Jordan, R. F. *Organometallics* **2008**, *27*, 4821–4824.

(8) Noda, S.; Nakamura, A.; Kochi, T.; Chung, L. W.; Morokuma, K.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, in press (DOI: 10.121/ja9047398).

(9) See the Supporting Information for experimetal details.

(10) For a similar purification method, see: (a) Gibson, V. C.; Tomov, A. *Chem. Commun.* **2001**, 1964–1965. (b) Li, X. F.; Li, Y. G.; Li, Y. S.; Chen, Y. X.; Hu, N. H. *Organometallics* **2005**, *24*, 2502–2510.

(11) The incorporation of a small amount of polar functional groups can change the surface properties of polyolefins. For example, isotactic polypropylenes modified with less than 1% of maleic anhydride can make the polymers exhibit better surface properties sufficient for the application to compatibilizing agents; see: Novák, I.; Borsig, E.; Hrćková, L.; Fiedlerová, A.; Kleinová, A.; Pollák, V. *Polym. Eng. Sci.* **2007**, *47*, 1207–1212.

JA9050839