J|A|C|S
COMMUNICATIONS

Alternating Copolymerization of Vinyl Acetate with Carbon Monoxide

Takuya Kochi,[†] Akifumi Nakamura,[†] Hirotsugu Ida,[‡] 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, and Tsukuba Research Laboratories, Kuraray Company, Ltd.,
41, Miyukigaoka, Tsukuba, Ibaraki 305-0841, Japan*

Received April 24, 2007; E-mail: nozaki@chembio.t.u-tokyo.ac.jp

Coordination polymerization of readily available polar vinyl monomers has been one of the major challenges in the field of olefin polymerization for decades[1] because it allows for syntheses of a wide range of polymer structures with polar functional groups,[2] which are not accessible with other polymerization methods, such as radical, cationic, or anionic polymerization. In spite of the considerable efforts devoted, however, only a limited number of polar vinyl monomers have been copolymerized via a coordination−insertion mechanism.[2−4]

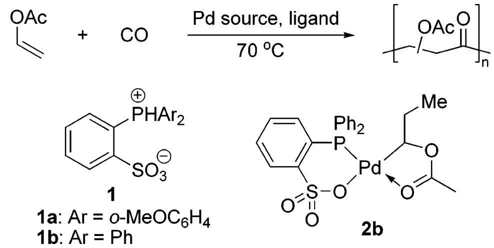
Alternating copolymerization of olefins with carbon monoxide catalyzed by late transition metals, such as palladium(II) catalysts, is one of the best methods for efficient synthesis of polar functionalized polymers by coordination polymerization of olefins.[5−7] The copolymerization reaction clearly demonstrates the functional group tolerance of palladium(II) catalysts, typically used for the reaction, because it proceeds in the presence of numerous carbonyl groups incorporated in the resulting γ-polyketones. However, no alternating copolymerization of carbon monoxide with polar vinyl monomers has ever been reported,[7] in contrast that several vinyl monomers linked to polar groups by one or more methylene spacers have been copolymerized with carbon monoxide.[8,9] A number of problems associated with the copolymerization have been identified, and one of the most serious drawbacks is low coordinating ability of the carbon−carbon double bond of polar vinyl monomers.[3,10−12]

Among polar vinyl monomers, coordination polymerization of vinyl acetate has been the most challenging target. Vinyl acetate is one of the most readily available and widely used polar vinyl monomers for polymer production. Nearly 5.0 Mt of vinyl acetate is produced worldwide each year.[13] However, unlike most of the other monomers,[14] vinyl acetate has been recognized as unique in the sense that the only way to polymerize it is a radical process.[15] Neither anionic, cationic, nor coordination polymerization has been efficiently applied to vinyl acetate.

In this report, we present the first example of alternating copolymerization of a polar vinyl monomer, vinyl acetate, with carbon monoxide. The results are also the first example of a nonradical pathway for polymerization of vinyl acetate.

We obtained the alternating copolymer of vinyl acetate with CO by using a mixture of $Pd(dba)_2$ and phosphine−sulfonic acid ligand (**1a**), which was originally reported by the group of Shell for the nonperfectly alternating copolymerization of ethylene with carbon monoxide.[16] When vinyl acetate was treated with 6.0 MPa of CO at 70 °C for 20 h in the presence of $Pd(dba)_2$ and **1a** as a catalyst, the corresponding alternating copolymer with M_n of 38000 was obtained with activity of 2.3 $g\cdot mmol^{-1}\cdot h^{-1}$ (Table 1, entry 1). Higher activity and molecular weights of the copolymers were achieved with the methoxy-substituted ligand **1a**, rather than the unsubstituted one **1b** (entries 1 and 2). Molecular weight of the copolymer increase as the reaction is carried out for a longer time period up to 20 h (entries 1, 3, and 4), but when the reaction was performed for 70 h, no significant increase in the molecular weight was observed (entry 5). As a Pd source, $Pd(OAc)_2$ can also be used, but the yield and the molecular weight of the copolymer became lower (entry 6). Neither **1** nor $Pd(dba)_2$ catalyzed the copolymerization in the absence of the other, which indicates that Pd complex formation with **1** was necessary for the copolymerization to proceed.

Table 1. Alternating Copolymerization of Vinyl Acetate and CO[a]



1
1a: Ar = o-$MeOC_6H_4$
1b: Ar = Ph
2b

entry	Pd source	ligand	time (h)	TOF (h^{-1})	activity ($g\cdot mmol^{-1}\cdot h^{-1}$)	M_n ($\times 10^3$)	M_w/M_n
1	$Pd(dba)_2$	**1a**	20	20	2.3	38	1.4
2	$Pd(dba)_2$	**1b**	20	9.2	1.1	26	1.3
3	$Pd(dba)_2$	**1a**	1.0	24	2.7	4.9	1.1
4	$Pd(dba)_2$	**1a**	5.0	26	3.0	18	1.2
5	$Pd(dba)_2$	**1a**	70	7.6	0.87	41	1.7
6	$Pd(OAc)_2$	**1a**	20	9.2	1.1	34	1.4
7	**2b**		20	15	1.7	31	1.2
8[b]	**2b**		20	14	1.6	25	1.4
9	**2b**		0.5	37	4.2	3.0	1.0

[a] Conditions: 0.010 mmol of Pd source, 0.012 mmol of ligand, 6.0 MPa of CO pressure, 2.5 mL of vinyl acetate, 70 °C. [b] Galvinoxyl (0.050 mmol) was added.

The structure of the alternating copolymers was confirmed by mass spectrometry and NMR spectroscopy. The polymers were analyzed by MALDI-TOF mass spectrometry using the materials with relatively low molecular weights, and signals with intervals of 114 were observed, which clearly indicates the formation of alternating copolymers. ^1H and ^{13}C NMR spectra of obtained materials were also in good agreement with the structure of the alternating copolymer, which was distinct from poly(vinyl acetate). ^{13}C NMR spectroscopy using inverse-gated decoupling[17] showed that nearly equal amount of each carbon of the repeating unit was contained in the polymer, including two carbons of carbonyls corresponding to keto groups (201−204 ppm) of the main chain and acetoxy groups (169−171 ppm). Head-to-tail structure is suggested to be less controlled based on the existence of multiple peaks for methyne and methylene of the main chain in both ^1H and ^{13}C NMR spectra.

A possible mechanism of the alternating copolymerization is shown in Figure 1. Copolymerization is initiated by migratory insertion of vinyl acetate into a Pd−H bond which was formed via

---

[†] The University of Tokyo.
[‡] Kuraray Company, Ltd.

10.1021/ja072859n CCC: $37.00 © 2007 American Chemical Society

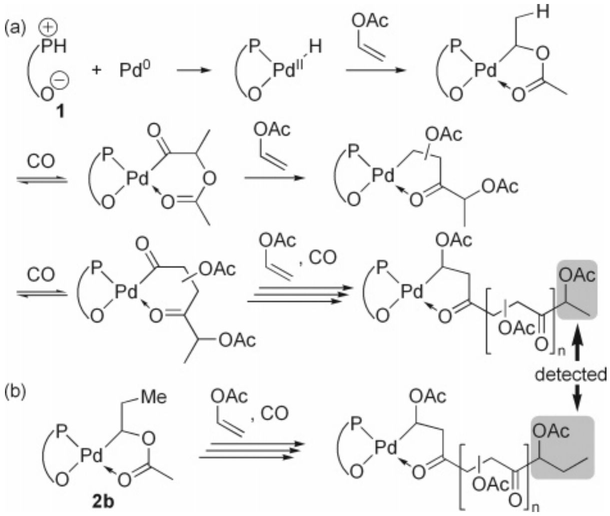


Figure 1. A possible mechanism of copolymerization of vinyl acetate and CO catalyzed by (a) **1** and Pd(dba)$_2$, or (b) **2b**.

protonation of Pd(0) species. 2,1-Insertion should occur more frequently than 1,2-insertion, as theoretically predicted[10] and experimentally observed in other systems.[18] The 2,1-insertion product forms a stable five-membered chelate, into which only CO can be inserted. Vinyl acetate, which was anticipated to have low coordinating ability of the carbon−carbon double bond,[12] coordinates to the palladium center and is inserted to the acylpalladium species.[19] Further alternating insertion of carbon monoxide and vinyl acetate in an alternating fashion leads to the formation of alternating copolymers. The initiation step, 2,1-insertion of vinyl acetate into Pd−H, is consistent with the existence of a 1-acetoxyethyl group in a copolymer as was confirmed by its ^{1}H NMR spectrum.

When a palladium complex bearing a 1-acetoxypropyl group (**2b**) was employed as a catalyst for the copolymerization,[20] the 1-acetoxypropyl group was observed by ^{1}H NMR as the initiating end group, instead of the 1-acetoxyethyl group. Copolymerization with **2b** showed higher activity than the mixture of **1b** and Pd(dba)$_2$ (Table 1, entries 7 and 9), suggesting efficient initiation of the copolymerization with **2b**. In addition, the major series of peaks on the MALDI-TOF mass spectrum of the copolymer obtained with **2b** were assigned to a completely alternating copolymer initiated by CO insertion to 1-acetoxypropylpalladium and removed from the metal by protonolysis of alkylpalladium resulting from the last insertion of vinyl acetate.

Polymerization via radical intermediates is unlikely, based on the following observations. Copolymerization using catalyst **2b** in the presence of galvinoxyl, a well-known radical trap, showed similar activity and provided the copolymer with similar molecular weight (Table 1, entry 8). When an radical initiator AIBN was used instead of the Pd catalyst, poly(vinyl acetate) was obtained as a sole product. Therefore, we believe a coordination−insertion mechanism operates for the copolymerization as observed with other Pd-catalyzed alternating copolymerization of alkenes with carbon monoxide.

In summary, we report the first example of alternating copolymerization of a polar vinyl monomer and carbon monoxide using vinyl acetate. We believe the present result opens the possibility for efficient syntheses of a new type of highly functionalized γ-polyketones by alternating copolymerization of a variety of polar vinyl monomers with carbon monoxide. This is also the first nonradical pathway for polymer synthesis with vinyl acetate, one of the most inexpensive and readily available polar vinyl monomer, as a major component. Application of other polar vinyl monomers for alternating copolymerization with carbon monoxide is currently under investigation.

Acknowledgment. The authors are grateful to Prof. Y. Nishibayashi and Dr. Y. Miyake at the University of Tokyo for high-resolution FAB-MS analysis of **2b**. T.K. thanks the Japan Society for the Promotion of Science (JSPS) for a Research Fellowship for Young Scientists. This work was also supported by a Grant-in-Aid for Scientific Research on Priority Areas “Advanced Molecular Transformations of Carbon Resources”.

Supporting Information Available: Experimental procedures and characterization (PDF, CIF). 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*, 1479−1493.
(2) *Functional Polymers: Modern Synthetic Methods and Novel Structures*; Patil, A. O., Schulz, D. N., Novak, B. M., Eds.; ACS Symposium Series 704; American Chemical Society: Washington, DC, 1998.
(3) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888−899.
(4) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 744−745.
(5) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663−682.
(6) Bianchini, C.; Meli, A. *Coord. Chem. Rev.* **2002**, *225*, 35−66.
(7) *Catalytic Synthesis of Alkene-Carbon Monoxide Copolymers and Cooligomers;* Sen, A., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2003.
(8) Kacker, S.; Jiang, Z.; Sen, A. *Macromolecules* **1996**, *29*, 5852−5858.
(9) Lee, J. T.; Alper, H. *Chem. Commun.* **2000**, 2189−2190.
(10) Philipp, D. M.; Muller, R. P.; Goddard, W. A., III; Storer, J.; McAdon, M.; Mullins, M. *J. Am. Chem. Soc.* **2002**, *124*, 10198−10210.
(11) Kang, M.; Sen, A.; Zakharov, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **2002**, *124*, 12080−12081.
(12) Williams, B. S.; Leatherman, M. D.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2005**, *127*, 5132−5146.
(13) Gustin, J.-L.; Laganier, F. *Org. Process Res. Dev.* **2005**, *9*, 962−975.
(14) Vinyl chloride may be regarded as a polar vinyl monomer which can be polymerized only via a radical mechanism, but Endo et al. have reported that polymerization of vinyl chloride by *tert*-butyllithium or (C$_5$Me$_5$)Ti(OMe)$_3$ and MAO may proceed via a nonradical polymerization mechanism: (a) Endo, K.; Kaneda, N.; Waku, H. *Polymer* **1999**, *40*, 6883−6886. (b) Endo, K.; Saitoh, M. *J. Polym. Sci., Part A* **2003**, *41*, 248−256.
(15) Koumura, K.; Satoh, K.; Kamigaito, M.; Okamoto, Y. *Macromolecules* **2006**, *39*, 4054−4061.
(16) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 964−965.
(17) (a) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999**, *283*, 2059−2062. (b) Cotts, P. M.; Guan, Z.; McCord, E.; McLain, S. *Macromolecules* **2000**, *33*, 6945−6952.
(18) Formation of 1-acetoxypropyl chelates by vinyl acetate insertion into Pd−Me bonds has been reported for two other palladium complexes: Reddy, K. R.; Chen, C.-L.; Liu, Y.-H.; Peng, S.-M.; Chen, J.-T.; Liu, S.-T. *Organometallics* **1999**, *18*, 2574−2576. See also ref 12.
(19) This may be related to the unique nature of the Shell catalyst Pd−**1a**, which provided the nonperfectly alternating ethylene/CO copolymer. The successive ethylene insertion results from the olefin insertion into the γ-ketoalkyl chelate, which was never reported for any other catalyst systems. In other words, ethylene, a monomer with lower coordinating ability than CO, could compete with CO for insertion only when **1a** was employed.
(20) Complex **2b** was prepared by reaction of a phosphine−sulfonate methylpalladium complex[21] with vinyl acetate. This reaction afforded a crude mixture containing complex **2b** as a major product, which was presumably formed by 2,1-insertion of vinyl acetate into the Pd−Me bond. **2b** was isolated in 51% yield, and the structure was determined by X-ray crystallography. See Supporting Information.
(21) Kochi, T.; Yoshimura, K.; Nozaki, K. *Dalton Trans.* **2006**, 25−27. Unique catalytic activity of phosphine−sulfonate palladium complexes for ethylene/acrylonitrile copolymerization has also been studied in our group.[22]
(22) Kochi, T.; Noda, S.; Yoshimura, K.; Nozaki, K. Submitted for publication.

JA072859N