

Coordination–Insertion Copolymerization of Allyl Monomers with Ethylene

Shingo Ito,[†] Masafumi Kanazawa,[†] Kagehiro Munakata,[†] Jun-ichi Kuroda,[‡] Yoshikuni Okumura,[‡] and Kyoko Nozaki^{*,†}

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

[‡]Corporate Research and Development Center, Showa Denko K. K., 2 Nakanosu, Oita, Oita 870-1809, Japan

S Supporting Information

ABSTRACT: Coordination–insertion copolymerization of allyl monomers with ethylene was developed by using a palladium/phosphine–sulfonate catalyst. A variety of allyl monomers, including allyl acetate, allyl alcohol, protected allylamines, and allyl halides, were copolymerized with ethylene to form highly linear copolymers that possess in-chain $-\text{CH}_2\text{CH}(\text{CH}_2\text{FG})-$ units.

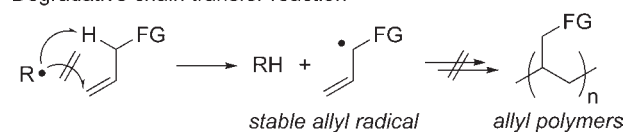
Despite its high potential utility in functionalized polyolefin synthesis, the polymerization of allyl monomers, $\text{CH}_2=\text{CHCH}_2\text{FG}$ (FG = OAc, OH, NH_2 , halogen, etc.), has received much less attention than that of the corresponding vinyl monomers.¹ Homopolymerization of allyl monomers is expected to give polymers corresponding to functionalized polypropylenes and thus has been the target of intensive research since the 1940s.^{1a} However, conventional free-radical polymerization of allyl monomers generally affords only oligomers or low-molecular-weight polymers because of facile “degradative chain transfer” to the allyl monomers and the low reactivity of the resulting allyl radical species (Scheme 1).^{1,2}

Although recent advances in metal-catalyzed coordination polymerization have enabled the use of various functionalized olefins,^{3,4} only a few catalysts have been found to be applicable to allyl monomer polymerization: Allyl alcohol^{5,6} and allylamine^{6,7} have been shown to undergo zirconocene-catalyzed copolymerization with ethylene when pretreated with a stoichiometric amount of alkylaluminum reagents to mask the functional groups. To our knowledge, there has been no example in the academic literature in which other allyl monomers have been copolymerized in metal-catalyzed coordination–insertion polymerization.^{8,9}

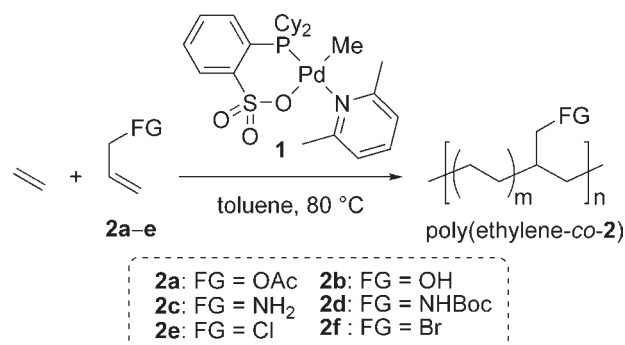
In recent research, we¹⁰ and others¹¹ have developed coordination–insertion copolymerization of fundamental polar vinyl monomers with ethylene by palladium catalysts bearing a phosphine–sulfonate ligand.^{3e} During further investigations to expand the scope of the copolymerization, the catalytic system was found to be applicable to allyl monomers. Herein we report the investigation of the coordination–insertion copolymerization of allyl monomers, including allyl acetate (**2a**), allyl alcohol (**2b**), allylamines (**2c**, FG = NH_2 ; **2d**, FG = NHBoc), and allyl halides (**2e**, FG = Cl; **2f**, FG = Br), with ethylene by Pd/alkylphosphine–sulfonate complex **1** (Scheme 2). The obtained ethylene/2

Scheme 1

Degradative chain transfer reaction



Scheme 2



copolymers have highly linear polyethylene structures with in-chain FGCH_2 groups and thus exhibit higher melting temperatures than the corresponding branched ethylene/vinyl monomer copolymers produced by conventional radical polymerization.

The copolymerization of allyl monomers and ethylene was performed in the presence of Pd complex **1** (0.10 mmol)^{10c} in toluene at 80 °C. The obtained copolymers were purified by reprecipitation from hot 1,2-dichlorobenzene/ CH_2Cl_2 to give an essentially pure form of the copolymers. As shown in entries 1–4 of Table 1, allyl acetate **2a** was successfully incorporated to form the linear copolymers.¹² Increasing the concentration of **2a** led to an increase in the **2a** incorporation ratio with a decrease in catalytic activity and molecular weight. Thus, the **2a** incorporation ratio could be increased up to 7.9% by conducting the copolymerization at a lower ethylene pressure (entry 4). When

Received: October 13, 2010

Published: January 4, 2011

Table 1. Copolymerization of Allyl Monomers with Ethylene by **1**^a

entry	monomer	monomer (mL)	toluene (mL)	ethylene (MPa)	yield (g) ^b	activity (g mmol ⁻¹ h ⁻¹)	M_n (10 ³) ^c	M_w/M_n	incorp. (%) ^d	T_{eim} (°C) ^e	T_{pm} (°C) ^f	T_{efm} (°C) ^g
1	2a (FG = OAc)	3.0	12.0	3.0	1.74	5.8	6.7 (15.3)	2.3	1.2	114.9	122.9	126.1
2	2a	7.5	7.5	3.0	1.64	5.5	6.1 (14.0)	2.3	2.4	96.0	115.5	119.3
3	2a	12.0	3.0	3.0	1.38	4.6	5.3 (12.1)	2.6	3.2	82.4	112.9	118.0
4	2a	12.0	3.0	1.5	0.45	1.5	4.4 (10.1)	1.7	7.9	55.2	87.7	103.5
5 ^h	2a	12.0	3.0	3.0	0.36	12.1	6.2 ^j (14.3)	2.3	3.4	86.7	113.4	120.2
6 ⁱ	2b (FG = OH)	3.0	12.0	4.0	0.19	0.04	1.5 (3.5)	1.7	5.7	80.0	92.7	103.2
7	2c (FG = NH ₂)	3.0	12.0	5.0	—	—	—	—	—	—	—	—
8	2d (FG = NHBoc)	(15 mmol)	15.0	3.0	1.18	3.9	4.5 (10.2)	2.4	1.8	110.2	117.2	120.6
9	2d	(30 mmol)	15.0	1.5	0.33	1.1	2.1 (4.8)	1.6	4.5	69.0	101.2	108.9
10	2e (FG = Cl)	3.0	12.0	3.0	0.47	1.6	4.2 (9.7)	2.3	0.9	115.4	124.5	128.0
11	2f (FG = Br)	3.0	12.0	3.0	0.27	0.90	2.8 ^j (6.3)	2.0	1.1	112.3	120.9	124.4

^a Copolymerization of **2** with ethylene was performed with **1** (0.10 mmol) in toluene at 80 °C for 3 h in a 50 mL autoclave, unless otherwise noted. ^b Determined after precipitation with MeOH. ^c Number-average molecular weight measured by size-exclusion chromatography with Shodex GPC AT-806MS columns using polystyrene as an internal standard and corrected by universal calibration. Molecular weights before universal calibration are shown in parentheses. ^d Molar ratio of incorporated allyl monomers determined by quantitative ¹³C NMR analyses. ^e Extrapolated onset melting temperature obtained using DSC. ^f Peak melting temperature obtained using DSC. ^g Extrapolated end melting temperature obtained using DSC. ^h Copolymerization was performed with 0.01 mmol of **1**. ⁱ Reaction time was 48 h. ^j Measured with Tosoh TSKgel GMH_{HR}-H(S)HT columns.

the reaction was conducted with 0.01 mmol of the palladium catalyst, the copolymerization gave the copolymer with almost the same composition and properties (entry 5). Allyl alcohol **2b** reacted sluggishly under 3.0 MPa ethylene but copolymerized at a higher ethylene pressure (4.0 MPa) to give the copolymer with a molecular weight of 1500 and a **2b** ratio of 5.7%, albeit with a low copolymerization activity (entry 6). The optimal reaction conditions were applicable to other allyl monomers containing nitrogen and halogen functionalities. Although allylamine **2c** was inert even under 5.0 MPa ethylene (entry 7), Boc-protected allylamine **2d** produced the copolymers with an activity comparable to that of **2a** (entries 8 and 9). Similarly, the copolymers with allyl halides such as allyl chloride **2e** (entry 10) and allyl bromide **2f** (entry 11) were obtained with ~1% allyl monomer incorporation. Since the transition-metal-catalyzed coordination copolymerization of vinyl halides with ethylene has rarely been achieved,^{13,14} the present protocol provides a novel strategy for incorporating halogen functionalities into highly linear polyethylenes.¹⁵

According to NMR analyses, the copolymers possess highly linear polyethylene backbones with FGCH₂ groups attached to the main chain. A representative ¹³C NMR spectrum measured under quantitative conditions (ethylene/**2e** copolymer) is shown in Figure 1. In all of the ethylene/**2** copolymers, the signals of the carbons α , β , γ , and δ to the FG group (*a*, *b*, *c*, and *d*, respectively) were observed in an exactly 1:1:2:2 ratio, indicating the presence of FGCH₂ groups linked to the linear polyethylene and no repeating unit of allyl monomers. In the case of **2a**, **2e**, and **2f**, two major chain ends were observed: an *n*-alkyl group (**I**) as an initiation chain end and a terminal vinyl group (**II**) as a termination chain end.¹⁶ The results strongly suggest that the copolymerization was initiated by the insertion of ethylene into the Pd–Me bond of **1** to form group **I** and terminated via β -H elimination after ethylene insertion or β -FG elimination after 2,1-insertion of an allyl monomer to form group **II**. It should be noted that the Pd–hydride species formed in situ by β -H elimination could be an initiator for the present copolymerization.¹⁷

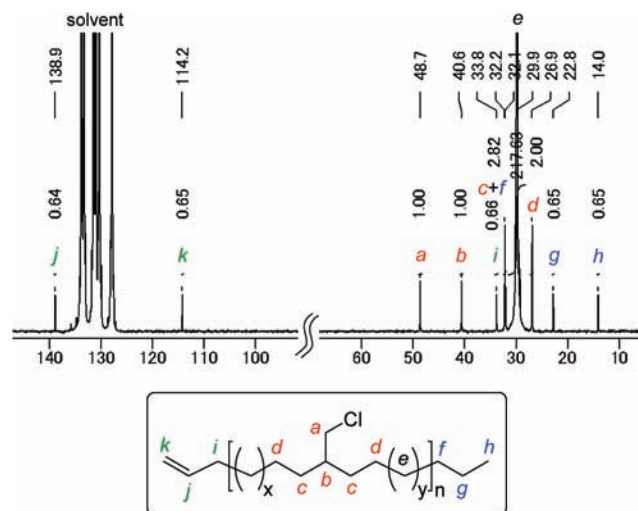
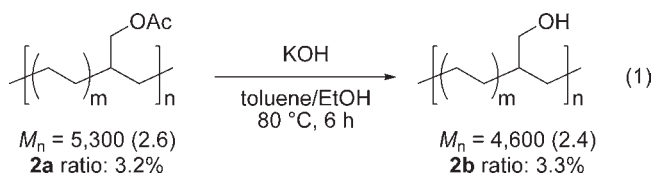


Figure 1. Quantitative ¹³C NMR spectrum of the ethylene/**2e** copolymer in entry 10 of Table 1 (1,2,4-trichlorobenzene, 120 °C).

In contrast, the ethylene/**2b** and ethylene/**2d** copolymers had an *n*-alkyl group (**I**) as the major chain end.¹⁸

The ethylene/**2a** and ethylene/**2d** copolymers can be deprotected to form the corresponding OH and NH₃Cl copolymers, respectively. Transesterification of ethylene/**2a** copolymers ($M_n = 5300$, $M_w/M_n = 2.6$, **2a** = 3.2%) in the presence of KOH in toluene/EtOH afforded the ethylene/**2b** copolymer without a significant decrease in molecular weight ($M_n = 4600$, $M_w/M_n = 2.4$) or FG ratio (**2b** = 3.3%) (eq 1):



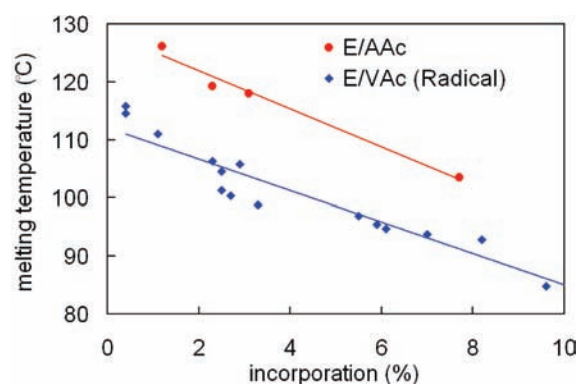
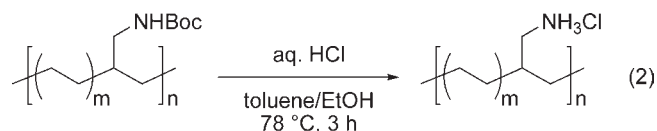


Figure 2. Comparison of extrapolated end melting temperatures (T_{fm}) measured by DSC for the present ethylene/2a copolymers (red) and ethylene/vinyl acetate copolymers produced by radical methods (blue).²⁰

Ethylene/2d copolymers were treated with aqueous HCl, which resulted in quantitative deprotection of the Boc group to afford ethylene/allylammonium copolymers (eq 2):



¹³C NMR analysis confirmed the complete disappearance of the Boc group, although the content of the NH₃Cl group could not be determined because of broadening of the signals of the carbons α and β to the NH₃Cl group.¹⁶

Differential scanning calorimetry (DSC) analyses revealed that the ethylene/2 copolymers showed melting behavior similar to that of linear low-density polyethylenes such as ethylene/1-hexene copolymers:¹⁹ as the incorporation ratio of 2 increased, the DSC traces gradually become broader along with a decrease in the melting temperature.¹⁶ The broadening of these traces could be explained by the increase of the heterogeneity of the ethylene/2 copolymers with the increasing comonomer content. Another significant feature is that the ethylene/2a copolymers (entries 1–4 in Table 1) exhibit higher melting temperatures than the moderately branched ethylene/vinyl acetate copolymers produced by radical processes (Figure 2),²⁰ indicating the potential applications of the present allyl copolymers as thermo-stable functionalized polyethylenes.

In summary, we have developed a general method for coordination–insertion copolymerization of allyl monomers with ethylene that uses the palladium/phosphine–sulfonate catalyst 1. A variety of allyl monomers, including allyl acetate, allyl alcohol, protected allylamines, and allyl halides, can be incorporated into linear polyethylenes within the range of 1–8% molar ratio. Although the catalytic activity still needs to be improved, the present method reveals the promising prospect of using allyl monomers in functionalized polymer synthesis.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures and product characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

nozaki@chembio.t.u-tokyo.ac.jp

■ ACKNOWLEDGMENT

This work was supported by a Grant-in-Aid for Scientific Research (A) (21245023 to K.N.), a Grant-in-Aid for Young Scientists (B) (22750083 to S.I.), and the Global COE Program “Chemistry Innovation through Cooperation of Science and Engineering” from MEXT, Japan.

■ REFERENCES

- (1) (a) Bartlett, P. D.; Altschul, R. *J. Am. Chem. Soc.* **1945**, *67*, 812–816. (b) Laible, R. C. *Chem. Rev.* **1958**, *58*, 807–843. (c) *Allyl Compounds and Their Polymers*; Schildknecht, C. E., Ed.; Wiley: New York, 1973. (d) Vorob'eva, A. I.; Prochukhan, Y. A.; Monakov, Y. B. *Polym. Sci., Ser. C* **2003**, *45*, 1–16.
- (2) High-molecular-weight polymers can be obtained when radical polymerization is performed in the presence of Bronsted or Lewis acids. For example, see: (a) Harada, S.; Hasegawa, S. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 27–31. (b) Iio, K.; Kobayashi, K.; Matsuo, M. *Polym. Adv. Technol.* **2007**, *18*, 953–958.
- (3) (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) Chen, E. Y.-X. *Chem. Rev.* **2009**, *109*, 5157–5214. (e) Nakamura, A.; Ito, S.; Nozaki, K. *Chem. Rev.* **2009**, *109*, 5215–5244.
- (4) Most of the polymerization systems using early-transition-metal catalysts deal with olefins possessing polar functional groups away from the olefinic locus of insertion. For recent examples, see: (a) Terao, H.; Ishii, S.; Mitani, M.; Tanaka, H.; Fujita, T. *J. Am. Chem. Soc.* **2008**, *130*, 17636–17637. (b) Yang, X.-H.; Liu, C.-R.; Wang, C.; Sun, X.-L.; Guo, Y.-H.; Wang, X.-K.; Wang, Z.; Xie, Z.; Tang, Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 8099–8102 and references cited therein.
- (5) (a) Imuta, J.; Kashiwa, N.; Toda, Y. *J. Am. Chem. Soc.* **2002**, *124*, 1176–1177. (b) Kashiwa, N.; Matsugi, T.; Kojoh, S.; Kaneko, H.; Kawahara, N.; Matsuo, S.; Nobori, T.; Imuta, J. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3657–3666.
- (6) Hagihara, H.; Tsuchihara, K.; Sugiyama, J.; Takeuchi, K.; Shiono, T. *Macromolecules* **2004**, *37*, 5145–5148.
- (7) Imuta, J.; Toda, Y.; Matsugi, T.; Kaneko, H.; Matsuo, S.; Kojoh, S.; Kashiwa, N. *Chem. Lett.* **2003**, *32*, 656–657.
- (8) In a patent application in 1988, Drent reported ethylene/allyl acetate/CO terpolymerization using a Pd(OAc)₂/dppp/CuOTf catalyst to obtain the corresponding terpolymers, although no mechanistic detail was described. See: Drent, E. *Eur. Pat. Appl.* 0272727, Jun 29, 1988.
- (9) In the patent literature, allyl phosphonate was employed for copolymerization with ethylene using a palladium/phosphine–sulfonate catalyst. See: (a) Matsuo, T.; Yamazaki, H.; Ishihama, Y.; Hirokane, K.; Sato, N.; Yamada, F. *Jpn. Kokai Tokkyo Koho* **2009**, 102521. (b) Matsuo, T.; Yamazaki, H.; Ishihama, Y.; Hirokane, K.; Sato, N.; Yamada, F. *Jpn. Kokai Tokkyo Koho* **2009**, 102554.
- (10) (a) Kochi, T.; Yoshimura, K.; Nozaki, K. *Dalton Trans.* **2006**, 25–27. (b) Kochi, T.; Noda, S.; Yoshimura, K.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 8948–8949. (c) Ito, S.; Munakata, K.; Nakamura, A.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14606–14607. Also see: (d) Nozaki, K.; Kusumoto, S.; Noda, S.; Kochi, T.; Chung, L. W.; Morokuma, K. *J. Am. Chem. Soc.* **2010**, *132*, 16030–16042. (e) Noda, S.; Nakamura, A.; Kochi, T.; Chung, L. W.; Morokuma, K.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14088–14100.
- (11) (a) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 744–745. (b) 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. (c) Luo, S.; Vela, J.; Lief, G. R.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 8946–8947.

(d) Weng, W.; Shen, Z.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 15450–15451. (e) Skupov, K. M.; Piche, L.; Claverie, J. P. *Macromolecules* **2008**, *41*, 2309–2310. (f) Borkar, S.; Newsham, D. K.; Sen, A. *Organometallics* **2008**, *27*, 3331–3334. (g) Guironnet, D.; Roesle, P.; Rünzi, T.; Göttker-Schnetmann, I.; Mecking, S. *J. Am. Chem. Soc.* **2009**, *131*, 422–423. (h) Bouilhac, C.; Rünzi, T.; Mecking, S. *Macromolecules* **2010**, *43*, 3589–3590. (i) Rünzi, T.; Guironnet, D.; Göttker-Schnetmann, I.; Mecking, S. *J. Am. Chem. Soc.* **2010**, *132*, 16623–16630. (j) Rünzi, T.; Fröhlich, D.; Mecking, S. *J. Am. Chem. Soc.* **2010**, *132*, 17690–17691.

(12) The copolymerization of **2a** with ethylene by **1** was not significantly affected by the presence of a radical inhibitor, galvinoxyl. See the Supporting Information for details.

(13) For a report on the coordination copolymerization of vinyl fluoride with ethylene, see ref 11d.

(14) (a) Endo, K.; Saito, M. *Polym. Bull.* **2003**, *49*, 411–416. Also see: (b) Misono, A.; Uchida, Y.; Yamada, K. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2366–2371. (c) Misono, A.; Uchida, Y.; Yamada, K.; Saeki, T. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2995–3001.

(15) Boz, E.; Wagener, K. B. *Polym. Rev.* **2007**, *47*, 511–541.

(16) See the Supporting Information for details.

(17) In entry 5, the number of produced polymer chains per Pd catalyst was calculated to be ~ 5.8 , suggesting the presence of the initiation pathway by Pd–H complexes in addition to the one by Pd–Me complex **1**.

(18) This suggests that the polymerization mechanism differs in the presence or absence of protic monomers. Detail will be reported elsewhere.

(19) For example, see: (a) Hosoda, S. *Polym. J.* **1988**, *20*, 383–397. (b) Quijada, R.; Scipioni, R. B.; Mauler, R. S.; Galland, G. B.; Miranda, M. S. L. *Polym. Bull.* **1995**, *35*, 299–306. (c) Kim, M.-H.; Phillips, P. J. *J. Appl. Polym. Sci.* **1998**, *70*, 1893–1905. (d) Starck, P.; Löfgren, B. *Eur. Polym. J.* **2002**, *38*, 97–107. (e) Sarzotti, D. M.; Soares, J. B. P.; Simon, L. C.; Britton, L. J. D. *Polymer* **2004**, *45*, 4787–4799.

(20) Bugada, D. C.; Rubin, A. *Eur. Polym. J.* **1992**, *28*, 219–227.