

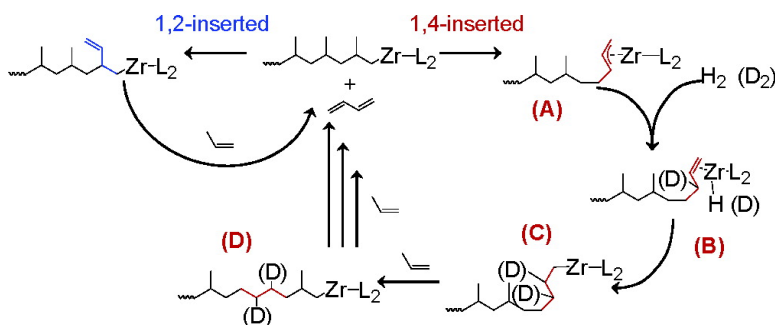
Communication

Hydrogenated 1,4-Insertion of Butadiene in the Copolymerization with Propylene Using an Isospecific Zirconocene Catalyst

Takeshi Ishihara, and Takeshi Shiono

J. Am. Chem. Soc., **2005**, 127 (16), 5774-5775 • DOI: 10.1021/ja050987a • Publication Date (Web): 02 April 2005

Downloaded from <http://pubs.acs.org> on March 25, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
 High quality. High impact.

Hydrogenated 1,4-Insertion of Butadiene in the Copolymerization with Propylene Using an Isospecific Zirconocene Catalyst

Takeshi Ishihara[†] and Takeshi Shiono^{*‡}

Japan Chemical Innovation Institute, AIST Tsukuba, Central 5-8, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan, and Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

Received February 16, 2005; E-mail: tshiono@hiroshima-u.ac.jp

Polypropylene (PP) is used worldwide since it provides excellent mechanical properties with low cost. The introduction of functional groups to PP enables it to be used for paint product, adhesion, print ink, or compatibilizer with other polar materials.

Polymerization methods enable the introduction of functional groups in precisely controlled structures.^{1–18} In the case of PP, the stereospecificity and the copolymerization ability should be simultaneously controlled, but the stereospecific catalysts with early transition metals are easily deactivated with polar functional groups. Copolymerization with monomers possessing nonpolar functional groups, so-called reactive monomers, attracts attention because of its productivities and its conversion to various functional groups in post-polymerization processes.⁹ Although simple diolefins, divinylbenzene, etc., were investigated due to their economical advantages compared to expensive reactive monomers, there are many problems, including cross-linking, cyclization, and low productivities.^{13–19}

Chung et al. found that additions of styrene (or its derivatives) and hydrogen together in propylene polymerization gave styryl-terminated PPs because hydrogen transfer selectively occurred after styrene insertion, which forms dormant species.^{7b–d} Conjugated diolefins, such as 1,3-butadiene, also deactivate α -olefin polymerization. The formation of stable π -allyl species after 1,4-butadiene insertion should be one of the reasons for low activities. The introduction of hydrogen into the propylene–1,3-butadiene copolymerization should reactivate the π -allyl zirconocene species formed by 1,4-inserted butadiene units (1,4-BD) to give Zr–H species and PP having a double bond at the chain end and pendant vinyl groups derived from 1,2-inserted butadiene units (1,2-BD). The polymer thus obtained can be useful as a precursor of functional PP and an aliphatic macromonomer.

Copolymerization of propylene and 1,3-butadiene was conducted using an isospecific zirconocene catalyst, *rac*-dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium dichloride (**1**), activated with modified methylaluminoxane (MMAO). The copolymerization results are summarized in Table 1. Copolymerization activities were very low (runs 1 and 2), and the number-average molecular weight (M_n) of the copolymer (run 2) was also lower compared to that of polypropylene synthesized under the same conditions in the absence of butadiene (run 7). The introduction of hydrogen into the copolymerization enhanced the polymerization activity by about 1000 times (runs 2 and 3). An increase of butadiene concentration, however, caused a decrease of polymerization activities to some extent (runs 3–5). The M_n value of the polymer synthesized with hydrogen was roughly double compared to those without hydrogen (runs 2 and 3). The molecular weights of copolymers obtained with the different butadiene concentrations were approximately the same

Table 1. Results of Propylene–1,3-Butadiene Copolymerization with 1-MMAO^a

run	BD ^b	H ₂ (MPa)	time (h)	yield (g)	rate ^c (kg mol ⁻¹)	M_n^d ($\times 10^3$)	M_w/M_n^d	BD Units in PP ^e			T_m^f (°C)
								$f_{1,4}$	$f_{1,2}$	$f_{H-1,4}$	
1	0.46	0	1.0	trace							
2	0.46	0	15	0.025	1.7	12.6	2.5	3.3	5.4	0.0	102
3	0.46	0.1	1.0	1.77	1770	27.5	1.7	0.0	4.8	4.0	104
4	0.23	0.1	1.0	2.29	2290	26.4	2.0	0.0	2.8	2.5	125
5	0.69	0.1	1.0	0.47	474	25.4	1.8	0.0	6.1	5.7	94
6	0.0	0.1	1.0	2.92		65.8	6.3				159
7	0.0	0	1.0	2.91		243	7.2				

^a Polymerization conditions: 100 mL autoclave; toluene, 40 mL; polymerization temperature, 0 °C; **1**, 1 μ mol; Al/Zr (mol/mol), 10000; propylene concentration, 1.79 mol L⁻¹. ^b Butadiene concentration (mol L⁻¹). ^c Polymerization rate (kg/polymer mol⁻¹ h⁻¹). ^d Determined by GPC. ^e Mole fraction (mol %) of each unit calculated by ¹H NMR and ¹³C NMR; $f_{1,4}$ is the mole fraction of the 1,4-butadiene unit; $f_{1,2}$ is that of the 1,2-butadiene unit, and $f_{H-1,4}$ is that of the hydrogenated 1,4-butadiene unit in the copolymers. ^f Measured by DSC.

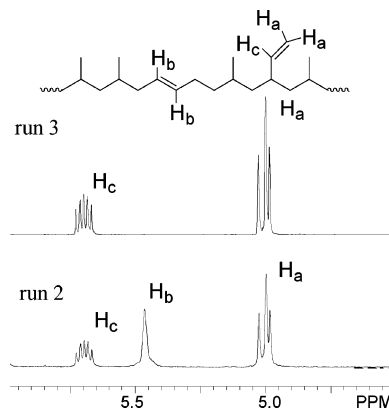


Figure 1. ¹H NMR spectra of poly(propylene-*ran*-butadiene) obtained with hydrogen (run 3) and without hydrogen (run 2).

(runs 3–5). These results rejected the selective hydrogen transfer after 1,4-butadiene insertion described above.

The ¹H NMR spectra of the copolymers obtained with and without hydrogen (runs 2 and 3) are shown in Figure 1. There are three signals in the olefinic proton region. The copolymers obtained without hydrogen (run 2) had two types of units derived from 1,3-butadiene, that is, 1,4-BD and 1,2-BD. The similar contents of these units indicate no selectivity of 1,2- and 2,1-(~1,4)-insertions for butadiene in this catalyst, whereas the copolymers obtained in the presence of hydrogen had only 1,2-BD (runs 3–5). An increase of butadiene concentration in the feed created a linear increase of the 1,2-BD contents in the copolymers. The structure of the copolymer synthesized with hydrogen (run 3) was then characterized by ¹³C NMR (Figure 2). The resonances at 113 and 145 ppm were assigned

[†] Japan Chemical Innovation Institute.

[‡] Hiroshima University.

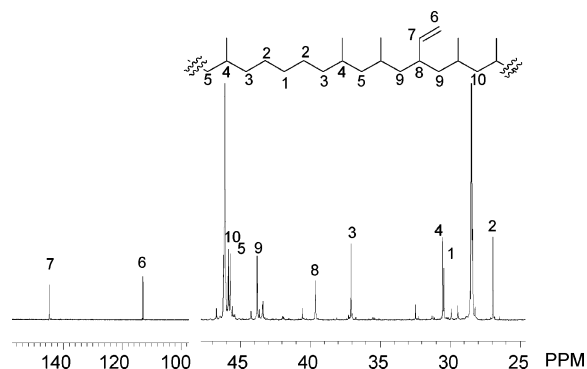
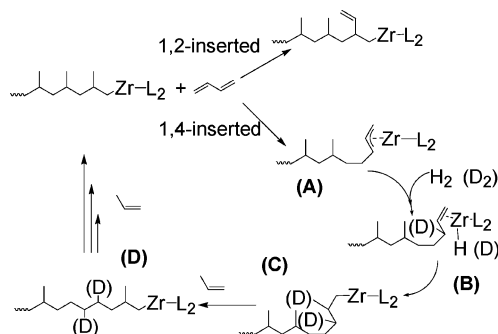


Figure 2. ^{13}C NMR spectrum of poly(propylene-*ran*-butadiene) obtained with hydrogen (run 3).

Scheme 1



to 1,2-BD. The existence of 1,2-BD was also confirmed by the resonances of aliphatic region signals at 39.6, 43.8, and 45.9 ppm, as shown in Figure 2. The sharpness of these resonances suggests the stereoregular insertion of 1,2-BD in the isotactic polypropylene sequence.

In addition, five relevant peaks were observed at 26.95, 30.46, 30.55, 37.1, and 45.7 ppm. These peaks were assigned to hydrogenated 1,4-butadiene units (H-1,4-BD) between two propylene units. The mole fractions of H-1,4-BD were calculated from the relative intensities of each unit compared to those of propylene in the ^{13}C NMR spectra. The contents of 1,2-BD and H-1,4-BD increased with an increase of butadiene concentration in the feed, while the ratio of 1,2-BD and H-1,4-BD was kept constant. The contents of total 1,3-butadiene units reached more than 10% (run 5). The T_m values of copolymers obtained with and without hydrogen decreased in accordance with the content of butadiene unit in the copolymers.

The results described above, that is, the sharp rise of the copolymerization activities and the formation of H-1,4-BD in the presence of hydrogen, can be explained by Scheme 1. 1,3-Butadiene inserted via 1,2-addition does not inhibit the insertion of the next monomer and forms 1,2-BD. On the other hand, the 1,4-inserted butadiene forms π -allyl Zr species and retards the insertion of the next monomer. Hydrogen reacts with the π -allyl species to give Zr-H species and a vinyl-terminated PP (B). The vinyl-terminated PP reinserts into the Zr-H bond to form the Zr-alkyl species (C), which accepts the successive propylene insertion very smoothly and results in the formation of H-1,4-BD (D).

Deuterium was used instead of hydrogen in the propylene-1,3-butadiene copolymerization in order to confirm the reaction scheme. Deuteriums were selectively introduced at 2- and 3-positions of 1,4-BD, which also supports the mechanism shown in Scheme 1.

Poly(propylene-*ran*-1,3-butadiene) that contained pendant vinyl units was successfully synthesized by the isospecific zirconocene complex (1) activated with MMAO in the presence of hydrogen. Hydrogen selectively transformed the π -allyl zirconocene species formed by the 1,4-inserted butadiene to the Zr-alkyl species, which resulted in the high activity of the copolymerization and the selective introduction of pendant vinyl groups.

Acknowledgment. This work was supported by the New Energy and Development Organization (NEDO) through a grant for "Project on Nanostructured Polymeric Materials" under the Nanotechnology Program. We also thank Dr. Hoang The Ban and Ms. Hiroko Kobashi for the characterization of copolymers.

Supporting Information Available: Experimental conditions, chemical shifts of plausible copolymer structures, and ^{13}C NMR spectra of a copolymer synthesized with deuterium. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Doi, Y.; Watanabe, S.; Ueki, S.; Soga, K. *Makromol. Chem. Rapid Commun.* **1983**, *4*, 533–537. (b) Doi, Y.; Murata, M.; Soga, K. *Makromol. Chem. Rapid Commun.* **1984**, *5*, 811–814. (c) Doi, Y.; Koyama, T.; Soga, K. *Makromol. Chem. Phys.* **1985**, *186*, 11–15. (d) Doi, Y.; Hizal, G.; Soga, K. *Makromol. Chem. Phys.* **1987**, *188*, 1273–1279. (e) Doi, Y.; Nunomura, M.; Ohgizawa, N.; Soga, K. *Makromol. Chem. Rapid Commun.* **1991**, *12*, 245–249. (f) Ueki, S.; Furuhashi, H.; Murakami, N.; Murata, M.; Doi, Y. *Stud. Surf. Sci. Catal.* **1995**, *92*, 359–362.
- (2) Yasuda, H.; Yamamoto, H.; Yokota, K.; Miyake, S.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 4908–4910.
- (3) (a) Shiono, T.; Yoshida, K.; Soga, K. *Makromol. Chem. Rapid Commun.* **1990**, *11*, 169–175. (b) Shiono, T.; Kurosawa, H.; Yoshida, K.; Soga, K. *Makromol. Chem. Phys.* **1992**, *193*, 2751–2761. (c) Kurosawa, H.; Shiono, T.; Soga, K. *Makromol. Chem. Phys.* **1994**, *195*, 1381–1388. (d) Shiono, T.; Kurosawa, H.; Soga, K. *Makromol. Chem. Phys.* **1994**, *195*, 3303–3309. (e) Shiono, T.; Kurosawa, H.; Soga, K. *Macromolecules* **1995**, *28*, 437–443.
- (4) (a) Fu, P. F.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 10747–10748. (b) Koo, K.; Marks, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 8791–8802. (c) Makio, H.; Koo, K.; Marks, T. J. *Macromolecules* **2001**, *34*, 4676–4679.
- (5) Xu, G.; Chung, T. C. *J. Am. Chem. Soc.* **1999**, *121*, 6763–6764.
- (6) Ringelberg, S. N.; Meetsma, A.; Hessen, B.; Teuben, J. H. *J. Am. Chem. Soc.* **1999**, *121*, 6082–6083.
- (7) (a) Lu, H. L.; Chung, T. C. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2795–2802. (b) Chung, T. C.; Dong, J. Y. *J. Am. Chem. Soc.* **2001**, *123*, 4871–4876. (c) Dong, J. Y.; Chung, T. C. *Macromolecules* **2002**, *35*, 1622–1631. (d) Dong, J. Y.; Wang, Z. M.; Hong, H.; Chung, T. C. *Macromolecules* **2002**, *35*, 9352–9359.
- (8) Nam, Y.-G.; Shiono, T.; Ikeda, T. *Macromolecules* **2002**, *35*, 6760–6762.
- (9) (a) Chung, T. C.; Janvikul, W. *J. Organomet. Chem.* **1999**, *581*, 176–187. (b) Chung, T. C.; Rhubright, D. *Macromolecules* **1993**, *26*, 3019–3025. (c) Chung, T. C.; Rhubright, D. *Macromolecules* **1991**, *24*, 970–972.
- (10) (a) Chung, T. C.; Lu, H. L. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 575–579. (b) Lu, H. L.; Hong, S.; Chung, T. C. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2795–2802.
- (11) Chung, T. C.; Dong, J. Y. U.S. Patent 6,096,849, 2000.
- (12) Hagihara, H.; Murata, M.; Uozumi, T. *Macromol. Rapid Commun.* **2001**, *22*, 353–357.
- (13) Dong, J. Y.; Hong, H.; Chung, T. C.; Wang, H. C.; Datta, S. *Macromolecules* **2003**, *36*, 6000–6009.
- (14) Uozumi, T.; Tian, G.; AHN, C.; Jin, J.; Tsubaki, S.; Sano, T.; Soga, K. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1844–1847.
- (15) (a) Ye, Z.; AlObaidi, F.; Zhu, S. *Ind. Eng. Chem. Res.* **2004**, *43*, 2860–2870. (b) Paavola, S.; Saarinen, T.; Löfgren, B.; Pitkänen, P. *Polymer* **2004**, *45*, 2099–2110. (c) Dolatkhan, M.; Cramail, H.; Deffieux, A.; Santos, J. M.; Ribeiro, M. R.; Bordado, J. M. *Macromol. Chem. Phys.* **2003**, *204*, 1889–1897. (d) Hustad, P. D.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 11578–11579.
- (16) (a) Monteil, V.; Spitz, R.; Barbotin, F.; Boisson, C. *Macromol. Chem. Phys.* **2004**, *205*, 737–742. (b) Galimberti, M.; Albizzati, E.; Abis, L.; Bacchilega, G. *Makromol. Chem.* **1991**, *192*, 2591–2601. (c) Kaminsky, W.; Schlobohm, M. *Makromol. Chem. Macromol. Symp.* **1986**, *4*, 103–118.
- (17) Pragliola, S.; Forlenza, E.; Longo, P. *Macromol. Rapid Commun.* **2001**, *22*, 783–786.
- (18) Pragliola, S.; Costabile, C.; Bartolomeo, F. D.; Longo, P. *Macromol. Rapid Commun.* **2004**, *25*, 995–999.
- (19) Ishihara, T.; Shiono, T. *Macromolecules* **2003**, *36*, 9675–9677.

JA050987A