Selected Paper

Direct Incorporation of Hydroxy Groups into Isotactic Polypropylene via Metallocene-Catalyzed Copolymerization of Ester Group Containing Vinyl Monomer Treated with Dialkylaluminum Hydride and Propylene

Ryuichi Sugimoto*[1] **and Tomoaki Matsugi**[2]

[1]School of Environmental Science and Engineering,
Kochi University of Technology, Miyanokuchi,
Tosayamada, Kami, Kochi 782-8502

[2]Research Center, Mitsui Chemicals, Inc.,
580-32 Nagaura, Sodegaura, Chiba 299-0265

E-mail: sugimoto.ryuichi@kochi-tech.ac.jp

Received: May 12, 2015; Accepted: June 5, 2015;
Web Released: June 12, 2015

Methyl 10-undecenoate treated with 2 equivalents of diisobutylaluminum hydride was quantitatively converted into a 10-undecenoxy aluminum compound, which was successfully utilized for metallocene-catalyzed copolymerization with propylene to produce functional polypropylene with hydroxy groups in its side chains.

Incorporation of polar functional groups (e.g., hydroxy, carboxy, or amino groups) into polyolefin chains has been a great issue to broaden applications of polyolefin. Many attempts focusing on copolymerization of polar vinyl monomer and olefin, using both early and late transition metal catalyst have been done.[1] Especially, by the development of the group 4 metallocene and non-metallocene single-site catalysts, whose catalytic performance is excellent, new polyolefin has been created (e.g., high activity, single-site active site, and good polymerization ability for higher α-olefins, cyclic olefins and diene compounds, etc.). However, direct copolymerization of olefin and polar vinyl monomer has not been achieved because of polar groups interfering with the catalyst. To avoid attacks by the heteroatom in polar monomers on the positively charged active center of catalyst, protected polar monomers have been used for copolymerization. In the case of vinyl monomers containing hydroxy groups, as protection methods to obtain hydroxy functionalized polyolefin, use of alkyl aluminums[2] and excess methylalumoxane (MAO)[3–5] has been reported. Polyolefin functionalized by hydroxy groups is expected to improve physical properties such as wetness, adhesion and paintability. In addition, with its high reactivity, it can also be used as synthetic tools for novel block and graft copolymers.[6–9]

Table 1. The reaction of UnCOOMe with alkyl aluminums and MAO (50 °C, 1 h)

Entry	Aluminum	[Al]/[UnCOOMe] m.r.	Conversion /%[a)]	Yield /%[b)]
1	DIBAL-H	1.0	53	53
2	DIBAL-H	2.0	100	100
3	TEAL	2.0	51	4.0
4	TIBAL	2.0	14	12
5	MAO	2.0	4.3	0

a) UnCOOMe conversion: determined by GC (retention time: 8.83 min). b) The yield of UnOH: determined by GC (retention time: 8.61 min).

However, in general, hydroxy functional monomers such as 10-undecen-1-ol (UnOH) are so expensive that it is difficult to use them for copolymerization industrially. Therefore, we chose to use inexpensive vinyl monomer containing ester groups, which can be converted into alcohols by several reduction reagents.[10]

In this paper, we herein discuss an innovative procedure for incorporation of hydroxy groups into polyolefin via metallocene-catalyzed copolymerization of propylene and vinyl monomers containing ester groups.

To evaluate reactivity and the products of the above-mentioned reductive reaction of ester group in detail, reaction of methyl 10-undecenoate (UnCOOMe), a relatively inexpensive vinyl monomer, with diisobutylaluminumhydride (DIBAL-H) was examined in toluene solution at 50 °C.[11] For comparison, reaction of two kinds of trialkyl aluminum (triethylaluminum: TEAL and triisobutylaluminum: TIBAL) and methyl 10-undecenoate (UnCOOMe) was also examined. Conversion of UnCOOMe and yield of reaction products were determined by gas chromatography (GC) of organic layers after treating reaction mixture with 1 M HCl aq. to remove alkyl aluminum residue. The results of the reaction for 1 h are summarized in Table 1.

All of the UnCOOMe was converted into UnOH by treatment with 2 equivalents of diisobutylaluminum hydride DIBAL-H (Entry 2 in Table 1). No by-product was detected by GC, suggesting all the ester groups were effectively converted into alcohol. The time profile of yield of UnOH shows that reaction was rapidly completed within 3 min (Figure 1).

Structures of the resulting mixture were confirmed by ^{1}H NMR measurement. (Figure 2A) shows the ^{1}H NMR spectrum of UnCOOMe. The peaks arising from an ester group ($–CH_2COOCH_3$, $\delta = 2.27–2.33$ and 3.66 ppm) of UnCOOMe disappeared after treatment of UnCOOMe with DIBAL-H (Figure 2B). Meanwhile the peaks attributed to aluminum oxymethylene ($–AlOCH_2–$) and aluminum oxymethyl ($–AlOCH_3$) appeared in regions 3.65–3.73 and 3.46–3.53 ppm, respectively, whose peak intensity ratio was 3:2. And the peaks corresponded with isobutylaluminum groups ($–AlCH_2CH(CH_3)_2$, $\delta = -0.04–-0.01$, 1.76–1.89, and 0.86–0.95 ppm) observed. After hydrolysis reaction and treating them with acidic H_2O, only UnOH was produced (Figure 2C). The vinyl proton peaks ($CH_2=CH–$, $\delta = 4.91–5.02$ ppm, $\delta = 5.76–5.82$ ppm) in Figure 2C retained reasonable peak areas assigned as UnOH, which showed the vinyl group was not affected by the reduction and hydrolysis reactions. These results reveal that one mole of diisobutylalu-

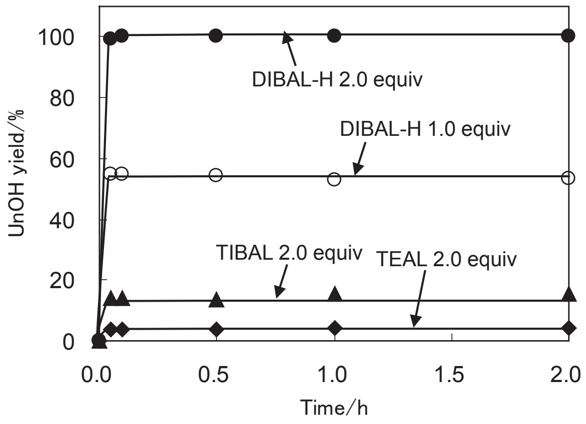


Figure 1. Time profile of the yield of UnOH generated by the reaction of UnCOOMe with alkyl aluminums.

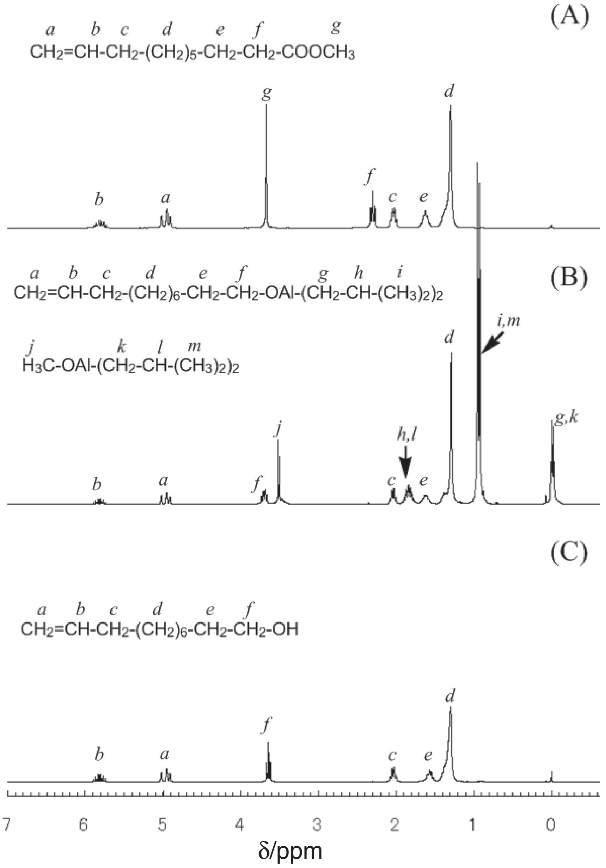


Figure 2. ^{1}H NMR spectra of (a) UnCOOMe, (b) the products after the reaction of a UnCOOMe with 2.0 equiv of TIBAL-H and (c) the hydrolyzed products (250 MHz, $CDCl_3$, 25 °C).

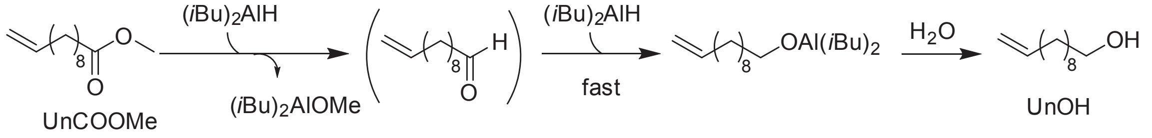
minum-protected UnOH (or a multi-complex based on them[12]) and equimolar diisobutyl aluminum methoxide was stoichiometrically produced by the reaction of UnCOOMe with 2 equivalents of DIBAL-H as described in Scheme 1.

The treatment of UnCOOMe with 1 equivalent of DIBAL-H also rapidly produced UnOH and the reaction yield was around 53% (Entry 1 in Table 1). The aldehyde species, a plausible reaction intermediate, was not detected after the reaction, showing that the rate of the 2nd reduction from aldehyde to alcohol was so fast compared to that of the 1st reduction that the resulting product was dominated by the alcohol compound. On the other hand, the treatment of UnCOOMe with 2 equivalents of TEAL and TIBAL were also converted to UnOH, although the yields of UnOH were relatively low (TEAL; 3%, TIBAL; 13%) with the generation of a by-product (two GC peak at 10.1 and 12.3 min in the case of TEAL and a GC peak at 12.4 min in case of TIBAL).

From the reaction time profile (Figure 1), the yield of UnOH was almost saturated within 3 min in both cases. It is reasonable to explain that the aluminum hydride species[13] (dialkyl aluminum hydride as the main one), which are known to be generated from trialkyl aluminum as an equilibrium reaction,[14] promoted the reduction to yield UnOH. From GC-MS measurements, the above-mentioned by-products are thought to be 1-alkylated 10-undecenol species[15] via a Grignard-type addition reaction mechanism as referred to in previously reported literature.[16] In addition, no UnOH was produced by the reaction of UnCOOMe with methylalumoxane (MAO).

The quantitative production of the 10-undecenoxy aluminum compound prepared from the reduction of UnCOOMe was expected to be applicable for inexpensive copolymerization in order to produce hydroxy-functionalized polyolefin. Therefore, copolymerization of in-situ prepared and protected UnOH with propylene was carried out using an ethylenebis(indenyl)zirconium chloride ($Et(Ind)_2ZrCl$)/MAO catalyst system under propylene atmospheric pressure at 50 °C in toluene.[17] UnCOOMe was treated with DIBAL-H, TEAL, and TIBAL for 5 min, and then an activated catalyst solution was added to start polymerization. After polymerization, the resulting solution was poured into acidic methanol to remove catalyst residue and hydrolyze alkyl aluminum species used for protection.

The polymerization results are summarized in Table 2. No polymer was obtained when 5.0 mmol of UnCOOMe was added without alkyl aluminum (Entry 2 in Table 2), suggesting that the ester group of UnCOOMe coordinated to the catalytic active center and prevented monomer insertion. When UnCOOMe was treated with 2.1 equivalents of DIBAL-H versus UnCOOMe, a white solid polymer was obtained with high yield (Entry 4 in Table 2). In contrast, no polymer was obtained when 1.0 equivalent of DIBAL-H, 2.1 equivalents of TEAL and TIBAL were added. We believe that the presence of unreacted UnCOOMe led to the catalytic deactivation.



Scheme 1. Reduction scheme of UnCOOMe by DIBALH.

Table 2. Copolymerization results of propylene with UnCOOMe using $Et(Ind)_2ZrCl_2$/MAO catalyst system[a)]

Entry	Functional monomer	Alkyl aluminum	Yield /g	Activity[b)]	C.C.[c)] /mol %	T_m /°C	M_n[d)] /g mol^{-1}	M_w/M_n[d)]
1	none	none	37.0	7.4	0	122.7	9600	1.91
2	UnCOOMe	none	0	0	—		—	—
3	UnCOOMe	DIBAL-H (1.2 equiv)	0	0	—		—	—
4	UnCOOMe	DIBAL-H (2.2 equiv)	29.6	5.9	0.46	121.5	12300	1.86
5	UnCOOMe	TEAL (2.2 equiv)	0	0	—		—	—
6	UnCOOMe	TIBAL (2.2 equiv)	0	0	—		—	—
7	UnOH	TIBAL (1.2 equiv)	35.0	7.2	0.40	117.7	12400	1.84

a) Conditions: 50 °C, 0.1 MPa pressure, toluene; 400 mL, propylene; 100 L h^{-1}, UnCOOMe or UnCOH: 5.0 mmol, $Et(Ind)_2ZrCl$ = 0.005 mmol, MAO; [Al] = 3.25 mmol. b) kg/mmol-cat./h. c) Comonomer content was determined by ^1H NMR measurement. d) M_w, M_n values; GPC analysis.

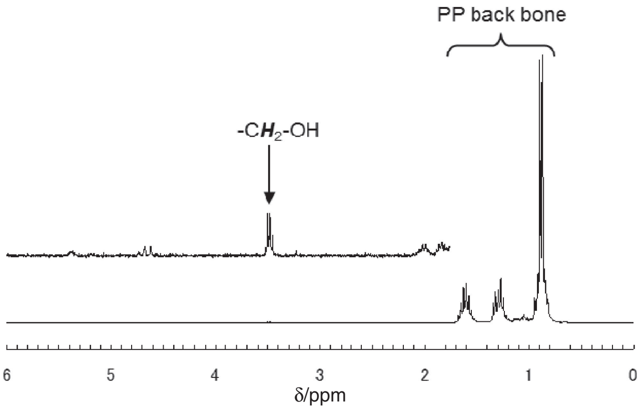


Figure 3. ^1H NMR spectra of hydroxylated polypropylene obtained by in-situ copolymerization of propylene with UnCOOMe treated with 2 equiv of DIBAL-H (Entry 4 in Table 2) (250 MHz, *o*-dichlorobenzen-d_4, 120 °C).

The molecular weight of the copolymer seemed to increase by the mutual interaction of polar groups of the spacer side chain (Entry 1, 4, and 7 in Table 2).

The structure of the obtained polymer (Entry 4 in Table 2) was analyzed by ^1H NMR measurement. No peaks corresponding to the ester group were observed, and the peak assigned to a methylene proton ($–CH_2–OH$) was observed at 3.49 ppm (Figure 3).

The catalytic activity (5.9 kg/mmol-Ti/h) and the content of hydroxy groups (0.46 mol %) were comparable to the case of 10-undecen-1-ol protected with TIBAL as shown in Entry 7 (Table 2). These results indicate that the 10-undecenoxy aluminum compound prepared by the treatment of UnCOOMe with 2 equivalents of DIBAL-H was highly effective and acts as comonomer for metallocene-catalyzed copolymerization.

In conclusion, we have demonstrated one-pot synthesis of hydroxy-functionalized polypropylene using vinyl monomer containing an ester group. Rapid 2-step reduction of the ester group by DIBAL-H led to the quantitative production of a 10-undecenoxy aluminum compound that successfully promoted metallocene-catalyzed copolymerization with propylene. Thus, a hydroxy-functionalized copolymer was produced with a relatively inexpensive monomer, giving rise to new polyolefin applications.

Supporting Information

Detailed reaction procedure of UnCOOMe with alkylaluminum and general polymerization procedure. This material is available electronically on J-STAGE.

References

1 a) L. S. Boffa, B. M. Novak, *Chem. Rev.* **2000**, *100*, 1479. b) T. C. Chung, *Prog. Polym. Sci.* **2002**, *27*, 39.

2 a) J. Imuta, Y. Toda, N. Kashiwa, *Chem. Lett.* **2001**, 710. b) J. Imuta, N. Kashiwa, Y. Toda, *J. Am. Chem. Soc.* **2002**, *124*, 1176. c) Y. Iizuka, J. Sugiyama, H. Hagihara, *Macromolecules* **2009**, *42*, 2321. d) S. Paavola, B. Löfgren, J. V. Seppälä, *Eur. Polym. J.* **2005**, *41*, 2861.

3 a) P. Aaltonen, B. Löfgren, *Eur. Polym. J.* **1997**, *33*, 1187. b) K. Hakala, B. Löfgren, T. Helaja, *Eur. Polym. J.* **1998**, *34*, 1093. c) P. Aaltonen, B. Löfgren, *Macromolecules* **1995**, *28*, 5353. d) P. Aaltonen, G. Fink, B. Löfgren, J. V. Seppälä, *Macromolecules* **1996**, *29*, 5255.

4 C.-E. Wilen, J. H. Nasman, *Macromolecules* **1994**, *27*, 4051.

5 M. M. Marques, S. G. Correia, J. R. Ascenso, A. F. G. Ribeiro, P. T. Gomes, A. R. Dias, P. Foster, M. D. Rausch, J. C. W. Chien, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2457.

6 T. Matsugi, S. Kojoh, N. Kawahara, S. Matsuo, H. Kaneko, N. Kashiwa, *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3965.

7 N. Kawahara, J. Saito, S. Matsuo, H. Kaneko, T. Matsugi, N. Kashiwa, *Adv. Polym. Sci.* **2008**, *217*, 79.

8 Y. Inoue, T. Matsugi, N. Kashiwa, K. Matyjaszewski, *Macromolecules* **2004**, *37*, 3651.

9 H. Kaneko, S. Matsuo, N. Kawahara, J. Saito, T. Matsugi, N. Kashiwa, *Macromol. Symp.* **2008**, *260*, 9.

10 H. Reinheckel, *Oleagineux* **1965**, *20*, 31.

11 The reaction procedure; see Supporting Information.

12 J. Turunen, T. T. Pakkanen, B. Löfgren, *J. Mol. Catal. A: Chem.* **1997**, *123*, 35.

13 0.6% in TEAL and 0.6% in TIBAL of aluminum hydride species (as AlH_3) were included in purchased TEAL and TIBAL.

14 K. Ziegler, W.-R. Kroll, W. Larbig, O.-W. Steudel, *Justus Liebigs Ann. Chem.* **1960**, *629*, 53.

15 As estimated by-products by GC-MS, TEAL treatment: 1-ethyl-10-undecenol and 1,1-diethyl-10-undecenol (GC peak area ratio of 12:88), TIBAL treatment: 1-isobutyl-10-undecenol.

16 K.-H. Shen, C.-W. Kuo, C.-F. Yao, *Tetrahedron Lett.* **2007**, *48*, 6348.

17 General polymerization procedure; see Supporting Information.