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The detailed analysis of the vinylidene structure of metallocene-catalyzed polypropylene

Nobuo Kawahara[a,*], Shin-ichi Kojoh[a], Yoshihisa Toda[b], Akira Mizuno[b], Norio Kashiwa[a]

[a]R and D Center, Mitsui Chemicals, Inc., 580-32 Nagaura, Sodegaura-shi, Chiba-ken 299-0265, Japan
[b]Analysis Research Laboratory, Mitsui Chemical Analysis and Consulting Service, Inc., 6-1-2 Waki, Waki-cho, Kuga-gun, Yamaguchi-ken 740-0061, Japan

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Abstract

The vinylidene structures in polypropylenes produced by ethylenebis(indenyl)zirconiumdichloride (En(Ind)$_2$ZrCl$_2$), **1**, and isopropyl(cyclopentadienyl)(fluorenyl)zirconiumdichloride (iPr(Cp)(Flu)ZrCl$_2$), **2**, were analyzed by ^{1}H NMR. The vinylidene group adjacent to the chain end was clearly distinguished from other internal vinylidene structures for the first time using 1,2-dichlorobenzene as solvent. The polypropylene produced by **2** had much internal vinylidene groups compared with one by **1**.

Keywords: Metallocene catalyst; Polypropylene; Analytical characterization

1. Introduction

The study on the chain end structure of polyolefins is one of the most interesting subjects for many scientists and engineers because it provides important key information on the elucidation of propagation and termination mechanisms in olefin polymerization. And also, the end structure often acts as a useful functional group in order to create new functional polyolefins. Furthermore, unsaturated chain end groups can be utilized for addition of a polar or other functional groups [1–6].

Since the discovery of metallocene catalyst system, the field of olefin polymerization has been extended from technology to science due to a homogeneous active site of the catalyst. And, it is well known that the metallocene-catalyzed polypropylene has vinylidene end group produced by β-hydride elimination [7,8]. Recently, the terminal chain end structures such as vinyl, butenyl and isobutenyl structures have been reported on polypropylene prepared by metallocenes that had different ligand structures [9,10]. However, the assignment of ^{1}H NMR peaks of those unsaturated structures, especially internal vinylidene structure, is actually difficult and complicated due to the peak overlapping with terminal vinylidene structure in polypropylene [11,12]. This paper briefly reports the separation of internal and terminal vinylidene peaks of polypropylene in ^{1}H NMR measurement by making use of the solvent effect, and the comparison of the amounts of those vinylidene structures between En(Ind)$_2$ZrCl$_2$, which is C_2 symmetrical, and iPr(Cp)(Flu)ZrCl$_2$, which is C_s symmetrical, too.

2. Experimental section

2.1. Materials

iPr(Cp)(Flu)ZrCl$_2$ was prepared according to the literature [13]. En(Ind)$_2$ZrCl$_2$ was purchased from Sigma-Aldrich Co. Methylalminoxane (MAO) was purchased as toluene solution (10 wt%) from Albemarle Co. and used without purification. Toluene purchased from Wako Pure Chemical Industries, Ltd. was dried over sodium metal and distilled. Propylene monomer (Mitsui Chemicals) was used without any further purification. Organometallic compounds were treated under the nitrogen atmosphere.

2.2. Polymerization

All polymerization experiments were carried out in 500 ml of glass flasks equipped with mechanical stirrer,

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[*] Corresponding author. Tel.: +81-438-64-2319; fax: +81-438-64-2377.
E-mail address: nobuo.kawahara@mitsui-chem.co.jp (N. Kawahara).

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thermocouples and monomer inlet tube. Into the reactor, 250 ml of dry toluene was introduced and saturated with propylene monomer gas. After heating the solvent to, 70 °C, MAO in toluene (5 mmol as Al atom) was added in the reactor, and then, the polymerization was started by addition of metallocene (0.005 mmol) in the reactor. That temperature was kept for 30 min under the constant feed, 100 NL/h, of monomer gas. After that, 5 ml of isobutanol was added to the reactor in order to terminate the polymerization. The reaction mixture was poured in 1 l of methanol. Resulting polymers were obtained by filtration and washed with methanol, then dried under the reduced pressure at 80 °C for 10 h. 12.86 g of polypropylene (PP-1) was produced by using En(Ind)$_2$ZrCl$_2$, and 2.33 g of polypropylene (PP-2) was produced by using iPr(Cp)(Flu)ZrCl$_2$.

2.3. Analysis of polymer

^{13}C NMR spectra were recorded on a JEOL GSX-400 spectrometer operating at 100 MHz under decoupling in Fourier transform mode. Instrument conditions were as follows: pulse angle, 45°; pulse repetition, 5.0 s; spectral width, 18,050 Hz; temperature, 118 °C; data points, 32k. NMR spectra were determined in ODCB.

^{1}H NMR spectra were recorded on a JEOL GSX-400 spectrometer operating at 400 MHz in Fourier transform mode. Instrument conditions were as follows: pulse angle, 45°; pulse repetition, 5.0 s; spectral width, 8000 Hz; temperature, 118 °C; data points, 32k. The NMR samples were prepared by dissolving 50 mg of polymer in 0.5 ml of decahydronaphthalene-d$_{18}$ (Decalin) or 1,2-dichlorobenzene-d$_4$ (ODCB) as solvent.

3. Results and discussion

Two metallocenes, En(Ind)$_2$ZrCl$_2$, **1**, and iPr(Cp)(Flu)ZrCl$_2$, **2**, were chosen in this study as typical C_2 and C_s symmetrical ones. Those metallocenes could produce isotactic polypropylene and syndiotactic polypropylene, respectively. Vinylidene structures of PP-1 obtained by **1** and PP-2 by **2** were investigated by ^{1}H NMR. In previous paper [14], it was mentioned that the terminal vinylidene structure changed to isobutenyl structure in case of using 1,1,2,2-tetrachloroethane-d$_2$ (TCE) as a solvent. Therefore, at first, decalin was used for the NMR measurement as a solvent. The NMR spectra of the vinylidene protons (4.50–4.80 ppm) were shown in Fig. 1. The peaks were assigned as follows [9–12]. The terminal vinylidene protons were observed at 4.62 and 4.69 ppm, respectively, because these two protons were in the different chemical environment. On the other hand, the internal vinylidene protons resonated at the same position of around 4.70 ppm. It was remarkable in PP-2 that the peak was more intense than the higher field one because of overlapping

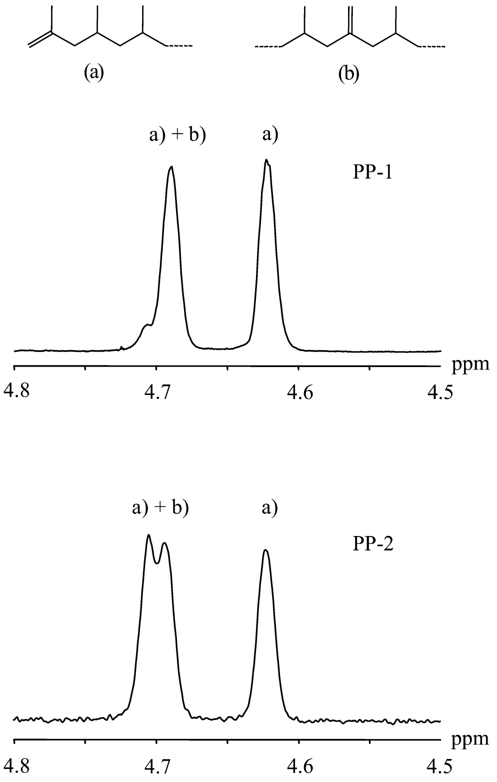

Fig. 1. Expanded ^{1}H NMR spectra between 4.5 and 4.8 ppm of PP-1 and PP-2 in decalin.

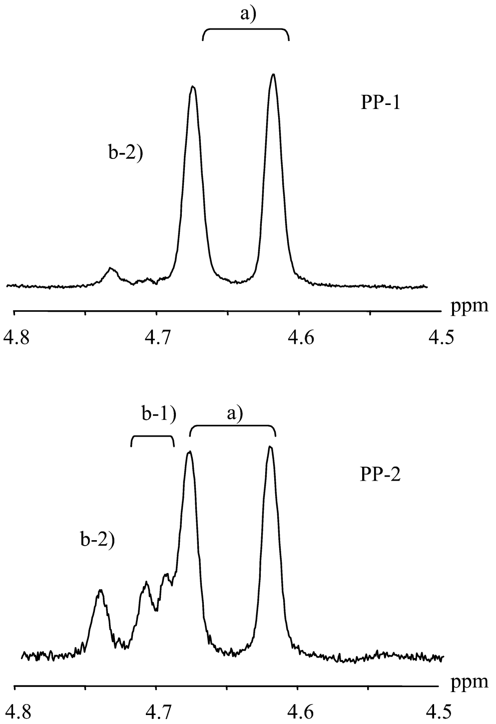

Fig. 2. Expanded ^{1}H NMR spectra between 4.5 and 4.8 ppm of PP-1 and PP-2 in *o*-dichlorobenzene.

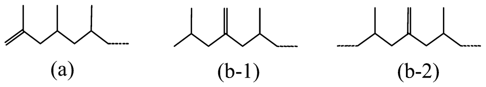

Fig. 3. Structures of vinylidene groups.

with the lower field peak of the terminal vinylidene protons like as same as using TCE.

Since that made the analysis complicated, we tried to make the peak separation, making use of the solvent effect induced by an aromatic compound. The ^{1}H NMR spectra of PP-1 and PP-2 observed in ODCB solution were presented in Fig. 2. It was noticeable that new peaks were observed in the range of 4.68–4.74 ppm in PP-2. We assigned the peaks at 4.69 and 4.71 ppm to the vinylidene protons adjacent to the chain end, where two vinylidene protons were in the slightly different chemical environment, and the lowest peak (4.74 ppm) to other internal vinylidene protons, respectively. The terminal vinylidene peaks at 4.61 and 4.67 ppm had the equal intensity, because internal vinylidene peaks were removed from the overlapping ones of vinylidene. Internal vinylidene might be produced via an allyl complex that was proposed by Schaverien [9].

The three types of vinylidene structures, which were confirmed by this study, were shown in Fig. 3. From the spectra in Fig. 2, three vinylidene structures, that is, Vd(a), Vd(b-1) and Vd(b-2), existed with the ratio of 92:3:5 in PP-1 and 60:31:9 in PP-2, indicating that the internal vinylidene structure was formed with the higher frequency with **2** than with **1**.

4. Conclusion

The vinylidene structures in metallocene-catalyzed polypropylenes were analyzed by ^{1}H NMR. The internal and terminal vinylidene structures were clearly distinguished using ODCB as solvent due to the effect of the ring current, and the vinylidene structure next to the chain end could be assigned for the first time as different peaks from the other vinylidene structures. iPr(Cp)(Flu)$ZrCl_2$ tended to produce internal vinylidene structures compared with En$(Ind)_2ZrCl_2$.

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