Polymerization of propene with catalyst systems composed of Al_2O_3 or $MgCl_2$-supported zirconocene and $Al(CH_3)_3$

Manabu Kaminaka* and Kazuo Soga†
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 227, Japan

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Six kinds of heterogeneous catalysts were prepared by supporting iPr(Flu)(Cp)$ZrCl_2$ (**1**) and Cp_2ZrCl_2 (**2**) on Al_2O_3, $MgCl_2$ and SiO_2, and propene polymerization was conducted with these supported catalysts using a common alkylaluminium, $Al(CH_3)_3$, as cocatalyst. The **1**/Al_2O_3 and **1**/$MgCl_2$ catalysts gave highly syndiotactic polypropylene whereas the **2**/Al_2O_3 and **2**/$MgCl_2$ catalysts gave atactic polypropylene in fairly good yields. In contrast, the SiO_2-supported catalysts were found to be inactive for propene polymerization.

(Keywords: supported catalysts; propene polymerization; Kaminsky–Sinn catalyst; zirconium compound; syndiotactic polypropylene; atactic polypropylene)

Introduction

Since the discovery of the 'Kaminsky–Sinn catalyst'[1–3], much effort has been paid to develop new types of catalysts without using methylaluminoxane (MAO) both for practical purposes and in order to understand the reaction mechanism.

Jordan *et al.* found that some dicyclopentadienyl zirconium alkyl complexes effectively catalyse ethylene polymerization in the absence of any cocatalyst[4].

Ewen *et al.* reported that cationic zirconium complexes such as $Et[IndH_4]_2ZrMe^+$, $iPr(Flu)(Cp)ZrMe^+$ (where $IndH_4$ = 4,5,6,7-tetrahydro-1-indenyl, Flu = fluorenyl and Cp = cyclopentadienyl), etc. show very high activities for propene polymerization without using MAO[5].

Zambelli *et al.* also found that some of the 4B group metallocene complexes are active for propene polymerization when a mixture of $Al(CH_3)_3$ and $AlF(CH_3)_2$ is used as cocatalyst[6].

We have recently reported that the heterogeneous catalyst system composed of Al_2O_3- and $MgCl_2$-supported $Et[IndH_4]_2ZrCl_2$ and $Al(CH_3)_3$ or $Al(C_2H_5)_3$ catalyses propene polymerization to give highly isotactic polypropylene in a fairly good yield[7].

More recently, we have found that both syndiotactic and atactic polypropylenes can be produced with similar catalyst systems by changing the auxiliary ligand of the zirconium compound to iPr(Flu)(Cp)$ZrCl_2$ and Cp_2ZrCl_2, respectively.

This communication reports preliminary results on the polymerization.

Experimental

Materials. Toluene and propene were commercially obtained from Takatiho Chemical Co. Ltd and were purified according to usual procedures[8]. Both SiO_2 (Fuji-Devison Chemical Ltd, no. 952) and γ-Al_2O_3 (Nishio Co. Ltd) were calcined at 400°C for 6 h.

Anhydrous $MgCl_2$ was provided by the Toho Titanium Co. Ltd and iPr(Flu)(Cp)$ZrCl_2$ (**1**) was prepared according to the literature[9]. Cp_2ZrCl_2 (**2**) purchased from Tokyo Kasei Co. Ltd was used without further purification. $Al(CH_3)_3$ and MAO were provided by Toso Akzo Co. Ltd and used without further purification.

Preparation of supported catalysts. Supported catalysts were prepared according to similar procedures as reported previously[7]. The contents of zirconium in the supported catalysts were measured by atomic absorption spectrophotometry (Shimadzu atomic absorption/flame spectrophotometer AA-610S). The zirconium contents were 1.2×10^{-2}, 1.0×10^{-2}, 2.8×10^{-2}, 2.7×10^{-2}, 2.3×10^{-2} and 2.9×10^{-2} mmol g^{-1} catalyst for **1**/Al_2O_3, **2**/Al_2O_3, **1**/$MgCl_2$, **2**/$MgCl_2$, **1**/SiO_2 and **2**/SiO_2 catalysts.

Polymerization and analytical procedures. Each of the supported catalysts was suspended in 15 cm^3 of toluene. To a 100 cm^3 stainless steel autoclave equipped with a magnetic stirrer were introduced the catalyst suspension, 10 cm^3 of additional toluene and a prescribed amount of $Al(CH_3)_3$ under nitrogen atmosphere. The reactor was degassed, followed by introduction of 7 l ($\sim$0.31 mol) of propene. The polymerization was carried out at 40°C and terminated by adding 500 cm^3 of acidic methanol. The precipitated polymer was adequately washed with methanol and dried *in vacuo* at 60°C for 8 h.

The molecular mass distribution of the polymer produced was measured at 145°C by g.p.c. (Waters 150C) using *o*-dichlorobenzene as solvent. The melting point (T_m) of the polymer was measured on the sample which had been previously melted and recrystallized using a Shimadzu DSC-50 calorimeter with a heating rate of 10°C min^{-1}. The ^{13}C n.m.r. spectrum was recorded at

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* On leave from Tokuyama Soda Co. Ltd, 1-1, Harumi-cho, Tokuyama-city, Yamaguchi 745, Japan
† To whom correspondence should be addressed

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Table 1 Results of propene polymerization[a]

Run no.	Catalyst (mmol Zr)	Cocatalyst	Amount of co-catalyst (mmol)	Polym. time (h)	Yield (g)	T_m (°C)	Activity (kg PP/ mol Zr)	M_n ($\times 10^{-3}$)	M_w/M_n
1	iPr(Flu)(Cp)$ZrCl_2/Al_2O_3$ (8.9×10^{-3})	$Al(CH_3)_3$	1	3	0.46	–	52	–	–
2	iPr(Flu)(Cp)$ZrCl_2/Al_2O_3$	$Al(CH_3)_3$	1	5	0.86	–	97	–	–
3	iPr(Flu)(Cp)$ZrCl_2/Al_2O_3$	$Al(CH_3)_3$	1	9	1.23	–	139	–	–
4	iPr(Flu)(Cp)$ZrCl_2/Al_2O_3$	$Al(CH_3)_3$	1	18	1.49	138	167	4.6	2.0
5	iPr(Flu)(Cp)$ZrCl_2/MgCl_2$ (2.1×10^{-2})	$Al(CH_3)_3$	10	3	1.06	–	51	–	–
6	iPr(Flu)(Cp)$ZrCl_2/MgCl_2$	$Al(CH_3)_3$	10	5	1.65	–	80	–	–
7	iPr(Flu)(Cp)$ZrCl_2/MgCl_2$	$Al(CH_3)_3$	10	10	2.67	–	129	–	–
8	iPr(Flu)(Cp)$ZrCl_2/MgCl_2$	$Al(CH_3)_3$	10	18	3.18	134	152	10.7	3.3
9	Cp_2ZrCl_2/Al_2O_3 (7.4×10^{-3})	$Al(CH_3)_3$	1	18	0.35	–	47	0.39[c]	–
10	$Cp_2ZrCl_2/MgCl_2$ (2.0×10^{-2})	$Al(CH_3)_3$	10	18	3.44	–	172	0.37[c]	–
11[b]	iPr(Flu)(Cp)$ZrCl_2$	MAO	13	1	3.03	123	758	39.3	1.8
12[b]	Cp_2ZrCl_2	MAO	10	1	1.32	–	132	0.33[c]	–

[a] Polymerization was conducted at 40°C in a 100 cm^3 stainless steel autoclave (see text)

[b] Polymerization was conducted in the presence of 4×10^{-3} mmol of iPr(Flu)(Cp)$_2ZrCl_2$ and 13 mmol of MAO (based on Al) or 1×10^{-2} mmol of Cp_2ZrCl_2 and 10 mmol of MAO (based on Al) in 200 cm^3 of toluene at 40°C under 10^5 Pa

[c] Estimated from the intensity ratio between the resonances of the methine carbon of polymer end groups and of the main chain

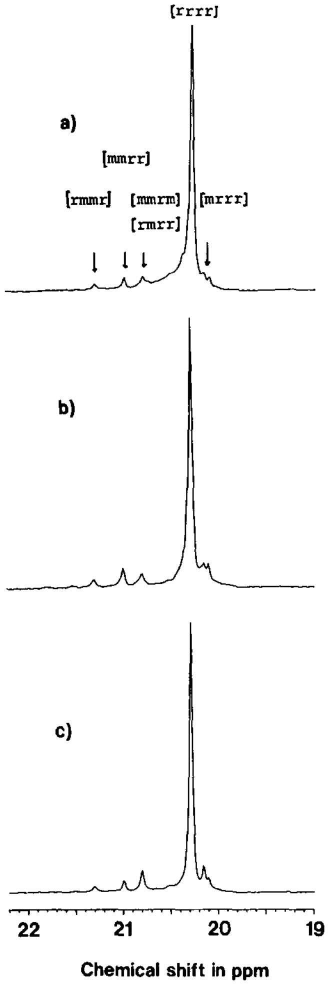

Figure 1 Expansions of the methyl region from the ^{13}C n.m.r. spectra of polypropylenes obtained with: (a) iPr(Flu)(Cp)$ZrCl_2/Al_2O_3$–$Al(CH_3)_3$ (run no. 4); (b) iPr(Flu)(Cp)$ZrCl_2/MgCl_2$–$Al(CH_3)_3$ (run no. 8); (c) iPr(Flu)(Cp)$ZrCl_2$–MAO (run no. 11)

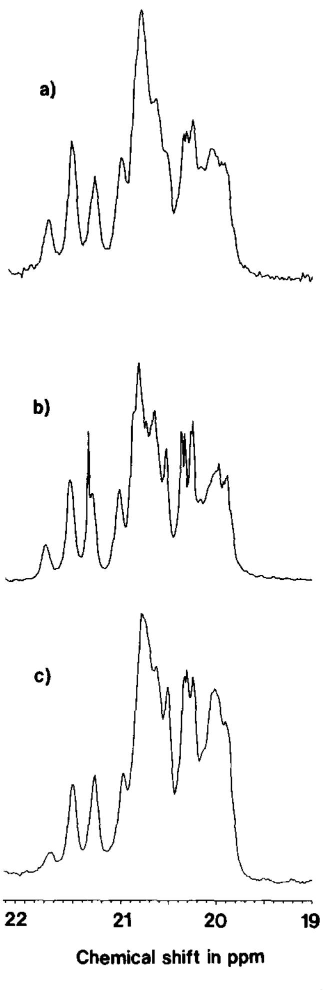

Figure 2 Expansions of the methyl region from the ^{13}C n.m.r. spectra of polypropylenes obtained with: (a) Cp_2ZrCl_2/Al_2O_3–$Al(CH_3)_3$ (run no. 9); (b) $Cp_2ZrCl_2/MgCl_2$–$Al(CH_3)_3$ (run no. 10); (c) Cp_2ZrCl_2–MAO (run no. 12)

120°C using a Jeol GX-270 n.m.r. spectrometer operating at 67.8 MHz. Polymers were dissolved in 1,2,4-trichlorobenzene/benzene-d_6 (9/1 v/v) up to 10 wt%.

Results and discussion

Polymerization of propene was conducted at 40°C with the six kinds of supported catalysts, **1**/Al_2O_3, **2**/Al_2O_3, **1**/$MgCl_2$, **2**/$MgCl_2$, **1**/SiO_2 and **2**/SiO_2, using $Al(CH_3)_3$ as cocatalyst. The homogeneous **1**–MAO and **2**–MAO catalysts were also used for reference. The results of polymerization with these catalyst systems are shown in *Table 1*. Propene polymerization took place even with the use of common alkylaluminium, instead of MAO, as cocatalyst, when Al_2O_3 or $MgCl_2$ were used as carrier. The results are in good agreement with those previously obtained for the polymerization of isotactic propene[7]. The ^{13}C n.m.r. spectra of polypropylenes produced with these catalysts are illustrated in *Figure 1*. Each spectrum displays a strong peak at 20.3 ppm attributed to the [*rrrr*] sequence[10]. The [*rrrr*] pentad fractions estimated from *Figures 1a, b* and *c* were 86, 81 and 77%, respectively. As shown in *Table 1*, the polymers produced with the **1**/Al_2O_3–$Al(CH_3)_3$ and **1**/$MgCl_2$–$Al(CH_3)_3$ catalysts showed higher T_ms compared to that produced with the homogeneous **1**–MAO catalyst system, which may reflect the difference in syndiotacticity. On the other hand, *Figure 2* shows the ^{13}C n.m.r. spectra of polymers produced with the **2**/Al_2O_3–$Al(CH_3)_3$, **2**/$MgCl_2$–$Al(CH_3)_3$ and **2**–MAO catalyst systems. These polymers gave very complicated spectra, which might be attributed to the atactic structure as well as to the end group resonances which are particularly intense due to the low molecular weight as shown in *Table 1*.

Thus, it was found that not only isotactic[7] but also syndiotactic and atactic polypropylenes can be obtained in fairly good yields by using a common alkylaluminium in place of MAO.

A further study is now being carried out with emphasis on the improvement of catalyst activity as well as on the mechanism of active sites formation. The results will be reported elsewhere.

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