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Isotactic polymerization of propylene with zirconocene catalysts in the presence of a Lewis base

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Summary

Polymerization of propylene was carried out at 0 °C in the presence of methyl methacrylate(MMA) or ethyl benzoate(EB) using rac-Et(Ind)$_2$ZrMe$_2$ or rac-Me$_2$Si(Ind)$_2$ZrMe$_2$ / Ph$_3$CB(C$_6$F$_5$)$_4$ as catalyst, which resulted in highly isotactic poly(propylene) with [mmmm] > 98 % , T_m = 160-161 °C and very few 1,3- or 2,1 regioirregular units. With the use of an achiral zirconocene Cp$_2$ZrMe$_2$, a polymer with T_m =139 °C was resulted as well. Base on these experimental fact that the zirconocene can form a C$_1$-symmetrical complex with a Lewis base.

Introduction

Recent development of metallocene catalysts shows that a C$_2$ symmetrical metallocene produces an isotactic poly(propylene)(iPP).$^{1)}$ Compared with the heterogeneous catalysts(e.g., TiCl$_3$$^{2)}$ or supported system TiCl$_4$/MgCl$_2$$^{3)}$), the homogeneous ones are usually less regio- and stereospecific,$^{1)}$ and hence produce iPP with a lower melting point. Much effort has been focussed on the design of metallocene ligands to suppress the formation of these defects.$^{4)}$ The polymerization temperature$^{5)}$ and the propylene concentration$^{6,7)}$ are known as the other factors affecting the isospecificity.

More recently, we have found that an addition of some Lewis bases, like methyl methacrylate(MMA), causes an increase of the regio- and stereospecificity of a C$_2$ symmetrical metallocene. The preliminary results are reported in this paper.

Results and Discussion

Propylene was polymerized at 0 °C in toluene with the rac-Et(Ind)$_2$ZrMe$_2$ / Ph$_3$CB(C$_6$F$_5$)$_4$ catalyst in the presence of MMA using tri(isobutyl)aluminium(TIBA) as cocatalyst. It was found that the polymer yield markedly increases when the catalyst system was contacted with propylene at -65 °C for 3 h before an addition of MMA.$^{8a)}$ The following polymerizations were therefore conducted using this method. It should be noted that the polymer yield during the prepolymerization is negligibly small.$^{8b)}$

The product(Run No.3) obtained at 0°C was fractionated with boiling THF. The soluble part was identified as isotactic PMMA$^{9)}$ by ^{1}H NMR ([mm] = 98%). The expanded ^{13}C NMR spectrum of the insoluble part is shown in Figure 1A. Although the polymer yield was quite lower as compared with that in the absence of MMA(Run No.1), the isotactic pentad [mmmm] was estimated to be as high as approximately 98.5%. Under similar conditions, rac-Me$_2$Si(Ind)$_2$ZrMe$_2$ also gave a highly isotactic PP(Run No.9). Whereas, the use of methyl

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alminoxane(MAO) in place of $Ph_3CB(C_6F_5)_4$ as cocatalyst yielded iPP with slightly lower Tm(Run No.5).

Table 1. Results of propylene polymerization in the presence of a Lewis base[a].

Run No.	Catalyst	Tp (°C)	Polymn.[b] time(h)	MMA (cm^3)	[MMA]/[Zr] ($x10^2$)	Yield[c] (g)
1	rac-$Et(Ind)_2ZrMe_2$	0	0.25	0.00	0.0	6.92
2	rac-$Et(Ind)_2ZrMe_2$	0	11	0.50	4.7	0.12
3	rac-$Et(Ind)_2ZrMe_2$	0	60	0.50	4.7	0.46
4[d]	rac-$Et(Ind)_2ZrMe_2$	0	60	0.20	1.9	0.76
5[e]	rac-$Et(Ind)_2ZrCl_2$	0	60	0.50	4.7	0.01
6	rac-$Et(Ind)_2ZrMe_2$	30	90	0.20	1.9	0.06
7	rac-$Et(Ind)_2ZrMe_2$	70	90	0.20	1.9	0.03
8	rac-$Et(Ind)_2ZrMe_2$	70	90	0.02	0.2	0.05
9	rac-$Me_2Si(Ind)_2ZrMe_2$	0	90	0.50	4.7	0.12
10[f]	rac-$Et(Ind)_2ZrMe_2$	0	60	——	——	0.04
11	Cp_2ZrMe_2	0	48	0.50	2.4	0.02

a) Polymerization conditions:[Zr] = [$Ph_3CB(C_6F_5)_4$] = 0.40 mM, [TIBA] = 40 mM, [MMA]/[$ZnEt_2$] = 4.7 in 25 cm^3 toluene. b) Polymerization time after addition of MMA. c) The amount of THF insoluble part, which is used for GPC or ^{13}C NMR measurement. d) The amount of THF soluble part (PMMA) was 0.12g (Mn = $79x10^3$, Tg = 54°C, [mmmm] = 94.3%). e) [MAO]/[$Et(Ind)_2ZrCl_2$] = 1000, for whole polymer. f) Ethyl benzoate(EB) was used in place of MMA(0.26 cm^3, [EB]/[Zr] = 190, other conditions are similar to Run No.4, without THF fractionation).

With a normal C_2 symmetrical zirconocene catalyst, the peaks assignable to the structures originated from 1,3- and 2,1-insertions are observed in the range of 30~40 ppm.[10,11,12] However, those peaks(e.g. a, b in Figure 2) are hardly observed in the spectra of the iPP produced in the presence of MMA(Figure 2A and 2B).

Further analytical results compiled in Tables 1 and 2 indicate that the iPP obtained in the presence of MMA has a high melting point. With an increase in the polymerization temperature from 0 to 70°C, the melting point of resulting polymer was decreased from 160 to154°C(Runs No.4, 7). The change of Tm along with the polymerization temperature is relatively mild as compared with normal C_2 symmetrical zirconocene catalysts.[5] Such a tendency has been recently observed with C_1 symmetrical zirconocenes.[13]

The polymerization of propylene was then carried out using an achiral catalyst, which also resulted in a polymer with a considerably highly melting point(Tm = 139°C, Run No.11).

A further study is now proceeding to make clear whether a complex[14] between the zirconocene and a Lewis base is formed in these systems, which might be the key to clarify the mechanism.

Table 2. Analytical results of poly(propylene).

Run No.	M_n a) ($\times 10^3$)	M_w/M_n a)	T_m b)	[mmmm] c) (%)
1	19.8	2.80	147.8	91.8
2	46.8	1.60	160.0	98.5
3	55.4	2.00	160.0	98.5
4	51.4	1.81	160.0	98.4
5 g)	----	----	152.2	----
6	19.6	3.10	158.5	----
7	7.8	3.28	153.5	----
8	4.2	3.31	134.8	----
9	116	2.00	161.0	98.7
10	65.5	1.96	160.7	----
11	11.8	3.90	139.3	---

a) Measured by GPC, calibrated with poly(styrene) standards. b) Melting point. c) Measured by ^{13}C NMR.

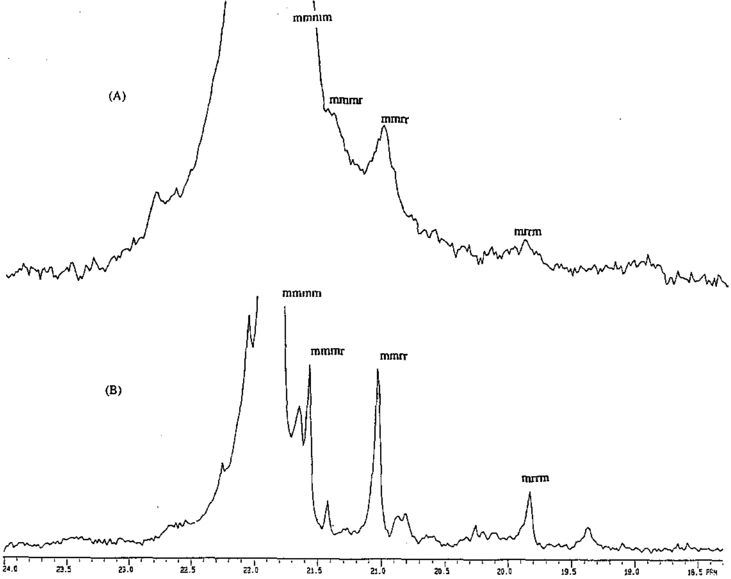

Figure 1. Expanded ^{13}C NMR spectra of iPP in the region of methyl group. A) rac-Et(Ind)$_2$ZrMe$_2$ / Ph$_3$CB(C$_6$F$_5$)$_4$ /TIBA / MMA (Run No. 3), B) rac-Et(Ind)$_2$ZrMe$_2$ / Ph$_3$CB(C$_6$F$_5$)$_4$ / TIBA (Run No. 1).

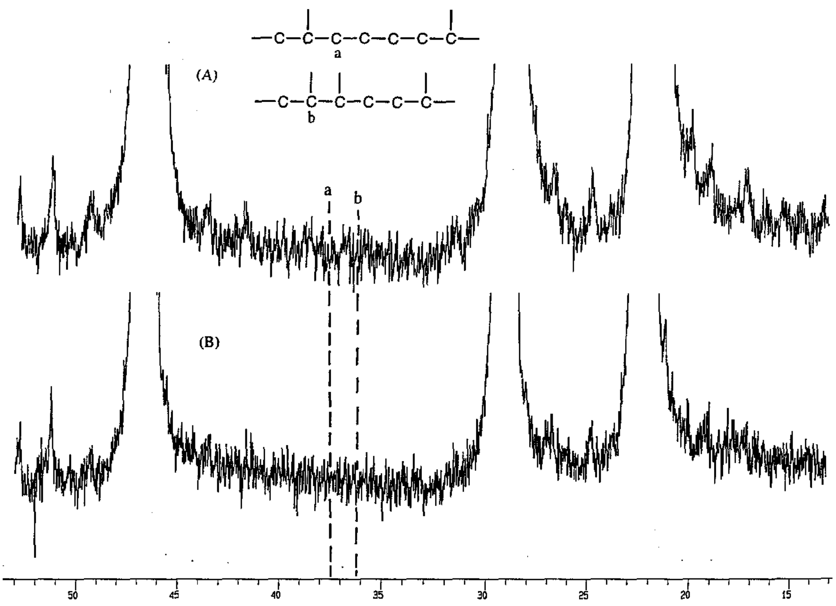

Figure 2. 75 MHz ^{13}C NMR spectra of iPP obtained with rac-Et(Ind)$_2$ZrMe$_2$ (A)(Run No.3) and rac-Me$_2$Si(Ind)$_2$ZrMe$_2$ (B) (Run No.9) in the presence of MMA. The assignments were made according to Ref.10-12.

Experimental

MMA, EB and toluene were dried over calcium hydride and distilled before use. rac-Et(Ind)$_2$ZrMe$_2$ [1a,1b] and rac-Me$_2$Si(Ind)$_2$ZrMe$_2$ [1b,1c] were synthesized according to the literature. Tri(isobutyl)aluminium (TIBA) and Ph$_3$CB(C$_6$F$_5$)$_4$ were donated from Tosoh Akzo Co. Ltd. The other chemicals (research grade) were purchased from commercial sources and used without further purification.

Polymerizations were carried out under dry nitrogen atmosphere in a 100 cm^3 autoclave equipped with a magnetic stirrer. Typical polymerization process is as follows: toluene (16.0 cm^3), 1.0 M toluene solution of TIBA (1.0 cm^3), 5.0 mM toluene solution of Ph$_3$CB(C$_6$F$_5$)$_4$ (2.0 cm^3) and 10 mM toluene solution of rac-Et(Ind)$_2$ZrMe$_2$ (1.0 cm^3) were injected into the autoclave. After the introduction of propylene (10.0 dm^3, STP), the autoclave was placed into a -65 °C bath for a 3 h prepolymerization . 5.0 cm^3 toluene solution of MMA (0.50 cm^3) and ZnEt$_2$ (2.0 M, 0.50 cm^3) were then added into the system at -78°C. The autoclave was warmed up to 0 °C for polymerization. The polymerization was quenched at 0 °C with methanol mixed with hydrochloric acid. The polymer produced was precipitated into methanol, followed by drying in vacuo at 60 °C for 8 h. The fractionations of iPP and iPMMA was carried out in boiling THF for 8 h.

The molecular weight and molecular mass distribution were measured by GPC (Senshu Scientific, SSC7100) at 145 °C using o-dichlorobenzene as a solvent and calibrated with poly(styrene) standards. The melting point (T_m) was measured with a Seiko DSC-220C calorimeter at a heating rate of 10 °C /min. The ^{13}C NMR spectra were measured in o-dichlorobenzene / benzene-d$_6$ (9/1 by vol.) at 140 °C with a Varian Gemini-300 spectrometer over 20000 transimients(Except Run No.1, recorded with 7000 transimients) using a delay time of 7.0 seconds. Broad band decoupling was used to remove the ^{13}C-^{1}H coupling. The main peak of methyl of iPP was used as the internal reference(21.78 ppm).

References

1) a) Kaminsky W, Kulper K, Brintzinger H-H, Wild F-R-W-P (1985)Angew. Chem. 97: 507. b) Chien J-C-W, Tsar W-M, M.D.Raush (1991)J. Am. Chem. Soc. 113, 8570. c) Herrmann W-A., Rohrmann J, Herdtweck E, Spaleck W, Winter A (1989)Angew.Chem.101,1536; d) Kei T, Soga K, Eds. Catalytic Olefin Polymerization Kodansha/Elsevier, 1989, Tokyo.

2) Corradini P, V.G-G Busico, Comprehensive Polymer Science; Pergamon Press: Oxford, 1988; Vol. 4, p29-50.

3) a)Barbe P-C, Noristi L, Baruzzi G (1992)Makromol. Chem. 193: 229; b) Barbe P-C, Cecchin G, Noristi L (1987)Adv. Poym. Sci. 81,1; c) Soga K, Shiono T, Prog. Polym.Sci., in press

4) Spaleck W, Kuber F, Winter A, Rohrmann J, Bachmann B, Antberg M, Dolle V, Paulus F-E (1994)Organometallics 13: 954.

5) Rieger B, Mu X, Mallin D-T, Rausch M, Chien J-C-W (1990)Macromolecules 23: 3559.

6) a) Buisco V, Cipullo R J. (1994)Am. Chem. Soc. 116: 9329. b)Resconi L, Fait A, F.Piemontesi, M.Colonnesi, H.Rychlicki, R.Zeigler (1995)Macromolecules 28: 6667.

7) Leclerc M-K, Brintzinger H-H (1995)J. Am. Chem. Soc. 117, 1651.

8) a) Without prepolymerization, iPP(T_m = 159.9 °C) was obtained in a very low yeild(0.10 g / 60 h). b) During the period of prepolymerization for 3 h at -65 °C, a trace amount of polymer was obtained, which was too small to be analyzed(ca. < 0.010 g).

9) a) Deng H, Shiono T, Soga K (1995)Macromolecules 28: 3067. b) Supplementary material.

10) Soga K, Shiono T, Takemura S, Kaminsky W (1987)Makromol. Chem., Rapid Commun. 8: 305.

11) a) Grassi A, Zambelli Z, Resconi L, Albizzati E, Mazzocchi R (1988)Macromolecules 21: 617. b) Cheng N-H, Ewen A-J (1989)Makromol. Chem. 190: 1931.

12) Busico V, Cipullo R, Chadwick C-J, J.Modder F, Sudmeijer O (1994)Macromolecules 27: 7538 .

13) a) Miyake S, Okumura Y, Inazawa S (1995)Macromolecules 28: 3074 . b) Unpublished results in our group.

14) Jordan F-R, Bajgur S-C, Willett R, Scott B (1986)J. Am. Chem. Soc. 108: 7410.