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Syndiospecific propene polymerization with polymer-supported metallocene catalyst

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Copolymers of styrene and a styrene derivative having a C_s symmetrical ligand moiety were synthesized and used as the carrier for the synthesis of supported-type zirconocene catalysts. Propene polymerization was conducted using the resulting catalyst together with methylalumoxane (MAO), which gave syndiotactic polypropene. The productivity of the polymer-supported catalyst (4010 kg PP (mol Zr)$^{-1}$ for 24 h) was, however, very low compared to that of the corresponding homogeneous catalyst (9130 kg PP (mol Zr)$^{-1}$ for 20 min). © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: metallocene catalyst; syndiotactic polypropene; polystyrene-supported catalyst)

INTRODUCTION

The discovery of syndiotactic propene polymerization with a C_s symmetrical metallocene catalyst by Ewen *et al.*[1] has attracted much interest in academic and industrial laboratories. Hitherto most articles related to this field have mainly investigated the effect of the substituents of metallocene ligands on the catalytic performance in order to generate a series of efficient soluble metallocene catalysts[2–4].

For isotactic propene polymerization, on the other hand, there has been an increasing number of investigations on heterogeneous supported-type metallocene catalysts. Polymerization tests have revealed that the isospecificity of C_2 symmetrical metallocene catalysts markedly increases when the metallocene is immobilized on a suitable solid carrier[5–9]. Even for a C_s symmetrical metallocene, its syndiospecificity is retained when combined with an SiO_2-supported methylalumoxane (MAO) as a cocatalyst. However, the stereospecificity of a C_s symmetrical metallocene catalyst frequently changes from syndiospecific to isospecific upon being immobilized rigidly on a solid carrier[10,11]. Therefore, it does not seem easy to develop immobilizing syndiospecific metallocene catalysts.

In this paper, we describe the preparation of polymer-supported syndiospecific metallocene catalysts using copolymer of styrene and 1-vinyl-4-(1-cyclopentadienyl-1-fluorenyl)ethylbenzene as the precursor, along with the results of propene polymerization using these catalysts.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) was distilled from sodium-benzophenoneketyl under nitrogen atmosphere. Styrene (from Kanto Chemical Co Ltd) was dried over calcium hydride for 12 h, followed by trap-to-trap distillation at 40°C. Cyclopentadiene was obtained by cracking dicyclopentadiene (from Wako Pure Chemicals/Industries Ltd). Fluorene, *p*-bromoacetophenone (from Wako Pure Chemical Industries Ltd), tetrakis(triphenylphosphine)-palladium(0) (from Tokyo Chemical Industries Ltd) and vinyltributyltin (from Aldrich Chemical Company Inc.) were used without further purification.

Synthesis of 6-(4′-bromophenyl)-6-methylfulvene (1)

In a 300 cm^3 glass reactor equipped with a magnetic stirrer was placed 120 cm^3 of THF solution of *p*-bromoacetophenone (23.1 g, 120 mmol); 120 cm^3 of 1.1 M THF solution of cyclopentadienyllithium was added dropwise under stirring at 0°C. After the mixture was kept stirring at 0°C for 3 h, it was refluxed for 1 h under nitrogen atmosphere. The mixture was cooled to room temperature and acidified with 50 cm^3 of 0.1 M hydrochloric acid. The organic layer was separated by extraction with ether, adequately washed with both saturated sodium hydrogencarbonate and sodium chloride aqueous solutions in this order followed by drying over chromatography, using *n*-hexane as a developing solvent, to give 6-(4′-bromophenyl)-6-methylfulvene as an oily product in 69% yield (20.5 g). ^{1}H n.m.r. (300 MHz, $CDCl_3$, 25°C) δ 7.54(2H,d) 7.27(2H,d) 6.61(1H,d) 6.59(1H,d) 6.50(1H,d) 6.14(1H,dd) 2.52(3H,s).

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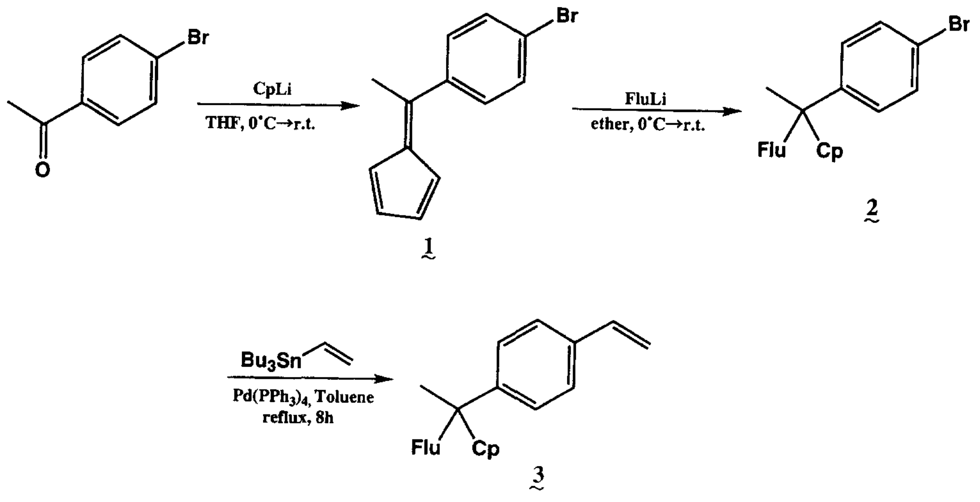
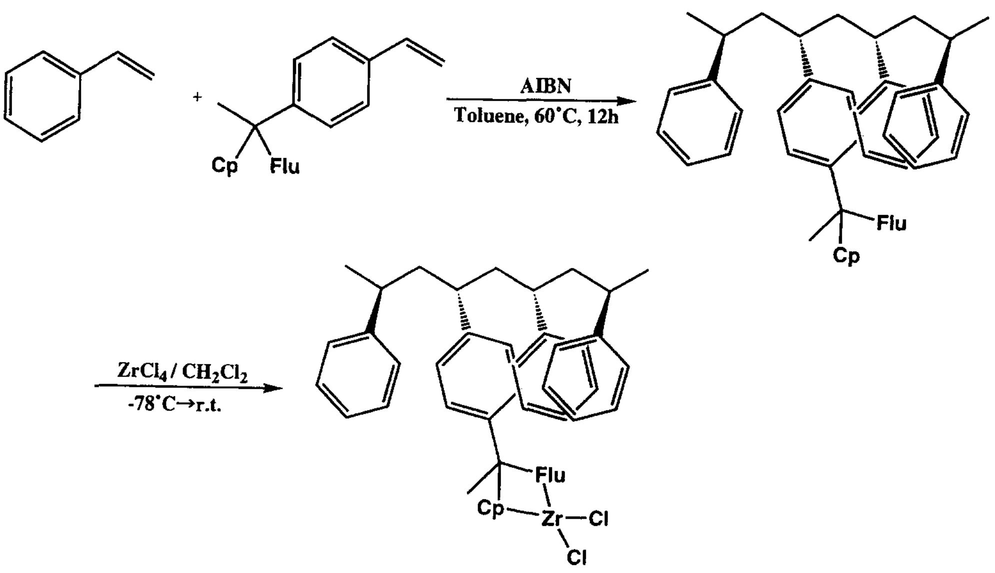


Scheme 1 Synthesis of 1-vinyl-4-(1-cyclopentadienyl-1-flurorenyl)ethylbenzene



Scheme 2 Synthetic route of a polystyrene-supported catalyst

Synthesis of 1-bromo-4-(1-cyclopentadienyl-1-fluorenyl) ethylbenzene (2)

In a 300 cm^3 glass reactor equipped with a magnetic stirrer was placed 100 cm^3 of ether solution of 6-(4′-bromophenyl)-6-methylfulvene (20.0 g, 81 mmol); 130 cm^3 of 0.7 M ether solution of fluorenyllithium was added dropwise at 0°C. The mixture was kept stirring at 0°C for 3 h and subsequently at 25°C for several hours. To the resulting solution was added 50 cm^3 of saturated aqueous solution of ammonium chloride. The organic layer was then separated by extraction with $CHCl_3$, followed by drying over anhydrous magnesium sulfate. After the removal of ether in vacuum, the product was adequately washed with dry acetone to obtain 1-bromo-4-(1-cyclopentadienyl-1-fluorenyl)ethylbenzene as a pale orange solid in 67% yield (22.3 g). mp: 184–186°C, ^{1}H n.m.r. (300 MHz, $CDCl_3$, 25°C) δ 7.71(2H,d) 7.48(2H,d) 7.44(2H,d) 7.30(2H,q) 7.08(2H,q) 6.86(1H,dd) 6.54(1H,d) 6.44(1H,d) 6.22(1H,dd) 4.29(1H,s) 3.06(1H,t) 1.07(3H,s).

Synthesis of 1-vinyl-4-(1-cyclopentadienyl-1-fluorenyl) ethylbenzene (3)[12]

In a 200 cm^3 glass reactor equipped with a magnetic stirrer were introduced 4.13 g (10 mmol) of 1-bromo-4-(1-cyclopentadienyl-1-fluorenyl)ethylbenzene, 0.23 g (0.2 mmol) of tetrakis(triphenylphosphine)palladium(0), and 40 cm^3 of toluene. After the addition of 3.49 g (11 mmol) of vinyltributyltin, the mixture was refluxed under nitrogen for 8 h. The resulting solution was then cooled to room temperature; this was followed by adding 50 cm^3 of saturated aqueous solution of ammonium chloride. The organic layer was separated by extraction with ether, dried over anhydrous magnesium sulfate and purified by recrystallization in THF to yield 1-vinyl-4-(1-cyclopentadienyl-1-fluorenyl)ethylbenzene as a white powder in 57% yield (1.20 g). For reference, the preparation method is schematically shown in *Scheme 1*. mp: 122–125°C, ^{1}H n.m.r. (300 MHz, $CDCl_3$, 25°C) δ 7.72(2H,d) 7.57(2H,d) 7.46(2H,d) 7.30(2H,q) 7.08(2H,q) 6.92(1H,dd) 6.78(1H,q) 6.52(1H,d) 6.44(1H,d) 6.24(1H,dd) 5.80(1H,d) 5.29(1H,d) 4.98(1H,s) 3.06(1H,t) 1.07(3H,s).

Preparation of catalyst precursor A

The precursor of polymer-supported catalyst was synthesized by the copolymerization of **3** with styrene as follows. In a 100 cm^3 glass reactor equipped with a

Table 1 Results of styrene and **3** copolymerization[a]

Precursor	Monomer ratio St.:**3**	Conversion[b] (%)	Ligand content[c] (mmol g^{-1})	Ratio St.:3	M_w ($\times 10^3$)	M_w/M_n
A	20:1	25	0.56	16.1	13.2	1.90
B	5:1	29	1.19	9.2	12.7	1.90
C	1:1	12	1.92	3.2	2.2	2.02

[a] Polymerization conditions: 12 h, 60°C in toluene, AIBN as the initiator
[b] Based on styrene
[c] From ^{13}C n.m.r.

Table 2 Results of propene polymerization with Cat-A[a]

Run No.	Polymerization temperature (°C)	Cocatalyst	Al/Zr ratio	Yield (g)	M_w ($\times 10^4$)	M_w/M_n	m.p. (°C)	Productivity (kgPP (mol Zr)$^{-1}$)	[rrrr]
1	40	MAO	17000	3.21	3.21	1.75	13.8	4010	0.86
2		MAO	3300	0.63	7.30	1.96	138	787	0.86
3		TIBA	3300	0	–	–	–	–	–
4[b]		MAO	3300	7.30	7.27	1.98	139	9130	0.89
5	70	MAO	17000	2.94	2.68	3.48	129	3700	0.75
6	0	MAO	17000	0.05	4.56	4.78	149	69	n.d.

[a] Catalyst: ca 0.02 g, Zr content: 4.0×10^2 mmol(g cat)$^{-1}$, polymerization time: 24 h, propene: 7 dm^3 (STP), toluene: 30 cm^3
[b] i-Pr(Cp)(Flu)ZrCl$_2$ (homogeneous) was used as catalyst: [Zr] $= 8.0 \times 10^{-4}$ mmol, polymerization time: 0.33 h
[c] Yield too low to be analysed

magnetic stirrer were introduced 5.82 g (56 mmol) of styrene, 1.00 g (2.8 mmol) of **3**, 0.184 g (1.12 mmol) of AIBN and 15 cm^3 of toluene under nitrogen atmosphere. The mixture was heated at 60°C for 12 h and methanol was added to stop the reaction. The polymer was separated by filtration and dried in vacuum at 60°C to afford 1.94 g of the catalyst precursor A. The content of **3** in the polymer was estimated to be 7 mol% (0.56 mmol g^{-1}) from the ^{13}C n.m.r.

Preparation of catalyst precursors B and C

Precursors B and C, with 1.19 mmol g^{-1} and 1.92 mmol g^{-1} contents of **3** respectively, were prepared according to the same procedure as that of precursor A.

Preparation of polymer-supported catalyst A (Cat-A)

In a 100 cm^3 glass reactor equipped with a magnetic stirrer were placed 1.50 g of precursor A and 15 cm^3 of THF. The reactor was substituted with nitrogen; this was followed by adding 1 cm^3 of 1.7 M *n*-hexane solution of *n*-butyllithium at 0°C. The mixture was slowly heated up to room temperature, after which the solvent was removed in vacuum and the solid products were adequately washed with pentane. Then, 8 cm^3 of 0.2 M ZrCl$_4$ suspension in CH$_2$Cl$_2$ was added dropwise at − 78°C. The mixture was slowly warmed up to room temperature and kept stirred for 18 h. The CH$_2$Cl$_2$ was removed in vacuum; this was followed by washing with plenty of hexane to obtain the polymer-supported catalyst A. The content of Zr in the catalyst was estimated to be 0.04 mmol g^{-1} from i.c.p. For reference, the preparation method is schematically shown in *Scheme 2*.

Preparation of polymer-supported catalysts B (Cat-B) and C (Cat-C)

Catalysts B and C, with 0.28 mmol g^{-1} and 0.31 mmol g^{-1} Zr contents respectively were prepared in a similar way to catalyst A.

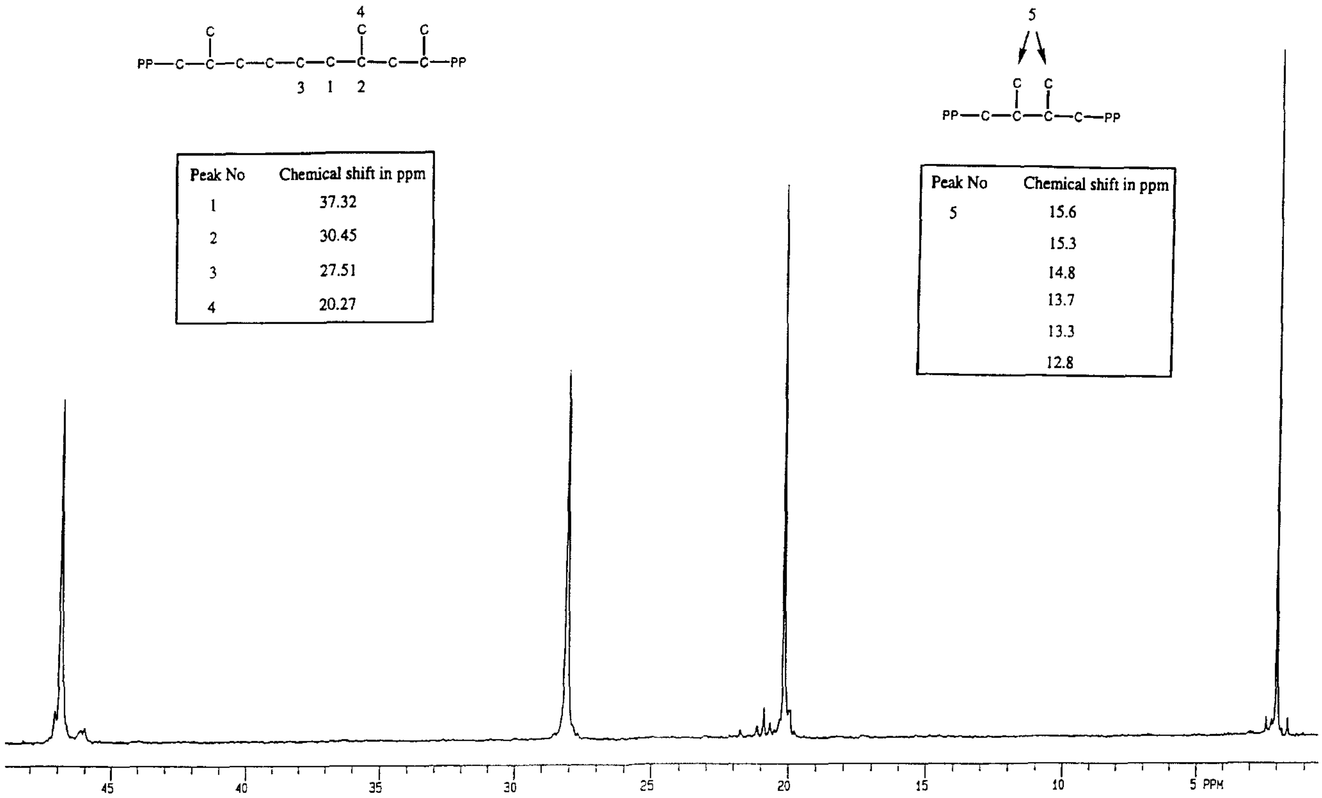
Polymerization and polymer analysis

Polymerization of propene (7 dm^3, STP) was conducted in a 100 cm^3 stainless steel autoclave equipped with a magnetic stirrer using MAO and toluene (30 cm^3) as the cocatalyst and solvent. Polymerization was stopped after 2 h by adding acidic methanol. The polymer obtained was adequately washed with ether, followed by drying in vacuum at 60°C. The ^{13}C n.m.r. spectra of the polymers were measured at 75 MHz in 1,2,4-trichlorobenzene at 135°C with a Varian Gemini 300 spectrometer. The chemical shifts were referred to HMDS added as an internal standard for $\delta = 2.0$. The molecular mass distribution (MMD) of the polymers was measured at 145°C by g.p.c. (Senshu Scientific Co Ltd SSC-7100) using *o*-dichlorobenzene as the solvent. The melting point of the polymers was measured by d.s.c. (Seiko Instruments SSC/5200) at a heating rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

To synthesize the catalyst precursor, copolymerizations of styrene and **3** were conducted with different monomer feed ratios at 60°C in toluene, using AIBN as the initiator. The copolymers produced were analysed by ^{13}C n.m.r. and g.p.c. The results are shown in *Table 1*.

The monomer reactivity ratios were estimated by the curve-fitting method to obtain r_1(styrene) $= 1.00$, r_2 (**3**) $= 0.30$ and hence $r_1 r_2 = 0.30$, indicating that the copolymer has a random structure. The supported catalysts were then prepared according to the methods of *Schemes 1* and *2*. The contents of Zr in the catalysts analysed by i.c.p. were Cat-A: 0.04 mmol g^{-1}, Cat-B: 0.28 mmol g^{-1} and Cat-C: 0.31 mmol g^{-1}; i.e., the contents of Zr in the supported catalysts were less than 25% as referred to the total ligands. To check the reason, a model reaction was conducted as follows: 5 mmol of isopropylidenecyclopentadienylfluorenyldilithium salt (i-Pr(CpLi)(FluLi)) was brought into contact with



Peak No	Chemical shift in ppm
1	37.32
2	30.45
3	27.51
4	20.27

Peak No	Chemical shift in ppm
5	15.6
	15.3
	14.8
	13.7
	13.3
	12.8

Figure 1 ^{13}C n.m.r. spectrum of SPP obtained with Cat-A

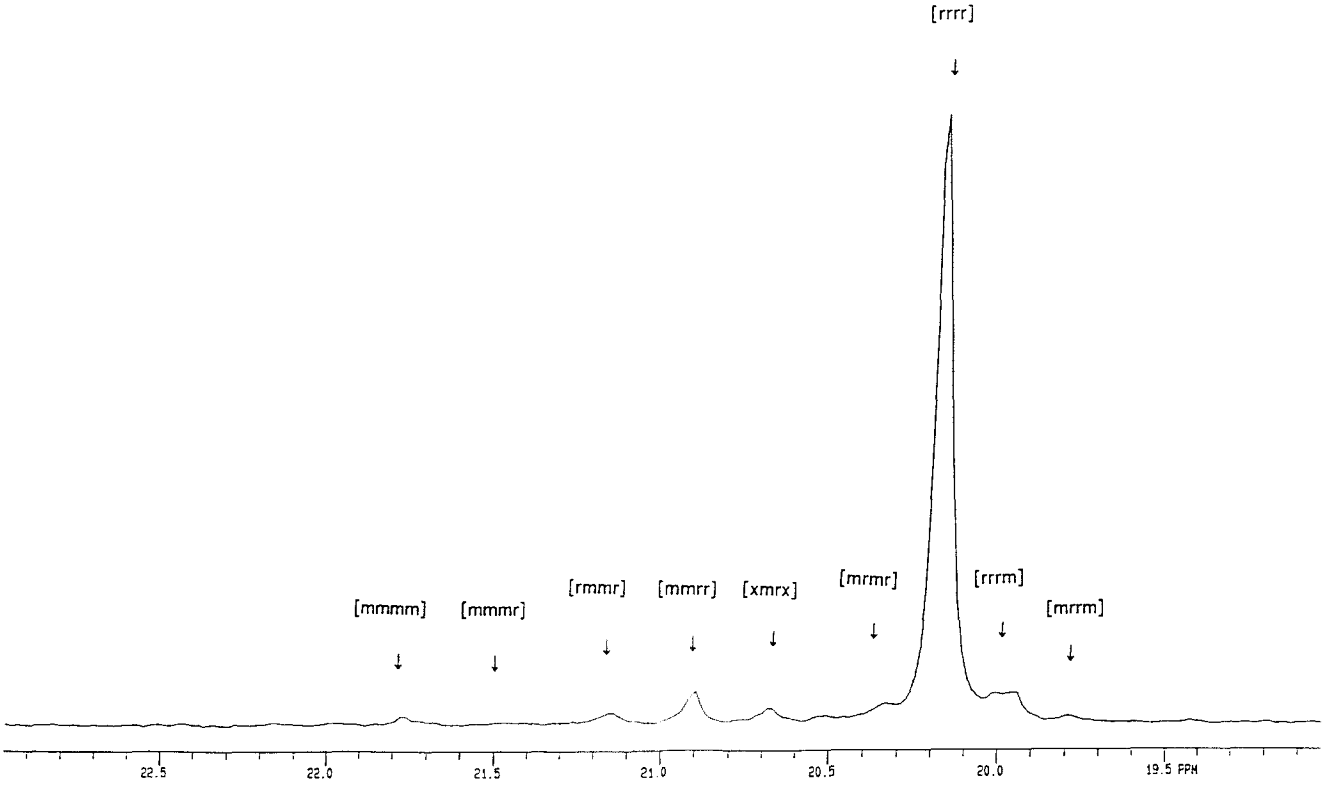


Figure 2 Expanded specrum of methyl region of *Figure 1*

5 mmol of $ZrCl_4$ in 30 cm^3 of CH_2Cl_2 at −78°C. The mixture was gradually heated to room temperature and kept stirred for 12 h. After removal of the solid part isopropylidenecyclopentadienylfluorenylzirconiumdichloride (i-Pr(Cp)(Flu)$ZrCl_2$)) by decantation and solvent by evaporation, the residue was analysed by g.c.-m.s. and ^1H n.m.r., which indicated the formation of approximately 1.5 mmol of 1,1-dimethyl-2-cyclopentadienyl-4-fluorenylcyclobutane (i-Pr(Cp)(Flu)CH_2). It seems, therefore, that such a side reaction causes a reduction

Table 3 Calculated and observed pentad distributions of SPP[a]

	i-Pr(Cp)(Flu)ZrCl$_2$		Cat-A	Cat-B	Cat-C	Cat-C
Pentad	(Calc.)[b]	(Obs.)	(Obs.)	(Obs.)	(Obs.)	(Insol. fract.)
[mmmm]	0.001	0.001	0.009	0.034	0.040	0.147
[mmmr]	0.001	0.003	0.000	0.014	0.008	0.077
[rmmr]	0.016	0.006	0.017	0.022	0.022	0.051
[mmrr]	0.033	0.021	0.032	0.046	0.042	0.088
[xmrx]	0.013	0.022	0.020	0.035	0.031	0.071
[mrmr]	0.003	0.013	0.011	0.025	0.029	0.029
[rrrr]	0.896	0.894	0.858	0.719	0.705	0.317
[rrrm]	0.037	0.073	0.049	0.102	0.114	0.146
[mrrm]	0.003	0.001	0.004	0.004	0.005	0.074

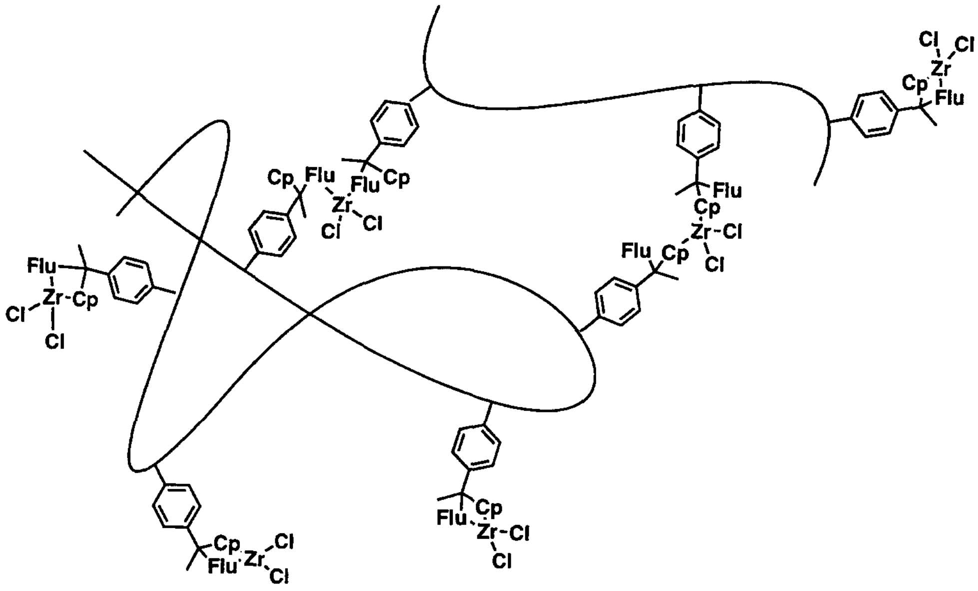
[a] Calculated using the general case model reported by Ewen *et al.* [15]

[b] [mm] = 0.010, [mr] = 0.056, [rr] = 0.934, $P_a = 0.010$, $P_b = 0.974$, $P_R = 0.026$, $P_s = 0.947$

Table 4 Results of propene polymerization with the supported catalysts[a]

Run No.	Catalyst	Zr content (mmol g^{-1})	Yield (g)	M_w ($\times 10^4$)	M_w/M_n	m.p. (°C)	Productivity (kg PP (mol Zr)$^{-1}$)	[rrrr]
2	Cat-A	0.04	0.63	7.30	1.96	138	787	0.86
7	Cat-B	0.28	1.14	1.95	2.34	131	204	0.72
8	Cat-C	0.31	0.70	4.65	2.61	125, 136	113	0.71

[a] Al/Zr ratio: 3300, polymerization time: 24 h, polymerization temperature: 40°C, propene: 7 dm^3 (STP)



Scheme 3 Plausible structure of the supported catalyst (insoluble fraction)

in the content of zirconium. From that viewpoint, THF was used in place of CH$_2$Cl$_2$ as the solvent for the catalyst preparation. The content of Zr in the resulting catalyst was, however, found to be much lower (1.50×10^{-2} mmol g^{-1}). Accordingly, the present catalysts were synthesized using CH$_2$Cl$_2$ as the solvent, as described in the Experimental section.

Polymerization of propene was conducted using approximately 0.02 g of Cat-A. *Table 2* shows the polymerization results, together with some analytical data of the resulting polymers. When MAO was employed as the cocatalyst, an appreciable amount of polymer was produced. The polymer yield was found to be dependent upon both the Al/Zr ratio and the polymerization temperature. Judging from the data, including the melting point listed in *Table 2*, syndiospecificity of the catalyst seems to decrease markedly with an increase in the polymerization temperature. For comparison, polmerization of propene was induced under similar conditions with the use of homogeneous analogue i-Pr-(Cp)(Flu)ZrCl$_2$ as catalyst. The result is also included in *Table 2*, indicating that the ^{13}C n.m.r. spectrum of a typical copolymer obtained with the supported catalyst (Run No. 1) is illustrated in *Figure 1*, which does not display any peak assignable to irregular bondings (1,3-insertion[13], head-to-head and tail-to-tail[14]), whereas almost all kinds of pentads are observed in the expanded spectrum of methyl region as shown in *Figure 2*.

The pentad distributions estimated from the ^{13}C n.m.r.

spectrum (Run No. 1) are given in *Table 3* together with those calculated according to the model reported by Ewen *et al.*[15]. The pentad distributions of polypropene obtained in Run No. 1 are not very different from those produced with the original homogeneous catalyst (Run No. 5) except for [mmmm]. To obtain some information as to the discrepancy of the [mmmm] pentad, polymerizations of propene were conducted with Cat-B and Cat-C having higher contents of Zr. The results of polymerization and the pentad distributions of the resulting polymers are given in *Tables 4* and *3*, respectively. Those catalysts produced less syndiotactic polymers.

It has been already reported that the syndiospecific i-Pr(Cp)(Flu)$ZrCl_2$ catalyst tightly fixed on the SiO_2 surface products not syndiotactic but high isotactic polypropene[10,11]. From such a viewpoint, solubilities of the three catalysts in toluene were checked at 40°C. The majority of Cat-A was quickly dissolved in toluene, whereas some portions of Cat-B and Cat-C remained as precipitates even after contact with toluene for several hours. It may be plausible to assume, therefore, that part of the zirconocene compound is connected with a couple of ligands in different polymer chains, as schematically shown in *Scheme 3*. Such irregular active species might produce atactic or isotactic polymers, depending upon the structures. Accordingly, polymerization of propene was conducted using the toluene-insoluble fraction of Cat-C. The microstructure of the resulting polymer is shown in *Table 3*. The structure is too complicated to be analysed in detail. However, the polymer seems to be composed of isotactic, atactic and syndiotactic blocks.

The result suggests that polypropenes produced with Cat-B and Cat-C contain more or less such irregular polymers. It is thus of importance to avoid the formation of these irregular active species for the synthesis of a polymer-supported syndiospecific metallocene catalyst. In addition, the activity of present catalysts is very low compared to that of the corresponding homogeneous catalyst.

REFERENCES

1 Ewen, J. A., Jones, R. L. and Razavi, A. *J. Am. Chem. Soc.* 1988, **110,** 6255

2 Erker, G., Nolte, R., Aul, R., Wilker, S., Kruger, C. and Noe, R. *J. Am. Chem. Soc.* 1991, **113,** 7594

3 Erker, G. and Temme B. *J. Am. Chem. Soc.* 1992, **114,** 4004

4 Mise, T., Miya, S. and Yamazaki, H. *Chem. Lett.* 1989, 1853

5 Soga, K. and Kaminaki, M. *Makromol. Chem., Rapid Commun.* 1993, **14,** 1745

6 Soga, K. and Kaminaka, M. *Makromol. Chem., Rapid Commun.* 1992, **13,** 221

7 Kaminsky, W. and Renner, F. *Makromol. Chem., Rapid Commun.* 1993, **14,** 239

8 Soga, K., Kaminaka, M. and Shiono, T. in MetCon'93, 1993, 65

9 Soga, K. in 'Catalyst Design for Tailor-made Polyolefins' (Eds K. Soga and M. Terano), Koudansha-Elsevier, Tokyo, 1994, p. 307

10 Kaminsky, W., Renner, F. and Winkelbach, H. in MetCon'94, 1994, Session III, 1

11 Soga, K., Kim, H. J. and Shiono, T. *Macromol. Chem. Phys.* 1994, **195,** 3347

12 McKean, D. R., Parrinello, G., Renaldo, A. F. and Stille, J. K. *J. Org. Chem.* 1987, **52,** 422

13 Soga, K., Takemura, S., Shiono, T. and Kaminsky, W. *Makromol. Chem., Rapid Commun.* 1987, **8,** 305

14 Tanaka, Y. *Kagaku no Ryouiki* 1983, **142,** 131

15 Ewen, J. A., Elder, M. J., Jones, R. L., Curtis, S. and Cheng, H. N. in 'Catalytic Olefin Polymerization' (Eds T. Keii and K. Soga), 'Studies in Surface Science and Catalysis 56', Koudansha-Elsevier, Tokyo, 1990, p. 439