

Synthesis of a dinuclear ansa-zirconocene catalyst having a biphenyl bridge and application to ethene polymerization

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Abstract

A novel dinuclear ansa-zirconocene catalyst ($\mu\text{-C}_{12}\text{H}_8\{\{\text{SiPh}(\text{Ind})_2\}\text{ZrCl}_2\}_2$) (**I**) was prepared by a Wurtz coupling reaction between two equivalent of bisindenylphenylchlorosilane and one equivalent of 4,4'-dibromobiphenyl in THF at reflux temperature for 12 h, followed by a successive reaction with $\text{ZrCl}_4 \cdot 2\text{THF}$ in THF at -78°C . Polymerization of ethene was conducted in a 300 cm³ glass reactor equipped with a stirrer at 40, 60, 80 and 100°C using MAO or $\text{Ph}_3\text{C}[\text{B}(\text{C}_6\text{F}_5)_4]$ as cocatalyst and toluene as the solvent. The catalyst (**I**) gave linear polyethene with a broader molecular mass distribution (MMD) in a much higher yield as compared to the corresponding mononuclear catalyst derived from $[\text{Ph}_2\text{Si}(\text{Ind})_2]\text{ZrCl}_2$ (**II**). The apparent activity increased monotonously from 40°C up to 100°C. The replacement of MAO with $\text{Ph}_3\text{C}[\text{B}(\text{C}_6\text{F}_5)_4]$ gave polyethene with a higher molecular weight. © 1998 Elsevier Science B.V.

Keywords: Dinuclear ansa-zirconocene catalyst; Biphenyl bridge; Ethene polymerization

1. Introduction

The practical application of metallocene catalysts still requires to improve their thermal stability for adaptation to the various existing olefin polymerization processes [1–4]. It was reported that some ansa-metallocenes with phenyl substitutions on a silicon bridge like $[\text{Ph}_2\text{Si}(\text{Ind})_2]\text{ZrCl}_2$, $[\text{Ph}_2\text{CCp}(\text{Flu})]\text{ZrCl}_2$, etc. display high activities to give linear polyethenes with high molecular weights even at elevated temperatures [5]. However, the molecular mass distributions of resulting polyethenes are very narrow ($M_w/M_n = 2\text{--}3$), which caused some

disadvantages on the processability due to the high shear viscosity and low melt extensional viscosity of the product [6,7]. To overcome those problems, combined metallocene catalysts like $\text{Cp}_2\text{TiCl}_2/\text{Cp}_2\text{ZrCl}_2$ [8] and $\text{Cp}_2\text{ZrCl}_2/\text{Cp}_2\text{HfCl}_2$ [9] have been developed. On the other hand, several kinds of dinuclear metallocene catalysts with diphenyl [10], phenylene [11] or siloxane bridge have also been synthesized and applied to olefin polymerizations [12,13].

In the present study, we have prepared a dinuclear ansa-zirconocene catalyst having a biphenyl bridge from bisindenylphenylchlorosilane and 4,4'-dibromobiphenyl using a modified Wurtz coupling reaction [14] and tested it to ethene polymerization. This paper reports the synthetic method of the dinuclear zirconocene

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catalyst together with preliminary results of ethene polymerization with it.

2. Experimental

2.1. Materials

Ethene of research grade purity donated by Mitsui Petrochemical Japan was further purified by passing through NaOH and P₂O₅ columns. Solvents (toluene, hexane, tetrahydrofuran (THF), dichloromethane and diethylether) were commercially obtained from Kanto Chemicals Japan and purified according to the usual procedures. Methylalumoxane (MAO), triethylaluminum (TEA) and Ph₃C[B(C₆F₅)₄] were donated by Tosoh Akzo Japan and used without further purification. Trichlorophenylsilane commercially obtained from Kanto Chemicals Japan was further purified by reduced distillation under nitrogen atmosphere. 4,4'-dibromobiphenyl and *n*-butyllithium were commercially obtained from Kanto Chemicals Japan and used without further purification.

2.2. Synthesis of bisindenylphenylchlorosilane

A modified method to prepare bisindenylchlorosilane [15] was employed for the synthesis of PhSi(Ind)₂Cl. A 500 ml three-neck flask was equipped with a reflux condenser, a dropping funnel and a magnetic stirring bar. Indenylmagnesiumbromide (22 g, 100 mmol) was added to the flask followed by the addition of 250 ml of diethylether. Then, trichlorophenylsilane (10.6 g, 8 ml, 50 mmol) in 100 ml of diethylether was added dropwise at room temperature and the reaction mixture was heated to reflux temperature with stirring for 10 h. After removing the solvent in vacuo, 300 ml of hexane was added followed by stirring at room temperature for 2 h. The solid fraction was removed by filtration through a Celite plug. Recrystallization of the filtrate from hexane gave 3.8 g (10.2 mmol, 20.4%) of PhSi(Ind)₂Cl as white solid powders, which was shown by ¹H-NMR (Fig. 1) to be the mixture of two diastereomers. ¹H-NMR (CDCl₃, 300 MHz, 25°C) δ = 7.59–7.38 (m, 10H, Ph), 7.32–7.01 (m, 16H, H-4, H-5, H-6, H-7), 6.98–6.90 (dd, 4H, H-3),

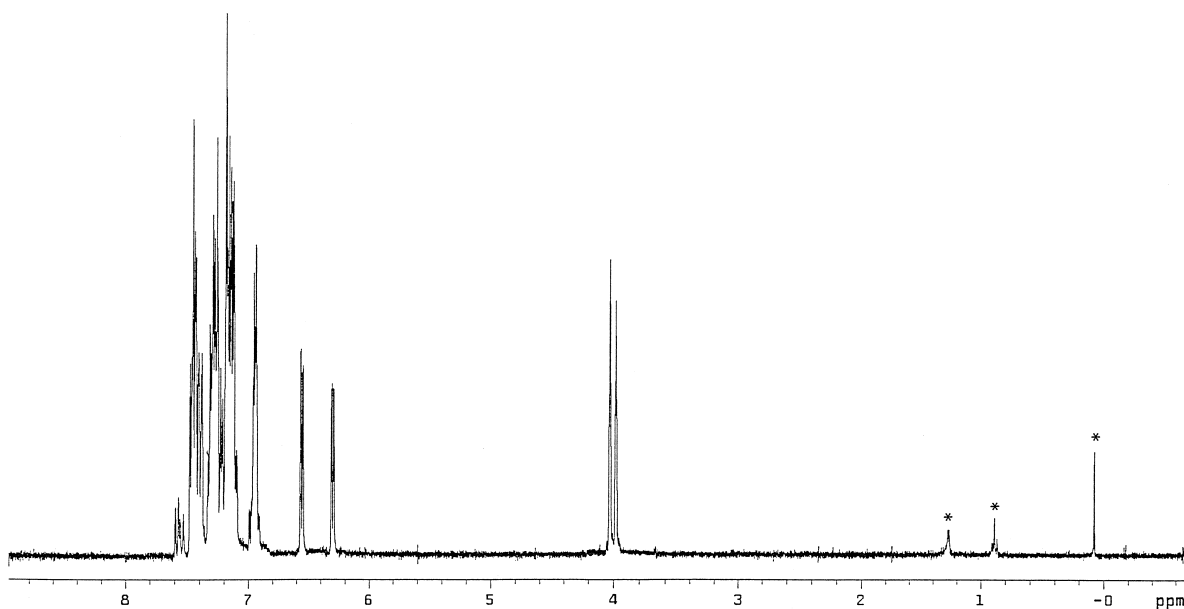


Fig. 1. ¹H-NMR (CDCl₃) spectrum of a mixture of two diastereomers PhSi(Ind)₂Cl (*: solvent impurity).

6.57–6.54 (dd, 2H, H-2), 6.31–.28 (dd, 2H, H-2), 4.03 (s, 2H, H-1), 3.98 (s, 2H, H-1). Further recrystallization from hexane gave a pure racemic isomer as white microcrystals, mp 130.3°C (Fig. 2). $^1\text{H-NMR}$ (CDCl_3 , 300 MHz, 25°C) $\delta = 7.50\text{--}7.42$ (m, 5H, Ph), 7.30–7.24 (m, 4H, H-4, H-5, H-6, H-7), 7.18–7.12 (m, 4H, H-4, H-5, H-6, H-7), 6.95–6.92 (dd, 2H, H-3), 6.31–6.30 (dd, 2H, H-2), 3.98 (s, 2H, H-1). The meso isomer was enriched in the mother liquor as a sticky yellow oil after removal of the recrystallization solvent.

2.3. Synthesis of the catalyst (**I**)

A modified method to prepare diphenyldi-*p*-biphenylsilane $(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_4\text{C}_6\text{H}_5)_2$ [14] was used to synthesize the catalyst precursor. To a 500 ml three-neck flask equipped with a reflux condenser, a dropping funnel and a magnetic stirring bar, were introduced 1.1 g (3.5 mmol) of 4,4'-dibromobiphenyl, 50 ml of THF and 0.5 g of sodium ribbon. Then, two equivalent of bisindenylphenylchlorosilane (the mixture of two diastereomers, 2.6 g, 7 mmol) in 50 ml of THF was added dropwise at room temperature. The reaction mixture was heated up to reflux temperature and kept standing with vigorous stirring for 12 h. After the THF was removed by distillation, 300 ml of toluene was added. The resulting suspension was stirred at room temperature for 2 h, and the solid fraction was removed by filtration through a Celite plug.

Recrystallization of the filtrate from toluene gave 2.2 g (2.7 mmol, 38.6%) of the catalyst precursor as a pale yellow powder. $^1\text{H-NMR}$ (CDCl_3 , 300 MHz, 25°C) $\delta = 7.60\text{--}7.38$ (m, 18H, Ph), 7.35–7.12 (m, 16H, H-4, H-5, H-6, H-7), 6.96–6.92 (m, 4H, H-3), 6.66–6.62 (dd, 2H, H-2), 6.42–6.40 (dd, 2H, H-2), 4.07 (s, 2H, H-1), 4.03 (s, 2H, H-1).

The catalyst (**I**) was prepared by an additional reaction of dilithiosalt of the precursor with a solution of $\text{ZrCl}_4 \cdot 2\text{THF}$ in THF at -78°C . The reaction mixture was slowly warmed up to room temperature and stirred over night. Lithium chloride was removed by adding toluene followed by filtration through a Celite plug. The filtrate was recrystallized from toluene to give 1.6 g (1.4 mmol, 51.8%) of the catalyst as orange powders. Despite much effort on further purification, the catalyst crystals could not be obtained at the present stage. We are trying to obtain the catalyst crystals by using pure isomers of $\text{PhSi}(\text{Ind})_2\text{Cl}$.

2.4. Polymerization and analytical procedures

All operations were carried out under nitrogen atmosphere. In a 300 cm^3 glass reactor equipped with a magnetic stirrer was introduced 100 ml of toluene solution of MAO ($[\text{Al}] = 0.6$ mmol/l). The reactor was thermostated at an appropriate polymerization temperature and saturated with ethene. An activated metallocene solution ($[\text{Zr}] = 1.0 \times 10^{-6}$ mol/l, $[\text{Al}](\text{MAO})$

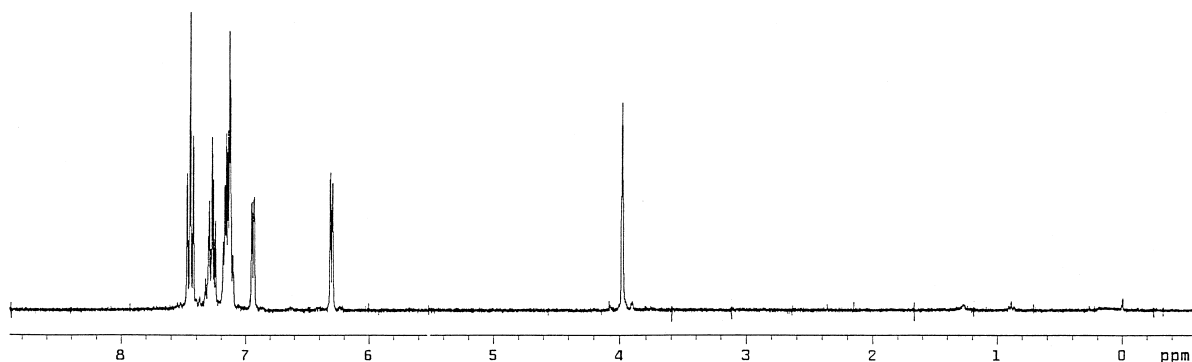


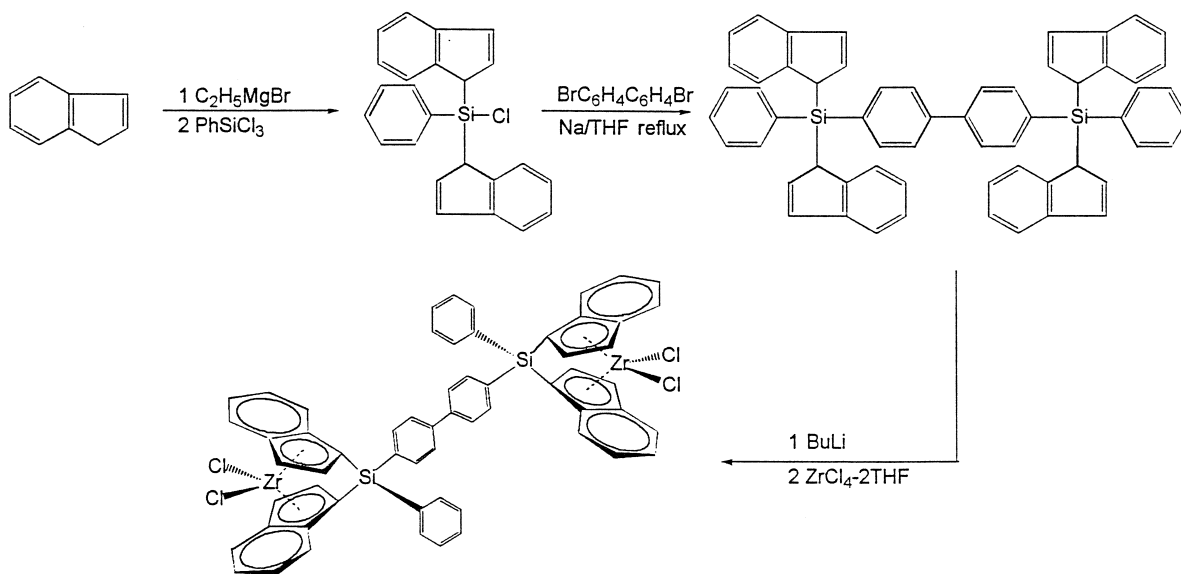
Fig. 2. $^1\text{H-NMR}$ (CDCl_3) spectrum of a pure racemic isomer of $\text{PhSi}(\text{Ind})_2\text{Cl}$.

= 0.4 mmol/l) was then injected to start the polymerization reaction. Ethene was continuously fed to the reactor to keep the pressure at 1 bar during the polymerization. The polymerization reaction was terminated by adding acidic methanol. The precipitated polymers were adequately washed with methanol and dried in vacuo at 60°C for 6 h. The weight average molecular weight (M_w) and molecular mass distribution (MMD) of polymers were measured at 145°C by GPC (gel-permeation chromatography, Senshu Scientific SSC7100) using *o*-dichlorobenzene as the solvent. The melting points of polymers (T_m) were measured by DSC (differential scanning calorimetry, Seiko DSC220C) at a heating rate of 10°C/min.

3. Results and discussion

The main objective of our present study is to prepare a metallocene catalyst with a high stability at elevated polymerization temperatures. The current catalyst structure stems from the model of poly(silylene)phenylene-supported metallocene catalysts which have been recently

developed in our laboratory [16]. The synthetic route of the catalyst (**I**) is illustrated in Scheme 1. The present catalyst having a $C_6H_5[Si(C_6H_4)_2C_6H_5]$ backbone looks highly rigid, suggesting that its thermal stability is much better than the corresponding zirconocene catalyst with a siloxane bridge [17,18]. In this study, we have conducted ethene polymerization as the first application of the catalyst (**I**). Therefore, the two diastereomers were used without separation. Polymerization of ethene was conducted in a 300 cm³ glass reactor at various temperatures using MAO or $Ph_3C[B(C_6F_5)_4]$ as cocatalyst, the results of which are summarized in Table 1. For reference, the corresponding mononuclear ansa-zirconocene catalyst derived from $[Ph_2Si(Ind)_2]ZrCl_2$ (**II**) was also prepared according to the literature [19] and tested to ethene polymerization. It is apparent from Table 1 that the catalyst (**I**) displays a much higher activity as compared to the catalyst (**II**). When MAO is used as cocatalyst, the polymerization activity increased monotonously from 40°C up to 100°C. Such a high activity and high thermal stability of the present catalyst might result from the



Scheme 1. A synthetic route of the catalyst (**I**) ($\mu-C_{12}H_8\{[SiPh(Ind)_2]ZrCl_2\}_2$).

Table 1
Results of ethene polymerization with the catalysts (I) and (II)

Run No.	Catalyst	Cocatalyst	T_p (°C)	[Et] ^a (mol/l)	Activity (kg/mol Zr [Et] h)	M_w ($\times 10^{-3}$)	M_w/M_n	T_m (°C)	ΔH (mJ/mg)	Crystallinity ^b (%)
1	I	MAO	40	0.109	11400	47.2	8.3	134.8	211.3	79.0
2	I	Ph ₃ C[B(C ₆ F ₅) ₄]	40	0.109	19900	87.7	10.8	136.8	204.9	76.0
3	I	MAO	60	0.085	3200	35.5	13.7	134.6	221.8	82.2
4	I ^c	MAO	60	0.169	44800	100.1	9.3	138.9	204.2	75.6
5	I ^d	MAO	60	0.255	44700	100.0	8.1	136.4	209.2	77.5
6	I	Ph ₃ C[B(C ₆ F ₅) ₄]	60	0.085	21500	42.3	7.3	138.3	211.7	82.1
7	I	MAO	80	0.065	69000	30.1	6.0	136.0	211.9	82.2
8	I	Ph ₃ C[B(C ₆ F ₅) ₄]	80	0.065	60000	36.8	4.2	136.5	226.2	83.8
9	I	MAO	100	0.028	70700	15.7	6.0	136.5	233.2	86.4
10	I	Ph ₃ C[B(C ₆ F ₅) ₄]	100	0.028	18200	19.3	5.6	137.6	234.5	86.9
11	II	MAO	40	0.109	3500	74.0	3.6	138.8	208.0	77.0
12	II	MAO	60	0.085	8000	70.1	3.4	135.6	213.4	79.0

Polymerization conditions: monomer pressure = 1 bar, [Zr] = 1.0×10^{-6} mol/l, Al(MAO)/Zr = 1000, Al(TEA)/Zr = 100 when Ph₃C[B(C₆F₅)₄] was used as cocatalyst, toluene = 100 ml, polymn. time = 10 min.

^aCalculated from literature [20].

^bCalculated from literature [21].

^cMonomer pressure = 2 bar.

^dMonomer pressure = 3 bar.

cooperating interaction between the two adjacent zirconocenes which are electronically coupled through a biphenyl bridge. However, the precise reasons are not clear at the moment. It is also uncertain why the replacement of MAO with $\text{Ph}_3\text{C}[\text{B}(\text{C}_6\text{F}_5)_4]$ caused a marked decrease in the activity at 100°C. Whereas, the weight average molecular weight (M_w) of polyethene decreased substantially with an increase in the polymerization temperature. The use of $\text{Ph}_3\text{C}[\text{B}(\text{C}_6\text{F}_5)_4]$ as cocatalyst yielded polyethene with a slightly higher M_w . The catalyst (**I**), especially combined with MAO, yielded polyethene with a broader molecular mass distribution (MMD), which may reflect the difference in catalytic performance between the two diastereomers.

Then, the effect of ethene pressure on the activity and M_w was briefly investigated, the results of which are shown in Table 1 (runs No. 4 and 5). Both the activity and the M_w of polyethene increased markedly with raising the ethene pressure from 1 to 2 bar. However, a further increase in the ethene pressure did not change the activity of the catalyst or the M_w of polyethene. Since the activity of the present dinuclear zirconocene catalyst is extremely high, a lot of polyethene was produced under such conditions. The use of a bigger reactor equipped with a mechanical stirrer might be necessary to evaluate those values more precisely.

4. Conclusion

A novel dinuclear zirconocene catalyst having a biphenyl bridge has been prepared and applied to ethene polymerization at elevated temperatures. It was found that the dinuclear catalyst shows an extremely high activity for ethene polymerization to give linear polyethene with a high molecular weight and a broad molecular mass distribution (MMD) even at

100°C. We are now preparing similar catalysts using the pure meso and racemic isomers of $\text{PhSi}(\text{Ind})_2\text{Cl}$. The detailed characterization of those catalysts together with the results of propene polymerization over them will be reported elsewhere.

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