High-Temperature Ethylene/α-Olefin Copolymerization with a Zirconocene Catalyst: Effects of the Zirconocene Ligand and Polymerization Conditions on Copolymerization Behavior

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ABSTRACT: Copolymerizations of ethylene and α-olefin with various zirconocene compounds at a high temperature were carried out to study the relationship between the ligand structure of zirconocene compounds and the copolymerization behavior. All of the indenyl-based zirconocene compounds in combination with dimethylanilinium tetrakis(pentafluorophenyl)borate/triisobutylaluminum produced only low molecular weight copolymers at a high temperature, regardless of the substituents and bridged structures of the zirconocene compounds. However, zirconocene compounds with a fluorenyl ligand gave rise to a significant increase in the activity and molecular weight of the copolymers by the selection of a diphenylmethylene bridge structure even at a high temperature. Ethylene/1-hexene copolymers obtained with the fluorenyl-based catalysts contained inner double bonds accompanied by the generation of hydrogen, presumably because of a C—H bond activation mechanism. The contents of the inner double bonds were significantly influenced by the polymerization conditions, including the 1-hexene feed content, polymerization temperature, and ethylene pressure. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 4641–4648, 2000

Keywords: zirconocene; indenyl; fluorenyl; high temperature; chain-transfer reaction

INTRODUCTION

A great amount of interest has been focused on the copolymerization of ethylene and α-olefin with soluble metallocene catalysts because copolymers obtained with these catalysts have a narrow molecular weight distribution and a narrow chemical composition distribution.[1] However, the most significant problem of ordinary metallocene catalysts is that the molecular weight of the copolymers is relatively low in comparison with copolymers obtained with a Ziegler–Natta catalyst. Therefore, the design of metallocene compounds is needed for the production of high molecular weight copolymers, especially in high-temperature polymerizations.[2] However, few articles have been published so far concerning catalyst performance in high-temperature polymerizations.[3] Bujadoux et al.[4] applied various metallocenes activated with methylaluminoxane (MAO) to an ethylene/α-olefin copolymerization at a high temperature under high pressure, but no catalyst produced high molecular weight copolymers.

We also indicated that ethylene(bisindenyl)zirconium dichloride [Et(Ind)$_2$ZrCl$_2$] and (dimethylsilylene)bis(2,4-dimethylcyclopentadienyl)zirconium dichloride [Me$_2$Si(2,4-Me$_2$Cp)$_2$ZrCl$_2$] activated with Me$_2$PhNH · B(C$_6$F$_5$)$_4$/triisobutylaluminum (i-Bu$_3$Al) produced only low molecular weight ethylene/1-hexene copolymers at a high tempera-

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ture.[5] However, it was reported that diphenylmethylene(cyclopentadienyl)(fluorenyl)zirconium dichloride [$Ph_2C(Cp)(Flu)ZrCl_2$] in conjunction with $Me_2PhNH \cdot B(C_6F_5)_4$/*i*-$Bu_3Al$ produced high molecular weight ethylene/α-olefin copolymers with good activity even at a high polymerization temperature,[6] and the MAO-activated catalyst also indicated high catalyst performance.[7] Furthermore, hafnocenes activated with $Me_2PhNH \cdot B(C_6F_5)_4$/*i*-$Bu_3Al$ showed high activity and good copolymerization reactivity in ethylene/α-olefin copolymerizations and produced high molecular weight copolymers.[8] These results suggested the possibility of the synthesis of high molecular weight copolymers with metallocene catalysts even at a high temperature. Nevertheless, the relationship between the ligand structure of metallocene compounds and the catalyst performance at a high temperature has not been clarified so far.

In this article, ethylene homopolymerizations and ethylene/1-hexene copolymerizations were conducted with various indenyl-based and fluorenyl-based zirconocene compounds in combination with $Me_2PhNH \cdot B(C_6F_5)_4)$/*i*-$Bu_3Al$ and MAO as cocatalysts under various polymerization conditions, and the effects of the ligand structures of the zirconocene compounds on the copolymerization behaviors under various polymerization conditions are discussed.

EXPERIMENTAL

Materials

Indenyl-based metallocene compounds such as $Et(Ind)_2ZrCl_2$, $(Ind)_2ZrCl_2$, $Me_2Si(Ind)_2ZrCl_2$, $Me_2Si(H_4{-}Ind)_2ZrCl_2$, $Ph_2Si(Ind)_2ZrCl_2$, $Me_2Si(Me{-}Ind)_2ZrCl_2$, and $Me_2C(Ind)_2ZrCl_2$ were synthesized according to the literature.[9] Fluorenyl-based metallocene compounds such as $Ph_2C(Cp)(Flu)ZrCl_2$, $Ph_2C(3\text{-}MeCp)(Flu)ZrCl_2$, $Ph_2C(3\text{-}i\text{PrCp})(Flu)ZrCl_2$, $Ph_2C(3\text{-}PhCH_2Cp)(Flu)ZrCl_2$, $Ph_2C(3\text{-}Me_3SiCp)(Flu)ZrCl_2$, $Ph_2C(Cp)(2,7\text{-}Me_2Flu)ZrCl_2$, $Ph_2C(Cp)(2,7\text{-}t\text{-}Bu_2Flu)ZrCl_2$, $Ph_2C(Cp)(H_8{-}Flu)ZrCl_2$,$Ph_2C(Cp)(2\text{-}Me_2NFlu)ZrCl_2$, and $Ph_2C(Cp)(2\text{-}MeONFlu)ZrCl_2$ were also synthesized according to the literature.[10] $Me_2PhNH \cdot B(C_6F_5)_4$, MAO, and *i*-$Bu_3Al$ from Tosoh Akzo Co. were used without purification. Toluene, C9–C12 hydrocarbon solvent, ethylene, 1-butene, and 1-hexene were commercially obtained and purified according to the usual procedures.

Polymerization Procedure

Slurry Polymerization

Polymerizations were carried out in a 2-L autoclave equipped with a magnetic stirrer, a thermometer tube, and various inlets. The autoclave was flushed several times with nitrogen and filled with 1 L of toluene, and the catalyst components were added. Ethylene was continuously supplied to keep the pressure constant during polymerization. After the polymerization time, ethylene was released, and the polymerization was terminated by the addition of ethanol. The obtained polymer was adequately washed with plenty of ethanol and dried at 60 °C under reduced pressure to a constant weight.

Solution Polymerization

Polymerizations were carried out in a 1-L autoclave equipped with a magnetic stirrer, a thermometer tube, and various inlets. The autoclave was flushed several times with nitrogen and filled with 600 mL of C9–C12 mixed hydrocarbon solvent; if needed, 1-hexene was added. Then, the autoclave was heated up to the polymerization temperature. The polymerization was started by the addition of the catalyst components. Ethylene was continuously supplied to keep the pressure constant during polymerization. After the polymerization time, ethylene was released, and the polymerization was terminated by the addition of ethanol. The obtained polymer was adequately washed with plenty of ethanol and dried at 60 °C under reduced pressure to a constant weight.

Ethylene/α-Olefin Copolymerization Procedure in a High-Pressure Process

Copolymerization reactions were carried out in our pilot plant, in which the operating conditions were very close to industrial conditions. The polymerization temperature could be changed from 120 to 280 °C. The ethylene pressure range was up to 2000 bar. The polymerization temperature was controlled by the catalyst feed rate. The average residence time was 60 s. Polymerization reactions were continuously carried out, and unreacted ethylene and α-olefin were recycled.

Characterization of the Polymers

Differential scanning calorimetry (DSC) measurements were made with a Seiko DSC-200 at a

Table I. Results of the Ethylene Polymerizations with Various Indenyl-Based Zirconocene Catalysts[a]

Run	Metallocene	μmol	Activity (kg/mmol · Zr · h)	Melt Flow Rate (g/10 min)
1	$Et(Ind)_2ZrCl_2$	1.0	31	>500
2	$(Ind)_2ZrCl_2$	1.0	48	>500
3	$Me_2C(Ind)_2ZrCl_2$	1.0	32	>500
4	$Me_2Si(Ind)_2ZrCl_2$	2.5	5	84
5	$Ph_2Si(Ind)_2ZrCl_2$	1.0	22	44
6	$Me_2Si(H_4$—$Ind)_2ZrCl_2$	2.5	6	25
7	$Me_2Si(Me$—$Ind)_2ZrCl_2$	2.0	14	13

[a] Polymerization conditions: solvent = C9–C12 hydrocarbon, 600 mL; ethylene pressure = 20 bar; polymerization temperature = 150 °C; polymerization time = 20 min; catalyst = metallocene/$Me_2PhNH \cdot B(C_6F_5)_4$/*i*—$Bu_3Al$ = 1/2/250.

heating rate of 10 °C/min. Melt-flow index measurements were carried out with an L244 melt indexer of (Takara Kogyo Co., Ltd.) with a standard weight of 2.16 kg to evaluate ethylene shear thinning behavior. The measurements were performed at 190 °C according to ASTM D 1238-79. The molecular weights and molecular weight distributions of the polymers were determined by gel permeation chromatography (GPC) with *o*-dichlorobenzene as a solvent. The number of short chain branches was analyzed from an IR spectrum measured with a PerkinElmer FTIR 1760X. ^1H NMR spectra were recorded from a 5 wt % 1,1,2,2-tetrachloroethane solution at room temperature with a JEOL GSX-400 at 400 MHz. ^{13}C NMR spectra of the polymers were recorded at 130 °C with a JEOL GSX-400 operating at 100 MHz. The solution was made in *o*-dichlorobenzene/benzene-d_6 (9/1 v/v) up to 10 wt %.

RESULTS AND DISCUSSION

Ethylene Polymerization with Indenyl-Based Zirconocene Catalysts

Ethylene polymerizations with various indenyl-based zirconocenes activated with $Me_2PhNH \cdot B(C_6F_5)_4$/*i*-$Bu_3Al$ at a high temperature were carried out to study the relationship between the ligand structures of zirconocene compounds and the catalyst performance. Table I shows the results of the ethylene polymerizations with various indenyl-based zirconocene catalysts at 150 °C. Nonbridged, ethylene-bridged, and isopropylidene-bridged bisindenyl zirconocene catalysts showed relatively high activity, but the molecular weight of the polyethylene obtained was not so high. Dimethylsilylene-bridged zirconocene catalyst produced higher molecular weight polyethylene than the other indenyl-based zirconocene catalysts did, although the activity was low. The activity and molecular weight of polyethylene were improved when the substituents in the bridge structure were changed from methyl to phenyl groups. Hydrogenation of indenyl ligands and the introduction of the methyl group into the 2-position of the indenyl ligand also affected the molecular weight of the polyethylene obtained and the activity. These results indicate that the electron-donative ligands and the rigidity of the bridge structure are needed for the production of high molecular weight polyethylene at a high temperature.

Table II. Effect of the Polymerization Temperature on the Ethylene Polymerizations with $Ph_2C(Cp)(Flu)ZrCl_2/Me_2PhNH \cdot B(C_6F_5)_4$/*i*-$Bu_3Al$[a]

Run	$Ph_2C(Cp)(Flu)ZrCl_2$ (μmol)	Temperature (°C)	Activity (kg/mmmol · Zr)	M_w ($\times 10^{-4}$)	M_w/M_n
8	0.25	150	172	11.2	2.0
9	0.25	170	134	8.3	1.9
10	0.50	200	50	5.5	1.8

[a] Polymerization conditions: ethylene pressure = 20 bar; solvent = C9–C12 hydrocarbon, 600 mL; polymerization time = 20 min; catalyst = $Ph_2C(Cp)(Flu)ZrCl_2/Me_2PhNH \cdot B(C_6F_5)_4$/*i*-$Bu_3Al$ = 1/2/250.

Table III. Effect of the Polymerization Temperature and 1-Hexene Content on the Molecular Weights and Structures of the Ethylene/1-Hexene Copolymers[a]

Run	$Ph_2C(Cp)(Flu)ZrCl_2$ (μmol)	Temperature (°C)	1-Hexene (mL)	Activity (kg/ mmol · Zr)	M_w ($\times 10^{-4}$)	M_w/M_n	Methyl (No/1000 C)
9	0.25	170	0	134	8.3	1.9	—
11	0.25	170	20	148	6.6	2.0	3.3
12	0.25	170	80	72	6.8	1.8	12.7
13	0.25	170	120	50	4.8	1.9	28.1
10	0.50	200	0	50	5.5	1.8	—
14	0.50	200	20	40	4.7	1.9	—

[a] Polymerization conditions: ethylene pressure = 20 bar; solvent = C9–C12 hydrocarbon, 600 mL; polymerization time = 20 min; catalyst = $Ph_2C(Cp)(Flu)ZrCl_2/Me_2PhNH \cdot B(C_6F_5)_4/i\text{-}Bu_3Al$ = 1/2/250.

Ethylene Polymerization with $Ph_2C(Cp)(Flu)ZrCl_2$-Based Catalyst

$Ph_2C(Cp)(Flu)ZrCl_2$ was first selected for the production of high molecular weight polyethylene at a high temperature. Table II shows the results of ethylene polymerizations with $Ph_2C(Cp)(Flu)ZrCl_2/Me_2PhNH \cdot B(C_6F_5)_4/i\text{-}Bu_3Al$ at a high temperature. It is clear that this catalyst can produce high molecular weight polyethylene even at a high temperature. We already reported that the change of the substituents in the bridge structure from phenyl to methyl groups resulted in a drastic decrease in the activity and molecular weight of the obtained polyethylene.[6] Actually, Razavi and Atwood[10(b)] indicated that the enhancement of the molecular weight in propylene polymerization was caused by the change of the substituents in the bridge structure from methyl to phenyl groups and concluded that the bridge structure of the fluorenyl-based metallocene compounds was important for the production of high molecular weight polyolefins.

Table III indicates the results of the ethylene/1-hexene copolymerizations with the $Ph_2C(Cp)(Flu)ZrCl_2$-based catalyst. The activity and molecular weight of the copolymers decreased with increasing 1-hexene feed content. Nevertheless, this catalyst produced high molecular weight copolymers with high 1-hexene contents even at a high temperature. Uozumi and Soga[11] previously indicated that C_s symmetric compounds such as $Me_2C(Cp)(Flu)ZrCl_2$ showed better copolymerization activity than C_2 symmetric metallocene compounds at low temperatures. Therefore, these results indicated that the $Ph_2C(Cp)(Flu)ZrCl_2$-based catalyst kept good copolymerization activity even at a high temperature.

Table IV. Effect of the Substituents in the Fluorenyl Ligand on the Ethylene/1-Hexene Copolymerizations at High Temperatures[a]

Run	Metallocene	μmol	1-Hexene (mL)	T_p (°C)[b]	Activity (kg/mmol · Zr)	M_w ($\times 10^{-4}$)	M_w/M_n	T_m (°C)[c]
15[d]	$Ph_2C(Cp)(2,7\text{-}t\text{-}Bu_2Flu)ZrCl_2$	0.25	20	170	144	8.6	1.7	120
16[d]	$Ph_2C(Cp)(2,7\text{-}Me_2Flu)ZrCl_2$	0.25	20	170	136	8.4	1.8	120
17[d]	$Ph_2C(Cp)(H_8\text{-}Flu)ZrCl_2$	3.00	20	150	1	5.6	2.6	125
11[d]	$Ph_2C(Cp)(Flu)ZrCl_2$	0.25	20	170	148	6.6	2.0	120
18[e]	$Ph_2C(Cp)(2\text{-}Me_2NFlu)ZrCl_2$	0.50	80	170	44	9.1	2.1	111
19[e]	$Ph_2C(Cp)(2\text{-}MeOFlu)ZrCl_2$	0.50	80	170	68	8.4	1.9	103
12[d]	$Ph_2C(Cp)(Flu)ZrCl_2$	0.25	80	170	72	6.8	1.8	99

[a] Polymerization conditions: ethylene pressure = 20 bar; solvent = C9–C12 hydrocarbon, 600 mL; polymerization time = 20 min.

[b] Polymerization temperature.

[c] Melting point of the copolymer.

[d] Catalyst = metallocene/$Me_2PhNH \cdot B(C_6F_5)_4/i\text{-}Bu_3Al$ = 1/2.0/250.

[e] Catalyst = metallocene/$Me_2PhNH \cdot B(C_6F_5)_4/i\text{-}Bu_3Al$ = 1/1.2/250.

Table V. Results of the Ethylene/1-Hexene Copolymerizations with Various Zirconocene Catalysts at High Temperatures[a]

Run	Metallocene	μmol	1-Hexene (mL)	T_p (°C)[b]	Activit (kg/mmol · Zr)	M_w ($\times 10^{-4}$)	M_w/M_n	T_m (°C)[c]
20[d]	$Ph_2C(3\text{-}MeCp)(Flu)ZrCl_2$	0.5	20	200	42	4.8	2.0	120
21[d]	$Ph_2C(3\text{-}i PrCp)(Flu)ZrCl_2$	0.5	20	200	54	3.3	2.2	121
22[d]	$Ph_2C(3\text{-}PhCH_2Cp)(Flu)ZrCl_2$	0.5	20	200	20	3.8	2.1	120
23[d]	$Ph_2C(3\text{-}Me_3SiCp)(Flu)ZrCl_2$	0.5	20	200	28	3.5	2.5	122
24[d]	$Ph_2C(3,4\text{-}Me_2Cp)(Flu)ZrCl_2$	0.5	20	200	24	6.8	2.1	123
14[e]	$Ph_2C(Cp)(Flu)ZrCl_2$	0.5	20	200	40	4.7	1.9	119

[a] Polymerization conditions: ethylene pressure = 20 bar; solvent = C9–C12 hydrocarbon, 600 mL; polymerization time = 20 min.

[b] Polymerization temperature.

[c] Melting point of the copolymer.

[d] Catalyst = metallocene/$Me_2PhNH \cdot B(C_6F_5)_4/i\text{-}Bu_3Al$ = 1/1.2/250.

[e] Catalyst = metallocene/$Me_2PhNH \cdot B(C_6F_5)_4/i\text{-}Bu_3Al$ = 1/2.0/250.

Modification of $Ph_2C(Cp)(Flu)ZrCl_2$

The effect of substituents in a fluorenyl ligand on the catalyst performance for ethylene polymerizations at 150 °C is shown in Table IV. The introduction of methyl or *t*-butyl substituents in the 2,7-positions of the fluorenyl ligand gave rise to an increase in the molecular weight of polyethylene without a decrease in catalytic activity. Propylene polymerization with these two metallocene compounds in combination with MAO was previously reported,[12] and the molecular weights of polypropylenes and their activity were not so different from those of the $Ph_2C(Cp)(Flu)ZrCl_2$/MAO catalyst, so the effect of the substituents on the ethylene or propylene polymerization behavior may be different. The copolymerization reactivity was not so changed by the introduction of alkyl substituents on the fluorenyl ligands, on the basis of the melting point of the copolymers. This means that these substituents did not inhibit the incorporation of the bulky α-olefin into the copolymers.

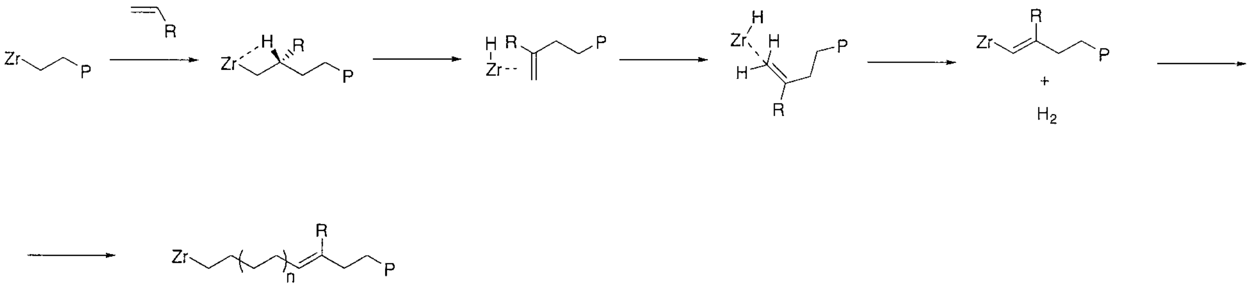
The hydrogenation of the fluorenyl ligand caused a decrease in activity, molecular weight, and 1-hexene incorporation into the copolymers. These phenomena were also observed for the MAO-activated catalyst. However, Shiomura et al.[13] reported that $Ph_2C(Cp)(H_8\text{–}Flu)ZrCl_2$/MAO showed high activity in propylene polymerization. Actually, we confirmed that this catalyst showed the same activity in ethylene polymerizations as the $Ph_2C(Cp)(Flu)ZrCl_2$-based catalyst at 40 °C.[10(c)] These results suggest that the stereorigidity of the ligand structure of metallocene compounds is a key factor in the production of high molecular weight polyethylene at a high temperature.

However, $Ph_2C(Cp)(2\text{-}MeOFlu)ZrCl_2$ and $Ph_2C(Cp)(2\text{-}Me_2NFlu)ZrCl_2$ activated with $Me_2PhNH \cdot B(C_6F_5)_4/i\text{-}Bu_3Al$ produced higher molecular weight copolymers than the $Ph_2C(Cp)(Flu)ZrCl_2$-based catalyst did, although they showed a slightly lower 1-hexene incorporation ability. The $Ph_2C(Cp)(2\text{-}MeOFlu)ZrCl_2$-based catalyst exhibited a higher

Table VI. Structures of the Ethylene/1-Hexene Copolymers Obtained with Fluorenyl-Based Catalysts[a]

Run	Metallocene	M_w ($\times 10^{-4}$)	M_w/M_n	Methyl (No/1000 C)	Vinylidene (No/1000 C)	Vinyl (No/1000 C)	Vinylene (No/1000 C)	Trisubstituted (No/1000 C)
12	$Ph_2C(Cp)(Flu)ZrCl_2$	6.8	1.8	12.7	0.07	0.09	0.28	0.40
19	$Ph_2C(Cp)(2\text{-}MeOFlu)ZrCl_2$	8.4	1.9	12.5	0.09	0.13	0.29	0.51
18	$Ph_2C(Cp)(2\text{-}Me_2NFlu)ZrCl_2$	9.1	2.1	10.4	0.06	0.07	0.26	0.34

[a] For polymerization conditions, see Table IV.



Scheme 1

1-hexene incorporation ability than the $Ph_2C(Cp)(2\text{-}Me_2NFlu)ZrCl_2$-based catalyst, but the molecular weight was lower than that of the copolymers obtained with the $Ph_2C(Cp)(2\text{-}Me_2NFlu)ZrCl_2$-based catalyst. Ewen[14] already indicated that the introduction of substituents containing oxygen or nitrogen atom such as Me_2N— or MeO— into fluorenyl ligand resulted in a drastic decrease in the molecular weight for propylene polymerization. These results suggest that the catalyst performance was affected by the interaction of substituents in the metallocene compounds with *i*-Bu_3Al.[15]

The results of the ethylene/1-hexene copolymerization with zirconocene compounds with a substituent in the cyclopentadienyl ligand in combination with $Me_2PhNH \cdot B(C_6F_5)_4$/*i*-$Bu_3Al$ at a high temperature are shown in Table V. These four kinds of C_1 symmetric zirconocene catalysts showed high activity even at a high temperature, but the molecular weights of the copolymers were roughly equal to or lower than those of the polymers obtained with the $Ph_2C(Cp)(Flu)ZrCl_2$ and $Ph_2C(3,4\text{-}Me_2Cp)(Flu)ZrCl_2$ catalysts, and the introduction of the huge substituents resulted in a decrease in the molecular weight. The variation of the substituents also affected the 1-hexene incorporation into the copolymers, and the introduction of a bulky substituent such as the trimethylsilyl group resulted in the decrease in the relative 1-hexene incorporation into the copolymers.

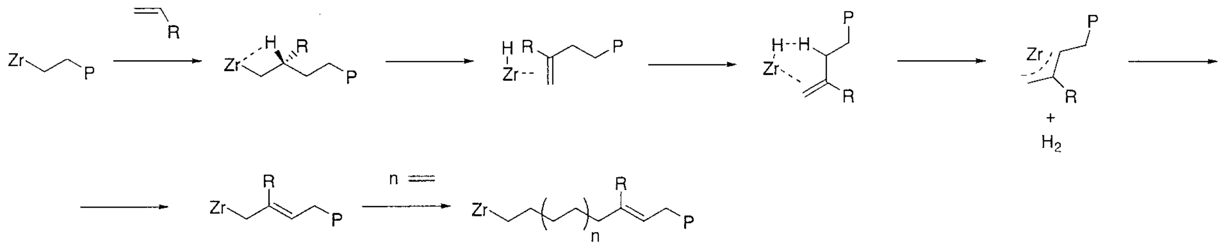
Formation of Inner Double Bonds Accompanied by the Generation of Hydrogen

Table VI shows the results of an unsaturated double-bond analysis for ethylene/1-hexene copolymers synthesized with various fluorenyl-based zirconocene catalysts at 170 °C. Trisubstituted double bonds were detected in addition to the vinyl, vinylidene, and vinylene double bonds. The formation of the terminal trisubstituted double bonds was already reported for an ethylene/1-butene copolymerization with metallocene catalysts.[16] However, Folie and Ruff[17] recently indicated the possibility of the formation of an inner trisubstituted double bond. The formation mechanism of the inner trisubstituted double bonds, based on a vinylic C—H bond activation, is shown in Scheme 1. On the basis of this mechanism, the hydrogen-liberation reaction was needed for the formation of the inner double bonds. Table VII shows the effect of the 1-hexene feed content on the amount of generated hydrogen. Hydrogen generation was detected, and the amount of it

Table VII. Effect of the 1-Hexene Feed Content on the Hydrogen Amount in Ethylene/1-Hexene Copolymerization[a]

Run	$Ph_2C(Cp)(Flu)ZrCl_2$ (μmol)	1-Hexene (mL)	Yield (g)	H_2 (ppm)	H_2/Polyethylene (ppm/g)
25	0.5	0	33.2	3200	96
26	0.5	20	37.5	5700	152
27	0.5	80	47.2	8700	184

[a] Polymerization conditions: ethylene pressure = 20 bar; solvent = C9–C12 hydrocarbon, 600 mL; polymerization time = 10 min; polymerization temperature = 170 °C; catalyst = metallocene/$Me_2PhNH \cdot B(C_6F_5)_4$/*i*-$Bu_3Al$ = 1/1.2/250.



Scheme 2

increased with increasing 1-hexene feed content. These results strongly suggest that the formation of inner trisubstituted double bonds were accompanied by the generation of hydrogen. However, Karol et al.[18] indicated the formation of an inner vinylene bond on the basis of an allylic C—H bond activation. Therefore, the formation of the trisubstituted double bonds can be explained by this mechanism, as shown in Scheme 2. An ^{1}H NMR spectrum of an ethylene/1-hexene copolymer (run 12) obtained with $Ph_2C(Cp)(Flu)ZrCl_2$ activated with $Me_2PhNH \cdot B(C_6F_5)_4/i\text{-}Bu_3Al$ at 170 °C is shown in Figure 1. It is clear that several kinds of trisubstituted double bonds (5.1–5.3 ppm) were formed in the copolymer backbone.[19] Now, we cannot conclude which mechanism is reasonable for the formation of the trisubstituted double bonds in ethylene/1-hexene copolymers synthesized at a high temperature. Further investigations are now in progress.

Another interesting point is that a large amount of hydrogen was detected even in ethylene homopolymerizations. However, we detected a trace amount of generated hydrogen in an ethylene homopolymerization at 40 °C, and the same tendency was reported for an ethylene polymerization with $Ph_2C(Cp)(Flu)ZrCl_2/MAO$.[20] These results suggest that the polymerization temperature affected the hydrogen-generation reaction, followed by the formation of the inner vinylene bonds for ethylene homopolymerization.

Ethylene/1-Butene Copolymerization in a High-Pressure Process

Table VIII shows the results of ethylene/1-butene copolymerizations with the $Ph_2C(Cp)(Flu)ZrCl_2$-based catalysts in a high-pressure process. Both catalysts produced high molecular weight ethylene/1-butene copolymers with high activity, although the copolymerization reactivity for these catalysts was slightly different. The introduction of the substituent in the fluorenyl ligand resulted in the decrease in the comonomer incorporation ability, presumably because of the steric effect of the substituents.

The most important point is that the detected amount of trisubstituted double bonds was slightly lower than that of copolymers obtained in a solution process, although the 1-butene content in the copolymers synthesized in a high-pressure process was higher than that of copolymers synthesized in a solution process. These results indicate that the formation of inner double bonds is controlled by the monomer concentration.

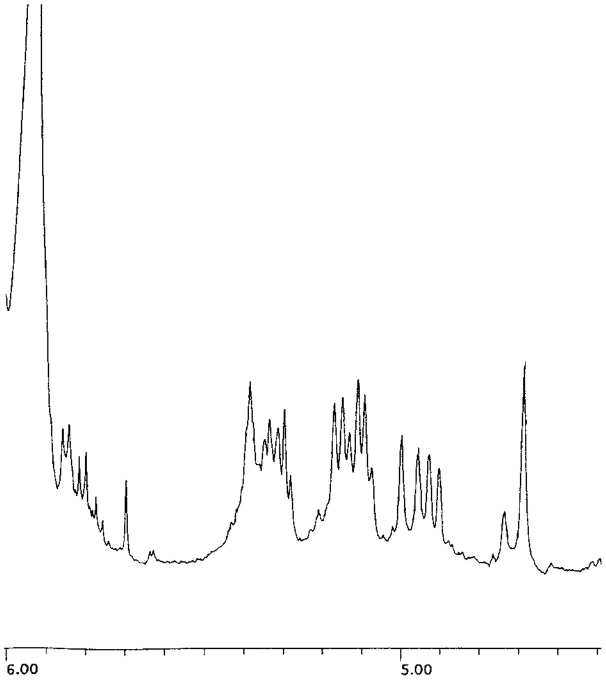


Figure 1. ^{1}H NMR spectrum of the ethylene/1-hexene copolymers obtained with $Ph_2C(Cp)(Flu)ZrCl_2/Me_2PhNH \cdot B(C_6F_5)_4/i\text{-}Bu_3Al$ at 170 °C (run 12).

Table VIII. Results of Ethylene/1-Butene Copolymerization in a High-Pressure Process[a]

Run	Metallocene	1-Butene (mol %)	Methyl (No/1000 C)	*trans*-Vinylene (No/1000 C)	Vinyl (No/1000 C)	Vinylidene (No/1000 C)	Trisubstituted (No/1000 C)
33	$Ph_2C(Cp)(Flu)ZrCl_2$	65	35.3	0.27	0.14	Trace	0.19
34	$Ph_2C(Cp)(2\text{-}Me_2NFlu)ZrCl_2$	72	36.9	0.26	0.07	0.08	0.08

[a] Polymerization conditions: ethylene pressure = 800 bar; polymerization temperature = 160 °C; catalyst = metallocene/$Me_2PhNH \cdot B(C_6F_5)_4/i\text{-}Bu_3Al$ = 1/1.2/250.

REFERENCES AND NOTES

1. (a) Kaminsky, W.; Miri, M. J Polym Sci Part A: Polym Chem 1985, 23, 2151; (b) Kaminsky, W.; Schlobohm, M. Macromol Chem Macromol Symp 1986, 4, 103.
2. Pietikäinen, P.; Seppälä, J. V. Macromolecules 1994, 27, 1325.
3. (a) Luft, G.; Batarseh, B.; Cropp, R. Angew Makromol Chem 1993, 212, 1547; (b) Bergemann, C.; Cropp, R.; Luft, G. J Mol Catal 1995, 102, 1; (c) Bergemann, C.; Cropp, R.; Luft, G. J Mol Catal 1996, 105, 87.
4. Bujadoux, K.; Adisson, E.; Olonde, X.; Gila, L. Metallocenes 95, Brussels, Belgium, April 1995; p 377.
5. Yano, A.; Sone, M.; Yamada, S.; Hasegawa, S.; Akimoto, A. Macromol Chem Phys 1999, 200, 917.
6. Yano, A.; Sone, M.; Hasegawa, S.; Sato, M.; Akimoto, A. Macromol Chem Phys 1999, 200, 933.
7. Yano, A.; Hasegawa, S.; Yamada, S.; Akimoto, A. J Mol Catal A: Chem 1999, 148, 77.
8. Yano, A.; Sone, M.; Yamada, S.; Hasegawa, S.; Akimoto, A. Macromol Chem Phys 1999, 200, 924.
9. (a) Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. Angew Chem Int Ed Engl 1985, 24, 507; (b) Dang, V. A.; Yu, L. C.; Balboni, D.; Dall'Occo, T.; Resconi, L.; Mercandelli, P.; Moret, M.; Sironi, A. Organometallics 1999, 18, 3781.
10. (a) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. J Am Chem Soc 1988, 110, 6255; (b) Razavi, A.; Atwood, J. J Organomet Chem 1993, 459, 117; (c) Yano, A.; Hasegawa, S.; Kaneko, T.; Sone, M.; Sato, M.; Akimoto, A. Macromol Chem Phys 1999, 200, 1542.
11. Uozumi, T.; Soga, K. Macromol Chem 1992, 193, 823.
12. Alt, H. G.; Zenk, R. J Organomet Chem 1996, 522, 39.
13. Shiomura, T.; Kohno, M.; Inoue, N.; Yokote, Y.; Akiyama, M.; Asanuma, T.; Sugimoto, R.; Kimura, S.; Abe, M. Stud Surf Sci Catal 1994, 89, 327.
14. Ewen, J. A. Macromol Chem Symp 1995, 89, 181.
15. Akimoto, A.; Yano, A. In Metalorganic Catalysts for Synthesis and Polymerization; Kaminsky, W., Ed.; Springer: Heidelberg, 1999; p 180
16. Rossi, A.; Zhang, J.; Odian, G. Macromolecules 1996, 29, 2331.
17. Folie, B.; Ruff, C. J. Polym Prepr (Am Chem Soc Div Polym Chem) 1998, 39, 201.
18. (a) Karol, F. J.; Kao, S.-C.; Wasserman, E. P.; Bradt, R. C. New J Chem 1997, 21, 797; (b) Wasserman, E.; His, E.; Young, W.-T. Polym Prepr (Am Chem Soc Div Polym Chem) 1998, 39, 425.
19. Resconi, L.; Piemontesi, F.; Camurati, I.; Sudmeijer, O.; Nifant'ev, I. E.; Ivchenko, P. V.; Kuz'mina, L. G. J Am Chem Soc 1998, 12, 2308.
20. (a) Yano, A.; Hasegawa, S.; Tanabiki, M.; Sato, M.; Akimoto, A. In Progress and Development of Catalytic Olefin Polymerization; Sano, T.; Uozumi, T.; Nakatani, H; Terano, M., Eds.; Technology and Education Publishers: Tokyo, 2000; p 233; (b) Karol, F. J.; Kao, S.-C.; Wasserman, E. P.; Yu, Z. In Metalorganic Catalysts for Synthesis and Polymerization; Kaminsky, W., Ed.; Springer: Heidelberg, 1999; p 629