

COPOLYMERIZATION OF ETHYLENE AND PROPYLENE WITH $(\text{CpCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\text{MCl}_2$ ($\text{M} = \text{Zr}, \text{Hf}$) AND Cp_2ZrCl_2 CATALYSTS

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Abstract $(\text{CpCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\text{MCl}_2$ ($\text{M} = \text{Zr}, \text{Hf}$)/MAO and Cp_2ZrCl_2 /MAO ($\text{Cp} = \text{cyclopentadienyl}$; MAO = methylaluminoxane) catalyst systems have been compared for ethylene copolymerization to investigate the influence of the ligand and transition metal on the polymerization activity and copolymer properties. For both $\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ substituted catalysts the catalytic activity decreased with increasing propene concentration in the feed. The activity of the hafnocene catalyst was 6–8 times lower than that of the analogous zirconocene catalyst. ^{13}C NMR analysis showed that the copolymer obtained using the unsubstituted catalyst Cp_2ZrCl_2 has greater incorporation of propene than those produced by $\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ substituted Zr and Hf catalysts. The melting point, crystallinity and the viscosity-average molecular weight of the copolymer decreased with an increase of propene concentration in the feed. Both $\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ substituted Zr and Hf catalysts exhibit little or no difference in the melting point and crystallinity of the produced copolymers. However, there are significant differences between the two zirconocene catalysts. The copolymer produced by Cp_2ZrCl_2 catalyst have much lower T_m and X_c than those obtained with the $(\text{CpCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\text{ZrCl}_2$ catalyst. The density and molecular weight of the copolymer decreased in the order: $(\text{CpCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\text{HfCl}_2 > (\text{CpCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\text{ZrCl}_2 > \text{Cp}_2\text{ZrCl}_2$. The kinetic behavior of copolymerization with Hf catalyst was found to be different from that with Zr catalyst.

Keyword Metallocene catalyst, Ethylene/propylene copolymerization, Methylaluminoxane

INTRODUCTION

The behavior of olefin polymerization is affected by changing the structure of metallocene catalysts, e.g. by variation of the transition metal, the steric and electronic properties of ligand. A few studies have looked at the differences in ethylene^[1–3] and propene^[2] homopolymerization and copolymerization of ethylene with α -olefin, with bridged and non-bridged zirconocenes and hafnocenes^[1–6]. On the other hand, Ewen^[1] and Chien^[7] have reported the effects of alkyl substitution on the Cp (cyclopentadienyl) rings for several zirconocenes. The steric and electronic factors of the substituents (on the Cp ligands) have a great effect on the catalyst activity.

To our knowledge, no report have been published on the use of zirconocene and hafnocene catalyst containing $\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ substituted Cp rings for the copolymerization of ethylene with propene. In this study we investigated the behavior of $(\text{CpCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\text{ZrCl}_2$ and $(\text{CpCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\text{HfCl}_2$ in ethylene/propene copolymerization and compared the results with those obtained with unsubstituted Cp_2ZrCl_2 catalyst.

EXPERIMENTAL

Materials

Toluene was purified by refluxing for 24 h over sodium metal, followed by fractional distillation. Polymerization grade ethylene, propene and nitrogen were used after purification by passing through columns of activated molecular sieve (4A).

$(\text{CpCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\text{ZrCl}_2$ and $(\text{CpCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\text{HfCl}_2$ were synthesized using $\text{Na}(\text{C}_5\text{H}_5)$,

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$\text{BrCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ and ZrCl_4 in tetrahydrofuran (THF)^[9]. The THF solution of $\text{Na}(\text{C}_5\text{H}_5)$ (0.2 mol) was added dropwise to the $\text{BrCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ (0.2 mol in THF) at room temperature and the mixture was stirred overnight. The resultant NaBr was filtered off. The solution was distilled under reduced pressure and then treated with sodium and THF solution at room temperature to yield the sodium salt, $(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\text{Na}$. To a suspension of ZrCl_4 or HfCl_4 (0.5 equiv) in THF, a THF solution of sodium salt was added dropwise and the reaction mixture was stirred at room temperature overnight. After filtration and concentration, *n*-hexane was added and a solid powder was obtained. Pure product was produced by reprecipitation from *n*-hexane. Cp_2ZrCl_2 was purchased from Fluka Co. Ltd. and used without further purification.

MAO (methylaluminoxane) was prepared from $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and trimethylaluminum (TMA) in toluene according to the literature reported^[10].

Copolymerization Procedure

All copolymerizations were carried out in a 0.5 L glass reactor equipped with a stirrer. Toluene was used as solvent. For every experiment, the reactor was purged with nitrogen and replaced with gas mixture of ethylene/propene at reaction temperature. 100 mL toluene and a solution of MAO were added consecutively. Copolymerization was initiated by the addition of the solution of metallocene in toluene. Gas mixture was continuously supplied to the reactor and the copolymerization was carried out at 1.06×10^5 Pa, 50°C for 0.5 h. Copolymerization was terminated by stopping the gas feed and quenched by adding ethanol containing hydrochloric acid. The copolymer was washed with ethanol and dried in vacuum at 60°C.

Polymer Characterization

The density of the polymer was measured by density gradient column techniques. A mixture of anhydrous ethanol and H_2O was used to prepare the density gradient at 25°C covering a density range of 0.82–0.95 g mL⁻¹. The melting points (T_m) of the copolymer were determined with a Perkin-Elmer Model DSC-7 instrument at a heating rate of 20 K/min. The crystallinity was calculated from the heat of fusion (ΔH_f)^[11]. The intrinsic viscosity was measured by an AVS 300 viscometer in dilute decahydronaphthalene solution at 135°C. The viscosity average molecular weight of the sample was calculated according to Scholte *et al.*^[12]. The ¹³C-NMR spectra were recorded on a JNM-FX100 instrument. The polymer solutions for the ¹³C-NMR measurement were prepared in *o*-dichlorobenzene-*d*₄. The propene content and the triad sequence distribution were calculated from the intensity of the signals according to the method reported by Hsieh and Randall^[13].

RESULTS AND DISCUSSION

Catalytic Activity

The $(\text{CpCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\text{ZrCl}_2/\text{MAO}$, $(\text{CpCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\text{HfCl}_2/\text{MAO}$ and $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalyst systems were used for copolymerization of ethylene/propene and the molar concentration of propene comonomer in the reaction feed was varied. The polymerization results and the physical properties of the copolymer obtained are presented in Table 1. Table 1 and Fig. 1 show that for all catalysts initial rate enhancement effects at low (< 4 mol%) propene concentration are observed. In the case of the two $\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ chain substituted catalysts, the variation of catalytic activity reach a maximum above which the activity slowly decreased with the increase of propene concentration. This is probably due to the lower catalytic activity toward the propene comonomer. However, a sharp increase in the activity on further increasing the propene concentration above 8 mol% with unsubstituted Cp_2ZrCl_2 catalyst is also observed. This case can be explained by the fact that at higher propene concentration the product was totally dissolved in the solvent and the reaction system was homogeneous allowing the comonomer to proceed toward the active centers more easily. It suggests that the activity of the catalyst also varied with the solubility of the copolymer in the solvent.

Comparison of $(\text{CpCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\text{ZrCl}_2$ and Cp_2ZrCl_2 catalyst revealed the effect of substituent $\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ in the Cp ring. $(\text{CpCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\text{ZrCl}_2$ shows higher ethylene homopolymerization activity, while, by contrast, always exhibiting lower activity for copolymerization of ethylene/propene E/P than unsubstituted Cp_2ZrCl_2 catalyst. This indicates that the steric hindrance of $\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ is greater than the

electronic effect in the copolymerization of E/P, as some earlier investigation have found that electron donation by an alkyl substituent increases polymerization rate whereas steric hindrance reduces it^[7, 14].

Table 1. Effect of comonomer addition on catalytic activity and copolymer properties^a

Catalysts	[Propene] in feed in mol%	Activity $\times 10^6$ in g/molM ^b · h	density in g/mL	T_m in °C	X_c^c in %	$M_v \times 10^{-5d}$
(CpCH ₂ CH ₂ CH=CH ₂) ₂ HfCl	0	0.76		134.58	66.1	5.39
	4	0.86	0.9345	126.84	58.0	4.28
	8	0.70	0.9284	123.82	55.9	3.53
	15	0.62		123.82	55.9	3.53
	20	0.50	0.9228	117.94	43.6	3.13
(CpCH ₂ CH ₂ CH=CH ₂) ₂ ZrCl	0	4.5		137.70	71.1	4.43
	4	5.6	0.9271	126.20	55.4	3.58
	8	4.4	0.9152	123.26	55.4	3.19
	1.5	4.1	0.9152	123.26	55.4	3.19
	20	3.8	0.9103	116.00	42.6	1.85
Cp ₂ ZrCl ₂	0	3.6	0.9103	116.00	42.6	1.85
	4	5.7	0.9156	124.3	56.2	1.62
	8	5.2	0.9076	117.2	48.7	1.08
	20	10.7	0.8997	93.8	48.7	0.12

a) Copolymerization conditions: [Zr] = 20 μ m Al/Zr = 2500, T = 50°C, t = 30 min, [Hf] = 40 μ m Al/Hf = 2500;

b) M = Zr, Hf; c) X_c = crystallinity; d) viscosity average molecular weight

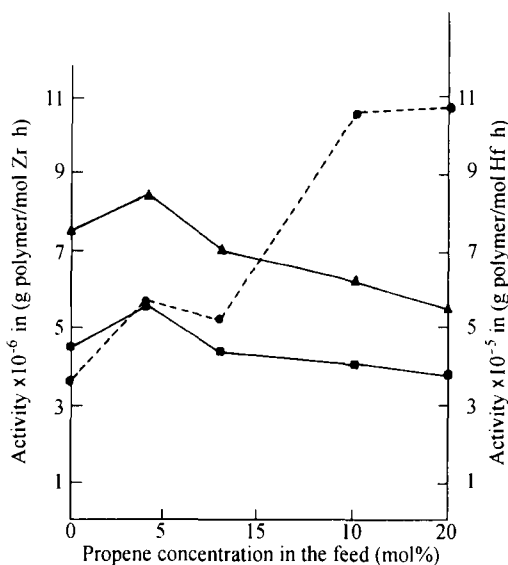


Fig. 1 The dependence of the activity on the propene concentration in the feed activity with different catalysts

● Cp₂ZrCl₂, ▲ (CpCH₂CH₂CH=CH₂)₂HfCl₂, ■ (CpCH₂CH₂CH=CH₂)₂ZrCl₂

The activity of the hafnocene catalyst was 6–8 fold lower than that of analogous zirconocene. This difference may be attributed to the greater number of active sites present in the Zr catalyst.

Composition of Copolymers

Table 2 shows the compositions of ethylene/propene copolymer produced with the different catalysts and measured by ¹³C-NMR. It can be seen that the propene incorporation of copolymer obtained with (CpCH₂CH₂CH=CH₂)₂ZrCl₂ catalyst was only slightly higher than that of (CpCH₂CH₂CH=CH₂)₂HfCl₂ catalyst at the same propene level in the feed. Both the substituted Zr and Hf catalysts have similar sequence distribution and number average sequence length. The unsubstituted Cp₂ZrCl₂ catalyst exhibits higher propene incorporation compared with both substituted metallocene catalysts and also has a different sequence distribution and number average sequence length. This indicates that the effect of CH₂CH₂CH=CH₂ chain in the cyclopentadienyl ring on propene insertion is greater and the effect of transition metal is less pronounced.

The NMR data also show no evidence of any PP diads and hence all the copolymers are random.

Table 2. Sequences and average sequence length

Catalyst	P	E	PP	PE	EE	PPP	PPE	EPE	PEP	PEE	EEE	n _p	n _E
(CpCH ₂ CH ₂ CH=CH ₂) ₂ ZrCl ₂	7.3	92.7	0	14.6	85.5	0	0	7.3	0	14.6	78.1	1	12.7
(CpCH ₂ CH ₂ CH=CH ₂) ₂ HfCl ₂	6.7	93.3	0	13.7	86.3	0	0	67	0	13.7	79.6	1	13.6
Cp ₂ ZrCl ₂	11.9	88.1	0	238	76.1	0	0	11.9	0	23.8	64.3	1	2.4

Copolymerization conditions: [Zr] = 20 mm, Al/Zr = 2800; [Hf] = 40 mm, Al/Hf = 2500; T = 50°C, t = 30 min, [propene] in feed = 20 mol%

Polymer Characterization

The results obtained for molecular weight, density, melting point and crystallinity of E/P copolymer are presented in Table 2.

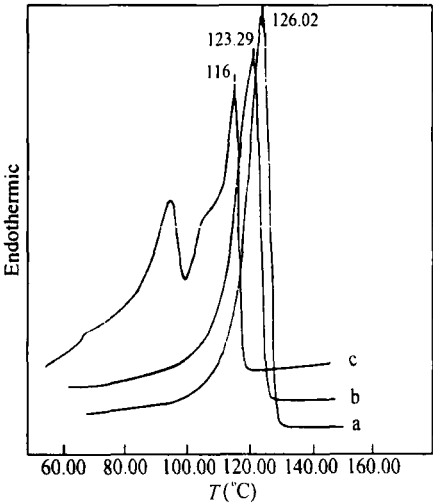


Fig. 2 DSC curves of E/P copolymers produced by (CpCH₂CH₂CH=CH₂)₂ZrCl₂ catalyst with various concentrations of propene in the feed a) 4 mol%, b) 8 mol%, c) 20 mol%

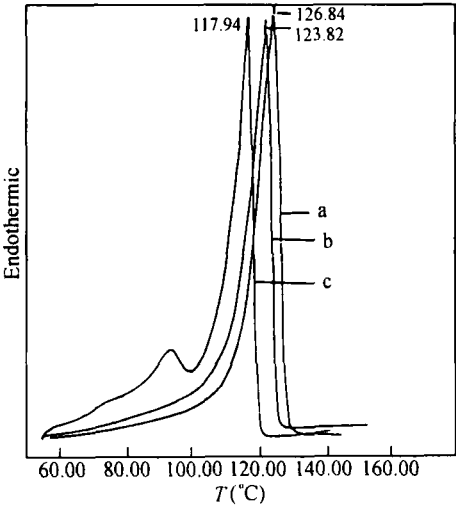


Fig. 3 DSC curves of E/P copolymer produced by (CpCH₂CH₂CH=CH₂)₂HfCl₂ catalyst with various concentrations of propene in the feed a) 4 mol%, b) 8 mol%, c) 20 mol%

As expected, the density, melting point and crystallinity of the copolymers decreased markedly with increasing concentration of propene in the feed, regardless of the type of the catalyst, as can be seen in Table 1. This indicates that the physical properties of the copolymers depend strongly on the concentration of comonomer and are attributed to the increasing incorporation of comonomer into the polymer chain which lowers the polymer chain length. Results from Table 1 also showed that for all the catalysts a decrease in the viscosity average

molecular weight was observed as the concentration of propene in the feed was increased. This can be explained by the chain transfer to the propene. The Hf catalyst produced higher molecular weight copolymer than the analogous Zr catalyst at the same propene level in the feed. The copolymer produced with Cp_2ZrCl_2 had the lowest molecular weight due to the highest incorporation of propene. The density of copolymer produced with Hf catalyst was higher than that of copolymer with analogous Zr catalyst at the same propene concentration whereas the $(\text{CpCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\text{ZrCl}_2$ catalyst produced higher density copolymer than unsubstituted Cp_2ZrCl_2 catalyst.

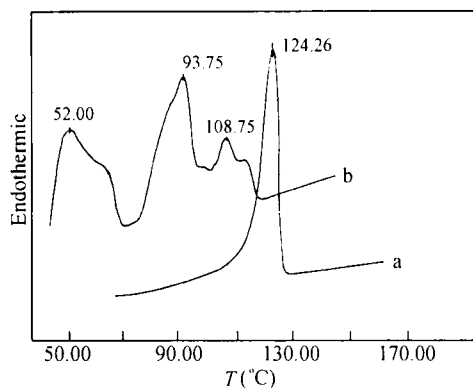


Fig. 4 DSC curves of E/P copolymer produced by Cp_2ZrCl_2 catalyst with various concentrations of propene in the feed
a) 4 mol%; b) 20 mol%

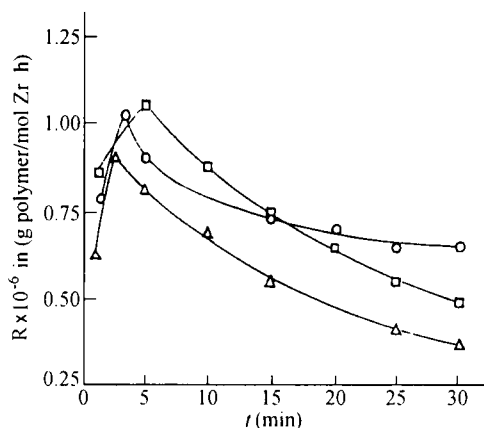


Fig. 5 Kinetic curves of E/P copolymerization with different concentrations of propene over $(\text{CpCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\text{HfCl}_2$ catalyst
Copolymerization conditions: 50 °C, $[\text{Hf}] = 40 \mu\text{M}$, $\text{Al/Hf} = 2500$, concentration of propene: $\square$ 4 mol%, $\circ$ 8 mol%, $\triangle$ 20 mol%

The melt temperature of the copolymers was measured together with melt enthalpy by DSC. By comparison, under the same conditions, both the $(\text{CpCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\text{ZrCl}_2$ and $(\text{CpCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\text{HfCl}_2$ catalysts exhibit little or no difference in the melting point and crystallinity of the obtained copolymers. However, there are significant differences between the two zirconocene catalysts. The copolymers produced by Cp_2ZrCl_2 catalyst have much lower T_m and X_c than those obtained with the $(\text{CpCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\text{ZrCl}_2$ catalyst. This can be attributed to the fact that copolymers produced by Cp_2ZrCl_2 catalyst contain more propene comonomer (Table 2). The DSC curves in Figs. 2–4 show that, as the propene concentration in feed increased to 20 mol%, the peaks became bimodal or multiple in number. According to the findings we can conclude that the molecular weight,

melting point and crystallinity were all strongly affected by the comonomer.

The kinetic behavior of ethylene/propene copolymerization with these catalysts was found to be different. Typical rate-time profiles are shown in Figs. 5~6.

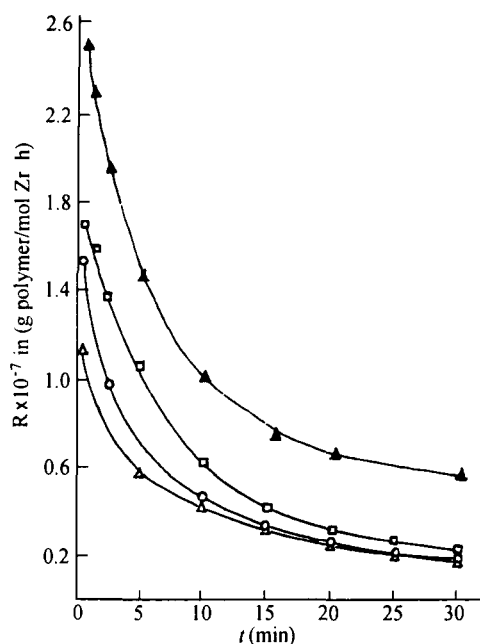


Fig. 6 Kinetic of E/P copolymerization with different concentration of propene over $(\text{CpCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\text{ZrCl}_2$ catalyst Cp_2ZrCl_2 Catalyst copolymerization conditions: 50°C , $[\text{Zr}] = 20\mu\text{M}$, $\text{Al}/\text{Zr} = 2500$, concentration of propene: □ 4 mol%, ○ 8 mol%, △ 20 mol%, ▲ 20 mol% for Cp_2ZrCl_2 catalyst

For the $(\text{CpCH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\text{HfCl}_2$ catalyst the kinetic profiles have an induction period of 3~6 min. After reaching a maximum, the rate decreases gradually with time (Fig. 5), which is similar to ethylene polymerization with Cp_2HfCl_2 catalyst^[1]. In contrast, the maximum rate of copolymerization for both Zr catalysts reaches a maximum within a very short time and then gradually decreases, and the Cp_2ZrCl_2 catalyst behaves somewhat differently with higher maximum rate of polymerization. These results suggest that the active-site formation in the reaction of hafnocene catalyst with MAO is lower than for zirconocene catalyst.

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REFERENCES

- 1 Mallin, D.T., Raush, M.D. and Chien, J.C.W., *Polym. Bull.*, 1998, 20: 421
- 2 Chien, J.C.W. and He, D., *J. Polym. Sci., Polym. Chem. Ed.*, 1991, 29: 1585
- 3 Yao, H. and Xiao, S., *Hecheng Shuzhi Ji Suliao* (Chinese), 1995, 12(4): 7
- 4 Kaminsky, W., Engehausen, R., Zoumis, K., Spaleck, W. and Rohrmann, J., *Makromol. Chem.*, 1992, 193: 1643
- 5 Koivumaki, J., *Polym. Bull.*, 1995, 34: 413
- 6 Heiland, K. and Kaminsky, W., *Makromol. Chem.*, 1992, 193: 601
- 7 Ewen, J.A., in "Catalytic Polymerization of Olefins" (Keii, T. and Soga, K. Eds.), Elsevier, Tokyo, 1986, p.271
- 8 Chien, J.C.W. and Wan, B.P., *J. Polym. Sci., Polym. Chem. Ed.*, 1990, 28: 15

- 9 Huang, Taisheng, M. Sc. Thesis, Chem. Depart. of Nankai University, Tianjin, 1994
- 10 Peng, K. and Xiao, S., *J. Mol. Catal.*, 1994, 90: 201
- 11 Mathot, V.B.F., "Calorimetry and Thermal Analysis of Polymers". Hanser Verlag, Munchen, 1994
- 12 Scholte, G., Meijerik, N.L.J., Schoffeleers, H.M. and Brands, A.M.G., *J. Appl. Polym. Sci.*, 1984, 29: 3763
- 13 Hsieh, H.L and Randall, J.C., *Macromolecules*, 1982, 15: 353
- 14 Chien, J.C.W. and Razavi, A., *J. Polym. Sci., Polym. Chem. Ed.*, 1988, 26: 2369