

Temperature effect on ethylene polymerization with a catalyst prepared by mixing $\text{Mg}(\text{C}_2\text{H}_5)(n\text{-C}_4\text{H}_9)$, $\text{Al}(\text{C}_2\text{H}_5)_{1.5}\text{Cl}_{1.5}$ and iron(II)bis (imino)pyridyl complex

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Summary

Ethylene polymerization was conducted with a catalyst prepared by mixing 2,6-bis{1-[2,6-(diisopropylphenyl)imino]ethyl}pyridine iron dichloride, $\text{Mg}(\text{C}_2\text{H}_5)(n\text{-C}_4\text{H}_9)$ and $\text{Al}(\text{C}_2\text{H}_5)_{1.5}\text{Cl}_{1.5}$ in the presence of common alkylaluminium as cocatalyst. Both the activity and the molecular weight of polymers produced were markedly dependent upon the polymerization temperature. The end-group analysis of polymers showed that the molecular weight of polymers produced at higher temperature was reduced by chain transfer with $\text{Al}(\text{C}_2\text{H}_5)_3$ in addition to β -hydrogen elimination.

Introduction

New late transition metal catalysts for olefin polymerization have recently attracted attention in academics and industry [1-8]. Several researchers have designed a variety of complexes with different ligands to develop a unique olefin polymerization catalyst. Such complexes activated with methylaluminoxane are known to produce unique polymers only by polymerizing ethylene monomer, e.g., polyethylenes with a broader molecular weight distribution or a higher branched structure.

More recently, it has been reported that some iron complexes: iron(II) bis(imino)pyridyl complexes, can promote ethylene polymerization only combined with common alkylaluminium compounds [9-11]. The results strongly suggest that new types of iron-based catalyst will be developed for producing polyethylene in an existing process without a drastic change in its system. However, the conventional iron-based catalysts, e.g., an iron complex combined with common alkylaluminium, can not be utilized for producing polyethylene in a commercial process, because they have no ability to control the polymer morphology. In order to overcome the disadvantage of them, it is necessary to develop a supported iron catalyst [12-15].

From such a view point, we have proposed a new type of MgCl_2 -supported iron catalyst and presented its ability for ethylene polymerization in our patent [16]. We have expected that our experiment might lead to a new development of superior MgCl_2 -supported iron catalysts. In fact, several researchers have developed spherical

MgCl₂-supported late transition metal catalysts, which can produce polyethylene with excellent polymer powder morphology [17-19].

In the present paper, we will first outline our MgCl₂-supported iron catalysts and then discuss the effect of polymerization temperature on their performance for ethylene polymerization.

Experimental

Materials

Commercial, extra pure grade heptane was dried by passing it through a molecular sieve 3 Å column in nitrogen atmosphere. Alkylaluminium compounds, ethyl-*n*-butyl magnesium (both from Tosoh Akuzo Co., Ltd.), ethylene (from Takachiho Chemical Co., Ltd.), anhydrous MgCl₂ (specific surface area: 80m²/g, from Toho Titanium Co.,Ltd.) and other chemicals were commercially obtained and used without further purification.

Preparation of the catalyst

The structures of iron complexes employed are illustrated in Figure 1. The complexes were synthesized according to the literature [1-4]. Catalyst I, II and III-a (Cat.I,II and III-a) were prepared according to the following procedure. 0.24 mmol of Al(C₂H₅)_{1.5}Cl_{1.5} was added to a heptane solution of Mg(C₂H₅)(*n*-C₄H₉) (0.06 mmol in 20 mL) at 25 °C under nitrogen atmosphere. After the mixture was stirred for 2 min, 0.002 mmol of iron complex (dark blue) was added and further stirred for 15 min. The resulting catalysts (light brown) suspended in 20 mL of heptane were used for ethylene polymerization. Catalyst III-b,c,d and e (Cat.III-b,c,d and e) were prepared by the same procedures as those for preparing Cat.III-a except for changing the amount of Mg(C₂H₅)(*n*-C₄H₉) in feed. Catalyst IV (Cat.IV) was prepared by the same methods as those for preparing Cat.III-a except for using 0.25 g of anhydrous MgCl₂ in place of 0.06 mmol of Mg(C₂H₅)(*n*-C₄H₉). The resulting catalyst suspensions (Cat.III-b,c,d,e and Cat.IV) were used for ethylene polymerization.

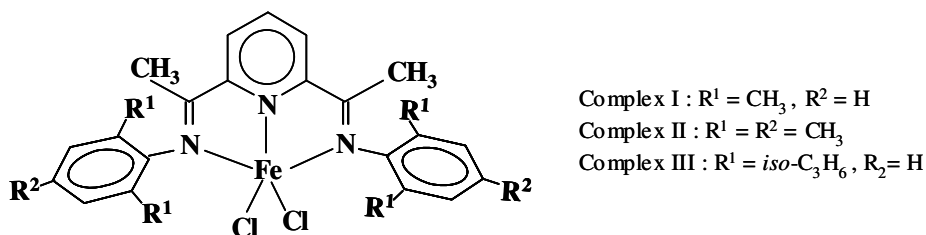


Figure 1. Molecular structures of iron complexes

Polymerization of ethylene

Heptane (400 mL), alkylaluminium (1mmol) and measured amount of the catalyst suspended in 20 mL of heptane (Fe: 0.002 mmol) were added in this order to a 1 L

stainless steel autoclave, which had been purged with nitrogen. The polymerization was started by quickly heating the reactor to the polymerization temperature along with the addition of 8 atm of ethylene. Ethylene was continuously fed at a constant pressure (8 atm). The polymerization rate was determined from the rate of ethylene consumption measured by a mass flow meter with a recorder. Polymers obtained were washed with methanol, filtered off, and dried under vacuum at 80 °C for 4 h.

Analytical procedures

The intrinsic viscosity of the polymers was measured at 135 °C in decalin containing 0.1 % of 1,2,4-*tert*-butyl-4-methylphenol (BHT). The molecular weight (MW) of the polymers were measured by gel-permeation chromatography (Waters Associate, Model 150) with five polystyrene gel columns at 145 °C using 1,2,4-trichlorobenzene (TCB) as the solvent. The MW calibration curve was obtained on the basis of a universal calibration with 10 standard samples of monodisperse polystyrene of MW between 3 600 to 820 000. Differential scanning calorimetry (DSC) measurements were carried out on a Perkin-Elmer 7 series thermal analysis system.

¹H and ¹³C NMR spectra of the polymers were recorded on a JEOL JNM-LA 500 spectrometer operated at 500.16 MHz and 126.65 MHz, respectively, in Fourier transform (FT) mode. The numbers of accumulated transients were 5 000 for ¹H NMR and 50 000 for ¹³C NMR. Solutions were made up in TCB/benzene-*d*₆ (vol.ratio =9/1) to 0.15 g/mL. FTIR spectra were recorded on a Nicolet MAGNA-IR560 spectrometer from 4 500 to 400 cm⁻¹ with a 2 cm⁻¹ resolution for 50 scans. Films of 200 μm thickness were obtained by compression-molding 0.2 g of sample under 6 MPa pressure at 200 °C for 60 sec. The vinyl content of polymers was determined from the peak intensity at 908 cm⁻¹ normalized by film thickness. The peak at 4322 cm⁻¹, which is correctly proportional to the film thickness of samples, was used for the normalization. A calibration curve for determining the vinyl content was obtained with the samples prepared by melt blending the mixture of polyethylene without vinyl group and various amounts of polyethylene with 0.049 mol-% of vinyl group.

Results and discussion

Ethylene polymerization was first carried out at 60 °C for 1 h using various kinds of iron-based catalysts activated with alkylaluminium (cocatalyst). The results are shown in Table 1. All the polymers produced were linear polyethylene (*T*_m: 135-137 °C) with higher molecular weight. The activity of Cat.III-a was much higher than that of Complex III when combined with Al(C₂H₅)₃ (*run 3 vs 12*). The present catalyst preparation is, therefore, effective for displaying the ability of Complex III for polymerizing ethylene.

As described in the introduction, it has been reported that the Complex III- Al(C₂H₅)₃ catalyst can polymerize ethylene with a relatively high activity [10,11]. However, the activity of the catalyst was very low in our experiment (*run12*). The discrepancy probably arose from the difference in the polymerization conditions adopted. A severe control of polymerization conditions may be necessary for employing Complex III- Al(C₂H₅)₃ catalyst for ethylene polymerization.

No polymerization took place only with Cat.III-a, i.e., in the absence of Al(C₂H₅)₃ (*run10*). Moreover, the performance of Cat.III-a was influenced by alkylaluminium

used (*run 3, 8 and 9*). These results show that alkylaluminium as cocatalyst is essential for converting the iron species in the present catalysts into the active species.

Table 1 Results of ethylene polymerization with various kinds of iron-based catalysts ^{a)}

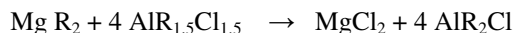
Run	Catalyst	Mg/Al ^{b)} (molar ratio)	Cocatalyst	Activity (kg-PE/g-Fe-h)	[η] ^{c)} (dL/g)
1	Cat.I	0.25	Al(C ₂ H ₅) ₃	80	2.66
2	Cat.II	0.25	"	70	3.05
3	Cat.III-a	0.25	"	317	8.47
4	Cat.III-b	0	"	0.15	-
5	Cat.III-c	0.15	"	148	7.80
6	Cat.III-d	0.40	"	289	8.68
7	Cat.III-e	1.0	"	0.05	-
8	Cat.III-a	0.25	Al(<i>i</i> -C ₄ H ₉) ₃	283	9.87
9	Cat.III-a	0.25	Al(<i>i</i> -C ₄ H ₉) ₂ H	119	7.88
10	Cat.III-a	0.25	none	0	-
11	Cat.IV	-	Al(C ₂ H ₅) ₃	237	11.0
12	Complex III	-	"	0.3	-

a) Polymerization was conducted at 60 °C for 1 h using the iron-based catalyst activated with 1 mmol of alkylaluminium compound

b) Molar ratio of Mg(C₂H₅)(*n*-C₄H₉) to Al(C₂H₅)_{1.5}Cl_{1.5} in the catalyst preparation

c) Intrinsic viscosity, 135 °C in decalin

Both the activity and [η] were strongly dependent upon the kinds of iron catalysts prepared. Especially, the Mg/Al ratio in the catalyst preparation markedly affected the activity of the resulted catalysts (*run 3-7*). It is widely accepted that Mg(C₂H₅)(*n*-C₄H₉) is easily chlorinated by Al(C₂H₅)_{1.5}Cl_{1.5} to produce magnesium chloride compounds. In fact, white colloidal solids instantaneously produced when 10 mmol of Mg(C₂H₅)(*n*-C₄H₉) was added to 40 mmol of Al(C₂H₅)_{1.5}Cl_{1.5} in 500 cm³ of heptane (Mg/Al molar ratio in feed: 0.25). The solid product was filtered, washed with plenty of heptane, and dried in vacuum at room temperature. Analysis of the product (white powder) thus obtained and the liquid phase transferred to another vessel at the filtration process revealed that MgCl₂ (Cl/Mg molar ratio in the solid product: 2.1) and AlR₂Cl (Cl/Al molar ratio: 1.0, R: alkyl group) were mainly produced in the reaction. Accordingly, the following reaction proceeded to provide an optimum catalyst formed at 0.25 of Mg/Al ratio, i.e., Cat.III-a



where the ethyl and *n*-butyl groups are represented by R for the simplification.

Since the catalysts prepared at 0 and 1.0 of Mg/Al ratio, at which MgCl₂ hardly produces, did not promote ethylene polymerization (*run 4 and 7*), the formation of MgCl₂ is a critical process of the present catalyst preparation. The formation of MgCl₂-supported iron catalyst is supported not only by the results obtained with Cat.IV which was prepared with MgCl₂ as a starting material (*run 11*) but also by the literature reported by Mao et al [18,19].

Ethylene polymerization was then conducted by changing the polymerization temperature with Cat.III-a-Al(C₂H₅)₃ system which showed the highest activity. The

activity and M_n of polymers obtained are plotted versus polymerization temperature in Figure 2. The M_w/M_n and M_z/M_w values of polymers are also shown as an index for molecular weight distribution. The activity was nearly constant in the 40-60 °C range but drastically decreased at higher temperatures. Whereas, M_n of polymers monotonously decreased with temperature. Moreover, the molecular weight distribution increased with temperature, suggesting that the increase in temperature brings about the increase in the inhomogeneity of the active species formed. Similar results have been reported by Mao et al. in ethylene polymerization using spherical $MgCl_2$ -supported iron catalysts combined with $Al(C_2H_5)_3$ [18,19]. However, their data are not sufficient for discussing such a drastic change in both the activity and the molecular weight of polymers produced.

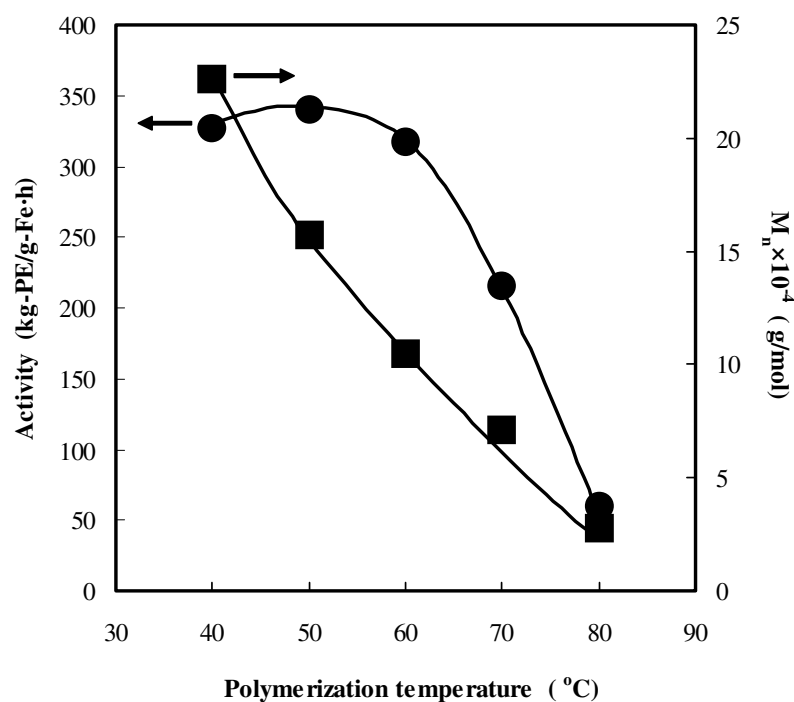


Figure 2. Activity and M_n of polymers as a function of temperature for ethylene polymerization with Cat.III-a- $Al(C_2H_5)_3$ catalyst

M_w/M_n ; 5.0 (40 °C), 5.4 (50 °C), 6.5 (60 °C), 6.7 (70 °C), 9.1 (80 °C)

M_z/M_w ; 2.7 (40 °C), 3.1 (50 °C), 3.9 (60 °C), 4.9 (70 °C), 7.4 (80 °C)

To get useful information on the change in the activity, we examined the kinetic curves of polymerization conducted at different temperatures. As illustrated in Figure 3, the rate-decay is pronounced by raising temperature. The drastic decrease in the activity shown in Figure 2 is, therefore, attributed to the deactivation of active species during the polymerization.

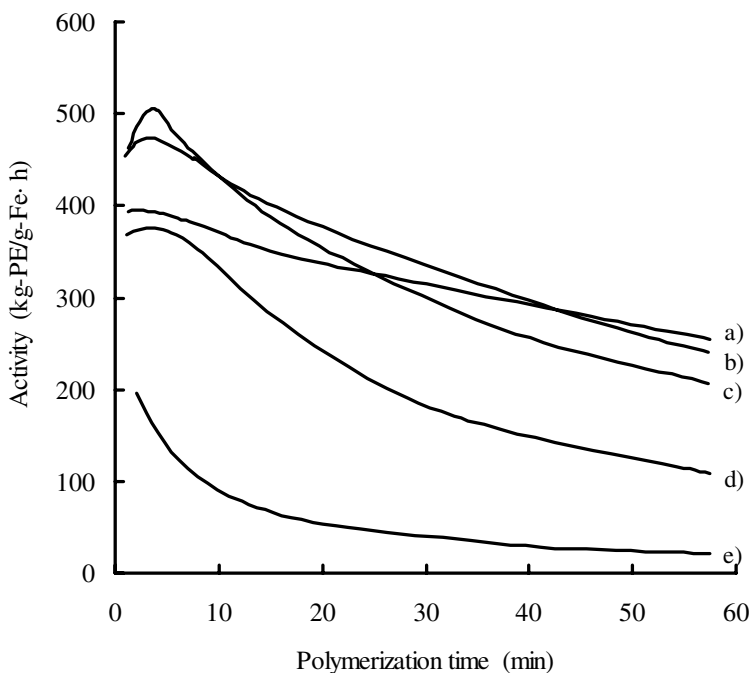


Figure 3. Kinetic curves of ethylene polymerization with Cat.III-a - $\text{Al}(\text{C}_2\text{H}_5)_3$ catalyst at a) 40 °C, b) 50 °C, c) 60 °C, d) 70 °C, e) 80 °C

Then, we investigated the polymerization mechanisms through the analysis of end-group of polymers plotted in Figure 2. The polymer produced at 80 °C was first analyzed by ^1H and ^{13}C NMR. The ^{13}C NMR is illustrated in Figure 4. Several weak resonances were observed besides the strong resonance attributable to main chain methylene carbons ($\delta = 30$ ppm). These signals were assigned to the chain-end *n*-butyl ($\delta = 14.1, 22.9, 29.6$ and 32.2 ppm) and vinyl ($\delta = 33.9$ and 114.3 ppm) carbons. Weak resonances assignable to the chain-end vinyl protons ($\delta = 2.0, 4.9$ and 5.8 ppm) were also observed in the ^1H NMR spectrum of the polymer. The concentration of the chain-end ethyl, i.e., *n*-butyl and vinyl groups were determined by ^{13}C NMR and ^1H NMR, respectively. Analysis of the end-groups revealed that the polymer contains 0.049 mol-% of terminal vinyl group and 0.12 mol-% of terminal ethyl group. If all the polymers were terminated by β -hydrogen elimination, the concentration of the chain-end vinyl group should be equal to that of chain-end ethyl group. However, the concentration of ethyl group was much higher than that of vinyl group. The results strongly indicate that the molecular weight of polymer produced at 80 °C was reduced not only by β -hydrogen elimination but also by chain transfer with alkylaluminum.

It is very difficult for polymers with higher molecular weight to analyze their end-groups by using NMR. The terminal vinyl group was then analyzed by FTIR to obtain information on the effect of temperature on chain transfer reactions. A clear absorption at 908 cm^{-1} assignable to the vinyl groups was observed in every sample investigated and the peak intensity increased with the polymerization temperature. Table 2 shows the vinyl contents of polymers and the calculated M_n values ($M_n^{\text{calc.}}$)

which were estimated by assuming that all the polymer chains were terminated by β -hydrogen elimination. The vinyl content increased with polymerization temperature. The $M_n^{\text{calc.}}$ values of polymers produced at 40 and 50 °C agree well with the corresponding observed values ($M_n^{\text{obs.}}$), indicating that the molecular weight of the polymers is predominantly controlled by β -hydrogen elimination at lower temperature. Whereas, the $M_n^{\text{calc.}}$ values of polymers produced at higher temperature (60 °C or above) were higher than the corresponding $M_n^{\text{obs.}}$ values. Especially, there was a great difference between $M_n^{\text{calc.}}$ and $M_n^{\text{obs.}}$ at 80 °C. Accordingly, the molecular weight of polymers produced at higher temperature was reduced by chain transfer with $\text{Al}(\text{C}_2\text{H}_5)_3$ in addition to β -hydrogen elimination. From these results, we concluded that the increase in temperature causes the frequency of the reaction between $\text{Al}(\text{C}_2\text{H}_5)_3$ and active iron species.

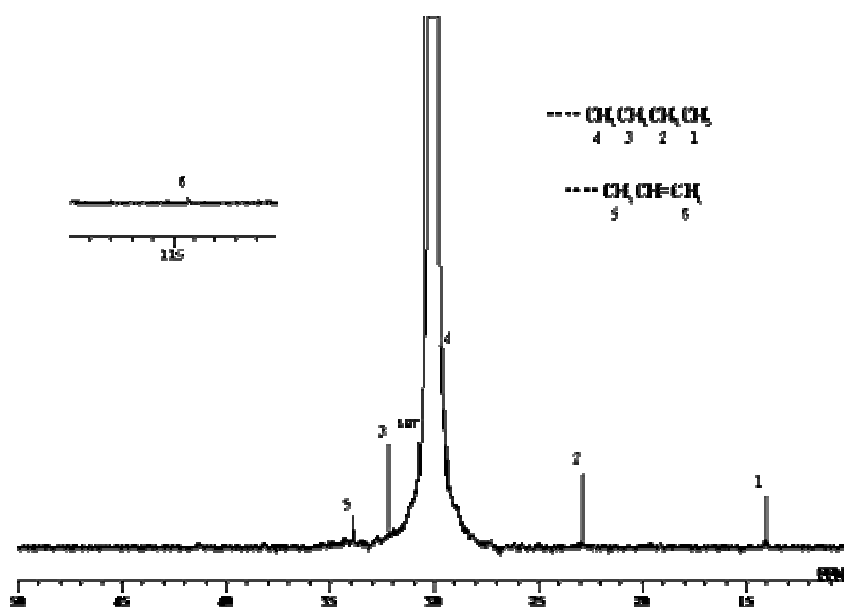


Figure 4. ^{13}C NMR spectrum of polyethylene produced with Cat.III-a- $\text{Al}(\text{C}_2\text{H}_5)_3$ catalyst at 80°C

Table 2. Observed and calculated M_n values of polyethylenes ^{a)}

Temperature (°C)	Vinyl content (mol-%)	$M_n^{\text{calc.}} \cdot 10^{-4}$ (g/mol)	$M_n^{\text{obs.}} \cdot 10^{-4}$ (g/mol)
40	0.011	23	23
50	0.019	15	14
60	0.021	13	11
70	0.032	9	7
80	0.049	6	3

a) The calculated M_n values were estimated by the vinyl content of polymers

Conclusion

We have demonstrated that MgCl_2 -supported iron catalyst can be simply prepared by using iron (II) bis(imino) pyridyl complexes, $\text{Mg}(\text{C}_2\text{H}_5)(n\text{-C}_4\text{H}_9)$ and $\text{Al}(\text{C}_2\text{H}_5)_{1.5}\text{Cl}_{1.5}$. Since such commercial reagents, i.e., Mg and Al compounds have been frequently utilized for preparing highly active MgCl_2 -supported Ti catalysts, the present method might be widely applied for the modification of the conventional catalysts.

The performance of the present MgCl_2 -supported iron catalysts was strongly influenced by polymerization temperature: the increase in temperature brought about a marked decrease in both activity and molecular weight of polymer. The end-group analysis of polymers revealed that the molecular weight of polymers produced at higher temperature was reduced by chain transfer with $\text{Al}(\text{C}_2\text{H}_5)_3$ in addition to β -hydrogen elimination.

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