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The effect of the compostion of heterogeneous polymerization catalyst on ethylene–1-butene copolymerization

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Abstract

The effect of ethylaluminium dichloride (EADC) in the heterogeneous Ziegler-Natta catalyst on the ethylene–1-butene copolymerization and the molecular structure of the resulting copolymer was investigated. SiO_2-supported $TiCl_4$ catalysts having different EADC/Ti molar ratio were prepared by changing the amount of EADC in feed during the catalyst preparation. Ti oxidation states of the prepared catalysts were changed with EADC/Ti molar ratio, and it contained the higher fraction of Ti(3+) and Ti(2+) at the higher EADC/Ti molar ratio. The change in EADC/Ti molar ratio of the catalyst was also shown to influence on the copolymerization performance. Xylene-solublility value corresponding to the fraction having low molecular weight with higher 1-butene content, decreased as EADC/Ti molar ratio decreased. The chemical compositional distribution of PE copolymer was shown not to be affected by EADC/Ti molar ratio of the catalyst significantly.

Keywords: Polymerization; Copolymer; Heterogenous catalysis; Chemical compositional distribution

1. Introduction

Since linear low density polyethylene (LLDPE) was commercialized and considered as an important bulk polymer in the mid-1970s, the copolymerization of ethylene and α-olefins has been studied due to its commercial importance [1,2]. Furthermore, the development of single-site metallocene catalyst boost up again the interest in new LLDPE grades which have not been produced with heterogeneous Ziegler-Natta catalysts, and a strong commercial attention has been paid to metallocene catalysts during the last two decades, resulting in the increase in the production of metallocene LLDPE. However, all LLDPE grades is not believed to be produced by metallocene catalyst, and the heterogeneous Ziegler-Natta catalyst has been rather studied significantly in the polyolefin industries to enhance the catalyst's performances such as the chemical compositional distribution (CCD), the lower risk of lump formation, and higher activity [1–4].

In the copolymerization of ethylene with α-olefins such as 1-butene and 1-hexene with heterogeneous Ziegler-Natta catalyst, the distribution of comonomer fraction in the polymer chains is quite important because it reflects the composition heterogeneity and determines the final properties of LLDPE. The properties of LLDPE are known to depend on molecular weight, molecular weight distribution, comonomer content, and chemical compositional distribution [5].

Ziegler-Natta catalysts are reported to produce ethylene–α-olefin copolymers with a broad CCD due to the heterogeneity in active sites [1,6]. Therefore, the capability of controlling active sites is quite important to optimize LLDPE properties and to ensure trouble-free operation of plant at lower densities [1–5]. In this study, the effect of chemical composition of catalyst on the molecular structures of ethylene–1-butene copolymer was examined with a SiO_2-supported $TiCl_4$ catalyst.

2. Experiments

2.1. Materials

All reactions were performed under a purified nitrogen atmosphere using standard glove box and Shlenk technique. Polymerization grade of ethylene was purified by passing it through columns of Fisher RIDOX catalyst and molecular sieve 5A/13X. Organic solvents were distilled from Na/benzophenone and stored over molecular sieves (4A). All other reagents

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were purchased from Aldrich and used without further purification.

2.2. Synthesis of catalyst

The heterogeneous Ziegler-Natta catalyst was prepared by the reaction of silica with ethylaluminium dichloride (EADC) for 1 h at room temperature, followed by the reaction with the solution of butyloctyl magnesium and 2-ethyl-1-hexanol for 4 h at 35 °C. The resulting catalyst precursor was reacted with $TiCl_4$ for 5 h at 50 °C. The catalyst was washed and dried under a nitrogen flow at 50 °C. The more detailed procedures for the preparation of catalyst were provided elsewhere [7].

2.3. Polymerization and characterization

A 3 L autoclave reactor was used. 1.8 L of isobutane was fed into a reactor as a reaction medium. After adding the solvent, the temperature of the reactor was raised to 85 °C. The catalyst and cocatalyst were fed into the reactor together with a 10 mL of pentane. A 10 wt% heptane solution of triethylaluminium (TEAL) was used as cocatalyst. Al/Ti molar ratio of 20:1 was maintained for copolymerization. The polymerization was started with the feeding of ethylene, and the total pressure during polymerization was maintained at 3.2 bar. Hydrogen was fed into the reactor with ethylene gas in the beginning of polymerization from the small cylinder (500 mL) filled with hydrogen at 3 bar. 1-Butene was fed into the reactor prior to the feeding of ethylene. Melting point and crystallinity for the copolymer were measured by DSC. DSC measurements were made by a PerkinElmer DSC thermal analyzer at a heating rate of 10 °C/min. Comonomer contents in the copolymers were measured by FT-IR method using the absorbance ratios [8]. Crystaf analysis was performed using CRYSTAF model 200 manufactured by PolymerChar S.A. The polymer was dissolved in trichlorobenzene (TCB) at a concentration of 0.1 mg/mL. During the dissolution step, the polymer solution was kept at a temperature of 160 °C for 1 h, then decreased to 95 °C and kept for 45 min. The polymer solution was then cooled at a constant rate of 0.1 °C/min to 30 °C. During the cooling process, aliquots of the polymer solution were collected and transferred to the in-line infrared detector. The infrared detector monitored the change in polymer concentration in solution with temperature, giving intergral Crystaf curve. The differential curve of Crystaf as reported in this article is obtained by numerical differentiation of the intergral curve, and more details are described in the literature [9]. The molecular weight and its distribution was measured by gel permeation chromatography (Waters 150CV) at 135 °C with 1,2,4-trichlorobenzene as solvent. Melt flow ratio, MFR(5) and MFR(21) is the output rate of polymer melt in gram that occurs in 10 min through a standard die of 2.0955 ± 0.0051 mm diameter and 8.000 ± 0.025 mm in length. During the measurement a fixed pressure is applied to the melt via a piston and a load of total mass of either 5 kg (MFR(5)) or 21.6 kg (MFR(21)) at a temperature of 190 °C.

The contents of metals such as Ti, Mg and Al in the catalysts were measured by flame atomic absorption using a nitrous oxide/acetylene flame. Chlorine was determined after dissolution in dilute sulphuric acid by potentiometric titration using a standard sliver nitrate solution. The measurements of Ti oxidation states were performed with about 0.5 g of catalyst. Chien's experimental methods were used to determine Ti oxidation states [10].

3. Results and discussion

To investigate the effect of EADC on the copolymerization performance the amount of EADC feeding during the preparation of catalysts was changed from 0.6 to 1.6 mmol EADC/g silica, and the metal contents and the distribution of Ti oxidation states were analyzed as shown in Table 1. The contents of Al and Cl were increased as the amount of feeding increased, confirming that the effect of Al and Cl on the catalytic performance in the copolymerization could be examined as the purpose of this study. The change in oxidation states was measured with respect to Al/Ti molar ratio in the preparation of catalyst. The distribution of Ti oxidation states were changed depending on the amount of EADC feeding as shown in Table 1. The fraction of Ti(4+) increased with decreasing EADC/Ti ratio, whereas the fractions of Ti(2+) and Ti(3+) decreased, and C-1.0 had highest Ti(4+) contents compared to C-1.2 and C-1.6. It is coincided well with the role of aluminium alkyls in the heterogeneous Ziegler-Natta catalyst, the reduction of Ti to produce the active sites for olefin polymerizations.

Using the C-1.6 catalyst, the copolymerizations with the different 1-butene/ethylene molar ratio from 0.0 to 1.5 in isobutene medium were performed. C-1.6 catalyst was used to be a reference to compare with other less EADC-contained catalysts such as C-1.2 to C-0.6. As a result, the comparison of catalyst performance using different catalyst in copolymerization was decided to be performed under the C_4/C_2 molar ratio of 1.06 in order to prevent a sticky gel-type copolymer.

The ethylene–1-butene copolymerizations were carried out with the C-0.6 to C-1.2 catalysts and compared to that of C-1.6 as shown in Table 2. All copolymerizations revealed to produce the powder type polymers without gel and lump in the reactor.

Table 1
Chemical composition of the catalysts

Catalyst lot	C-0.6	C-0.8	C-1.0	C-1.2	C-1.6
EADC/silica in feed (mmol EADC/g silica)	0.6	0.8	1.0	1.2	1.6
Ti (wt%)	2.07	2.18	1.90	1.88	1.96
Mg (wt%)	2.08	2.20	1.99	1.95	1.97
Al (wt%)	1.22	1.54	1.88	1.96	2.51
Cl (wt%)	9.06	10.11	10.54	11.00	12.55
Al/Ti (mol/mol)	1.05	1.25	1.76	1.85	2.27
Cl/Ti (mol/mol)	5.88	6.21	7.15	7.62	8.60
Ti(2+) (wt%)	–	–	0.12	0.19	0.37
Ti(3+) (wt%)	–	–	0.15	0.26	0.32
Ti(4+) (wt%)	–	–	1.79	1.48	1.20

(–): Not measured.

Table 2
Copolymerization results and properties of copolymers produced different catalysts

Catalyst lot	C-0.6	C-0.8	C-1.0	C-1.0	C-1.2	C-1.6
1-But (mL)	150	150	150	170	150	150
Activity (kg PE/g cat h)	5.65	7.61	8.15	7.85	9.50	7.87
Density (kg/m^3)	924.7	925.3	924.5	922.5	924.8	922.3
Comonomer content (wt%)	3.8	4.0	4.1	5.0	3.9	5.4
MFR(5) (g/10 min)	0.64	1.0	1.1	0.97	1.3	2.8
MFR(21) (g/10 min)	5.6	8.7	8.5	7.6	12.7	21.4
FRR(21/5)	8.7	8.7	8.0	7.9	9.5	7.6
Xylene-solubility (wt%)	1.07	1.23	1.37	2.76	1.17	5.83

A 3 L reactor, 1.8 L of isobutene, 1 h runs, P_t = 3.2 bar, temp = 85 °C, TEAL as cocatalyst, Al/Ti = 20.

The activity in copolymerization showed the maximum with C-1.2 catalyst and it downed to less than 5 kg PE/g cat hr with C-0.6 catalyst as shown in Fig. 1. Fig. 2 indicated the 1-butene content in the copolymer showed the similar comonomer response between C-0.6, 0.8, 1.0 and 1.2, but C-1.6 had higher comonomer response, resulting in the lowest density value of copolymer under the same copolymerization conditions. The melt flow rate (MFR), indicating the hydrogen response of catalyst, were compared as shown in Fig. 3, and the C-1.6 produced the lower molecular weight and molecular weight distribution compared to the other catalysts. It is coincided with the observation that C-1.6 had the higher comonomer response, resulting in the more frequent chain termination reaction due to the presence of 1-butene in the polymer chain. It is also in-line with the observation that FRR(21/5) (flow rate ratio, MFR(21)/MFR(5)) value was down to 7.6 in case of C-1.6.

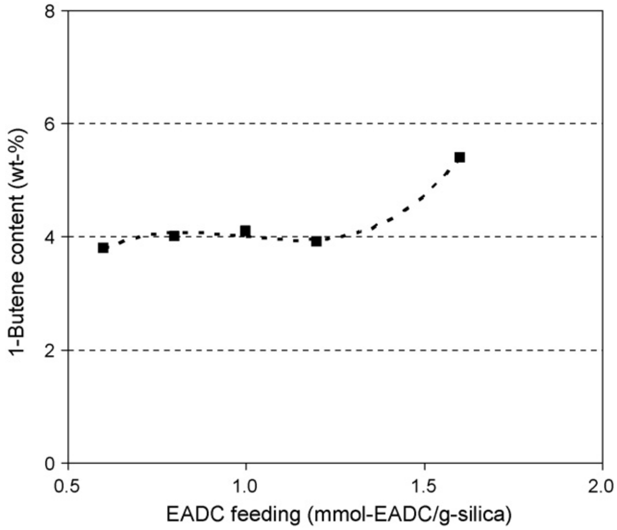

Fig. 2. Change in 1-butene content of copolymers with respect to EADC feeding (mmol EADC/g silica).

To investigate the effect of EADC on the copolymer structure the measurement of xylene-solubility (XS) and Crystaf analysis were performed. The amount of sticky material which could cause a lump formation during the production of LLDPE needs to be estimated in the laboratory scale, and it is closely connected to the microstructure of copolymer. The tendency of blocky insertion of 1-butene of catalyst should increase the fraction of short polymer chains with higher 1-butene content, resulting in higher solubility in xylene solvent at room temperature. It suggests low XS value could necessarily mean the better CCD in the range of lower crystallinity-copolymer which corresponds to the range of lower elution temperature in the cases of temperature-rising elution fractionation (TREF) and Crystaf analysis. As shown in Fig. 4, the XS values from C-0.6 to 1.2 were compared to that of C-1.6, a reference catalyst. The catalyst with the lower EADC content exhibited the lower XS value in the density range of 922–926 kg/m^3. All the lower EADC-contained catalysts decreased XS by about 40%. To observe the CCD of the copolymers, Crystaf analysis was performed and it is shown in Fig. 5. Crytaf analysis has a single-step solution crystallization process, where polymer molecules precipitate at different temperatures according to their crystallizabilities. The different crystallization temperature links to the CCD, the distribution of

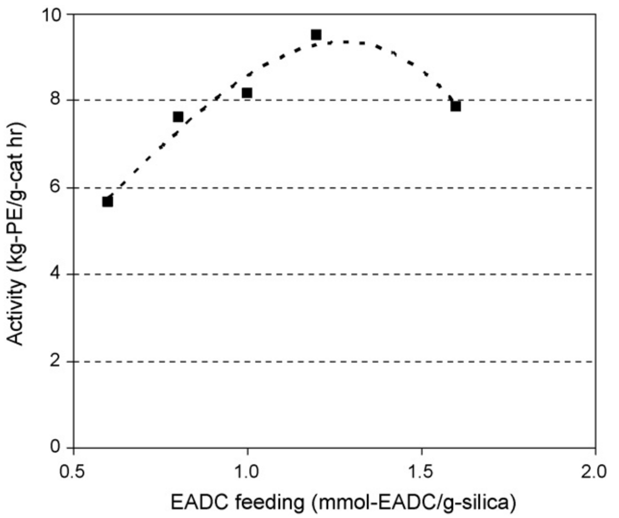

Fig. 1. Change in activity of copolymerization with respect to EADC feeding (mmol EADC/g silica).

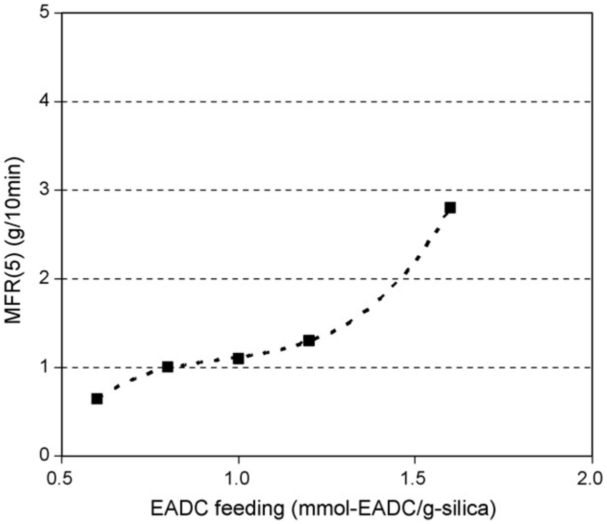

Fig. 3. Change in MFR5 of copolymers with respect to EADC feeding (mmol EADC/g silica).

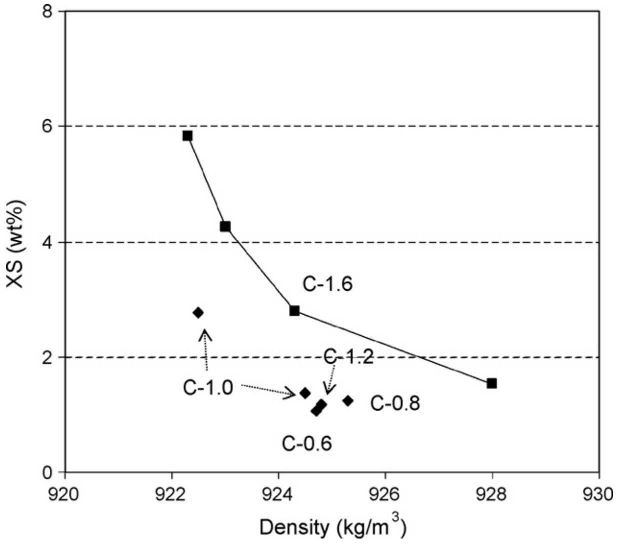

Fig. 4. Change in xylene-solubility of copolymers with respect to EADC feeding (mmol EADC/g silica).

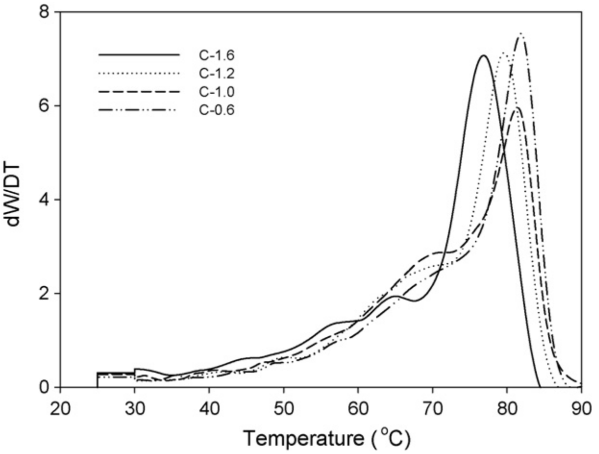

Fig. 5. Crystaf curves of copolymers produced using different catalysts.

comonomer fraction in polymer chains. Polymer chains with low comonomer content crystallize at higher temperature in the polymer solution [9]. Due to the difference in density values, the position of maximum peak was changed and the copolymer with the lower density value such as C-1.6 showed the lowest elution temperature for the peak. Al/Ti molar ratio in the catalyst did affect a little the CCD of ethylene–1-butene copolymer. The shape of Cystaf curve was similar to each others regardless of different Al/Ti ratio.

It has been reported that isolated and multinuclear Ti active sites in the heterogeneous Ziegler-Natta catalyst produced the copolymers with different CCD [4]. Multinuclear Ti active sites were known to show higher comonomer-insertion rate, but CCD became broader. Isolated Ti active sites produce narrower CCD with lower comonomer-insertion rate. Taking the results from XS and Crystaf analysis into consideration, it could lead the fact that isolated Ti active species was formed on the surface of heterogeneous Ziegler-Natta catalyst compared to the higher Al/Ti (or Cl/Ti) molar ratio such as C-1.6. The lower Cl/Al molar ratio could form the less multinuclear Ti active species due to the less amount of chlorine that played a role of bridge between two Ti metals. In addition, the ligands attached Ti metal is expected to be mainly alkoxy group, but not chlorine, meaning the active sites are changed from multinuclear Ti with chlorine to isolated Ti with alkoxy ligand group. It could be concluded that the isolated Ti sites produce ethylene–1-olefin copolymers with less composition heterogeneity and have the lower comonomer response. It did not affect the whole CCD of copolymer, but the fraction of copolymer having higher comonomer content with low MW.

4. Conclusions

The effect of EADC/Ti molar ratio of the heterogeneous Ziegler-Natta catalyst on the copolymerization and its resulting copolymer was investigated. The analysis of Ti oxidation states showed the higher fractions of Ti(3+) and Ti(2+) at the higher EADC/Ti molar ratio. The comonomer and hydrogen responses were dependent on EADC/Ti molar ratio of the catalyst. The less EADC/Ti molar ratio, the lower comonomer and hydrogen responses in the ethylene–1-butene copolymerization. XS value corresponding to the fraction of the low molecular weight with higher 1-butene content, decreased with the decrease in Al/Ti molar ratio. The CCD of whole PE copolymer was not shown to be affected by EADC/Ti molar ratio of the catalyst significantly.

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