Effect of Substituent on Titanocene/MMAO Catalyst for Ethylene/1-Hexene Copolymerization

M. Wannaborworn, B. Jongsomjit, T. Shiono

Abstract—Copolymerization of ethylene with 1-hexene was carried out using two *ansa*-fluorenyl titanium derivative complexes. The substituent effect on the catalytic activity, monomer reactivity ratio and polymer property was investigated. It was found that the presence of *t*-Bu groups on fluorenyl ring exhibited remarkable catalytic activity and produced polymer with high molecular weight. However, these catalysts produce polymer with narrow molecular weight distribution, indicating the characteristic of single-site metallocene catalyst. Based on ^{13}C NMR, we can observe that monomer reactivity ratio was affected by catalyst structure. The r_H values of complex 2 were lower than that of complex 1 which might be result from the higher steric hindrance leading to a reduction of 1-hexene insertion step.

Keywords—Constrained geometry catalyst, linear low density polyethylene, copolymerization, reactivity ratio

I. INTRODUCTION

THE discovery of metallocene catalyst brings to the development of polyolefin, especially linear low density polyethylene (LLDPE). This kind of polymer produces polymer with narrow molecular weight distribution (MWD) due to the single-site system. This leads to an improvement of mechanical polymer properties such as Young's modulus, tensile strength and impact strength [1], [2]. Therefore, it has been used to produce in many applications. Moreover, in the last two decade, Constrained geometry catalyst (CGC) initiated an increasing in the research and development for the LLDPE. It shows the high catalytic performance for copolymerization and has high thermal stability under polymerization reaction. In addition, many researchers have attempted to modify catalyst through the electronic and steric effect of ligand improve the catalytic property such as modification cyclopentadienyl (Cp) ring, variation donor fragment, metal atom and moreover. For example, Cai and coworkers [3] studied the effect of catalyst structure on the catalytic activity and polymer property using *tert*-butyl substituent at 2,7 and 3,6 position on the fluorenyl ring for producing propylene.

M. Wannaborworn is with Center of Excellence on Catalysis and Catalytic Reaction Engineering Department of Chemical Engineering, Faculty of Engineering Chulalongkorn University, Bangkok 10330, Thailand (e-mail: Mingkwan.W@Student.chula.ac.th).

B. Jongsomjit is with Center of Excellence on Catalysis and Catalytic Reaction Engineering Department of Chemical Engineering, Faculty of Engineering Chulalongkorn University, Bangkok 10330, Thailand (e-mail: bunjerd.j@chula.ac.th).

T. Shiono is with Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan (e-mail: tshiono@hiroshima-u.ac.jp).

It was found that the catalytic activity and average molecular weight were affected by the substituent. However, the modification Cp has not been studied so far. In this study, two-*ansa* fluorenyl derivative complexes (complex 1 and 2) (Scheme 1) were selected as a catalyst to copolymerize ethylene with 1-hexene activated by MMAO cocatalyst. The effect of catalyst ligand on catalytic activity, average molecular weight and microstructure of the obtained copolymer was examined.

II. EXPERIMENTAL PART

A. Materials

All operations were carried out under N_2 atmosphere using standard Schlenk techniques. The cocatalyst, modified methylaluminoxane (MMAO) was donated from Tosoh-Finechem Co., Ltd. All solvents for catalyst synthesis and polymerization were commercially obtained and dried with standard methods. Other commercially available reagents were purchased and used without purification.

B. Preparation of catalysts

The *ansa*-fluorenyl titanium (complex 1) was synthesized according to the literature procedure [4]. While the synthetic route for synthesized *ansa*-Oct (complex 2) is described below. The chemical structure of complex 1 and 2 are shown in Fig. 1.
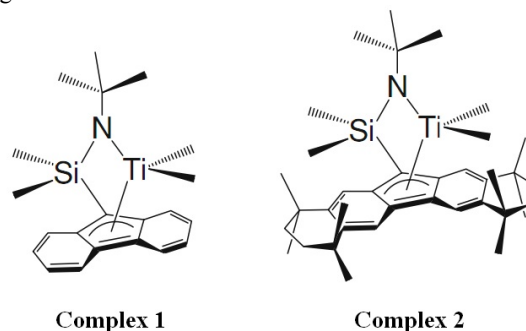

Complex 1   **Complex 2**

Fig. 1 presents the structure of complex 1 and 2

C. Synthesis of [t-BuNSiMe2Oct]TiMe2 ; complex 2

An octamethyloctahydrodibenzofluorene (Oct) was synthesized according to the literature [5]. An amount of 8.54 mmol of n-BuLi was added in the solution of Oct (3.0 g) in Et_2O (200 mL) at 273K, and then the mixture was stirred for 4 h. After that, it was transferred into the flask contained an excess of $(CH_3)_2SiCl_2$ (5.8 mL, 46 mmol) in hexane (40 mL) at 195K and stirred continuously overnight.

All volatiles were removed under vacuum and hexane (130 mL) was added in. The solvent was again removed under vacuum to yield an off-white solid. Next, t-BuNH$_2$ (8.3 mL, 13 mmol) was added in a solution of ClSiMe$_2$Oct in THF (50 mL) at 273K and stirred for 5 h. Then, the precipitated ammonium salt was removed provided an off-white ligand in 90.42% yield. n-BuLi (4.8 mL, 1.60 M) was added dropwise to a solution of ligand (3.0 g, 6.26 mmol) in Et$_2$O (120 mL) which resulting in orange suspension, and then it was stirred at 273K for 4 h. From this suspension, MeLi (15.28 mL, 17.42 mmol) was then transferred into and the reaction was allowed to warm to room temperature. A new flask, TiCl$_4$ (0.76 mL, 6.97 mmol) and hexane (35 mL) were added in, followed by the previously prepared mixture was transferred into. After stirring the solution overnight, the mixture was removed under vacuum and the residue was extracted with hexane 100 mL. This solution was concentrated and cooled at 243K provided red crystals of (t-BuNSiMe$_2$Oct)TiMe$_2$ (complex 2). C$_{37}$H$_{57}$NSiTi: Calcd. C 75.09, H 9.71, N 2; Found C 73.6, H 9.49, N 2.20.

D. Copolymerization

The polymerization was performed in a 100 mL glass reactor equipped with a magnetic stirrer. First, the reactor was charged with toluene and desired amount of MMAO. Then, 1 mL of the complex solution (20 μmol) in toluene was added to start polymerization. The polymerization was terminated by addition of acidic methanol. The precipitated polymer was filtered, washed with methanol, and dried under vacuum at 373K for 6 h.

E. Characterization

^{13}C NMR spectra were conducted on a 125.65 MHz JEOL GX 500 spectrometer with the pulse Fourier-Transform mode at 403K. The sample solution was prepared by dissolving 60 mg of obtained polymer in 1,1,2,2-tetrachloroethane-d$_2$. The ^{13}C NMR was taken with a 45° pulse angle and about 10,000 scans were accumulated in pulse repetition of 5.0 s. The average molecular weight and molecular weight distribution of the ethylene/1-hexene copolymer were measured at 408K in o-dichlorobenzene using Waters 150CV Gel Permeation Chromatography (GPC). The parameters for universal calibration were K=7.36×10-5, α = 0.75 for polystyrene standard.

III. RESULTS AND DISCUSSION

The synthesized catalyst (complex 1 and 2) using MMAO as cocatalyst for copolymerization ethylene/1-hexene were investigated. The results of copolymerization were summarized in Table I.

TABLE I
COPOLYMERIZATION OF ETHYLENE WITH 1-HEXENE USING COMPLEX 1 AND 2/MMAO

Run	1-hexene Feed (M)	Yield (g)	Activity[c]	M_n[d] (×10^{-4})	MWD[d]
1[a]	0.15	0.0227	5	2.5	1.54
2[a]	0.45	0.1290	30	2.2	1.49
3[a]	0.75	0.1335	32	2.1	1.40
4[a]	1.5	0.0510	12	1.1	1.36
5[b]	0.15	0.0299	359	5.1	2.38
6[b]	0.45	0.1093	1312	15.2	1.83
7[b]	0.75	0.1758	2110	19.1	2.09
8[b]	1.5	0.1738	2086	18.4	2.08

[a]Polymerization conditions: Complex 1, Ti=10μmol, MMAO as cocatalyst Al/Ti=400, solvent=toluene, total volume=30mL, temperature=273K, Time= 25 min.
[b]Polymerization conditions: Complex 2, Ti=1μmol, MMAO as cocatalyst Al/Ti=400, solvent=toluene, total volume=30mL, temperature=273K, Time=5 min.
[c]Activity in kg-polymer molTi^{-1}·h^{-1}.
[d]Calculated by GPC.

From Table I, we can notice that the catalytic activity of complex 1 was improved with an increase in the 1-hexene feed concentration. Until the 0.75 M of 1-hexene, the catalytic activity was decreased which might be attributed to the higher steric hindrance around the active sites, making the ethylene monomer difficulty inserted to the metal center [6]. A similar trend was observed in the case of complex 2 system. Moreover, when comparing the catalytic activities between complex 1 and complex 2, it can be observed that the *ansa*-sterically expanded complex 2 exhibited much higher catalytic activity than that obtained from complex 1. The enhancement catalytic activity may be related to the electronic effects of the substituent group on the ligand. The introduction of electron-donating t-Bu groups leads to an increase of electron density at the metal atom caused the improvement of the propagation rate for the ethylene/1-hexene copolymerization. This behavior is consistent with the work done by Price and coworkers [7] whose work revealed that an *ansa*-Oct ligand had a higher electron density compared to fluorenyl ring as confirmed by DFT calculation, and thus resulting in enhanced catalytic activity. The number-average molecular weight (M_n) and average molecular weight distribution (MWD) of the obtained copolymer was determined by GPC. As shown in Table I, it can be observed that complex 2 produced copolymer with higher molecular weight which is probably due to the fact that the presence of t-Bu caused the greater steric hindrance around active site, leading to a reduction in chain-termination step. Moreover, it was found that the molecular weight is also sensitive to the comonomer feed concentration and decreases with increase in the 1-hexene feed. This can be ascribed to the fact that a high concentration of 1-hexene makes more the chain transfer reaction to α-olefin easier [8]. The all polymers produced from each complex exhibited moderate molecular weight with narrow molecular weight distribution (MWD~2), indicating the characteristic for single-site catalyst. From this point, it can be concluded that t-Bu substituent not only increases the catalytic activity, but also increases the molecular weight. Additionally, to investigate the copolymerization behavior, the obtained copolymers were further using ^{13}C NMR. The triad distributions and 1-hexene comonomer incorporation are presented in Table II.

TABLE II
TRIAD DISTRIBUTION OF ETHYLENE/1-HEXENE COPOLYMERIZATION

Complex	H in Feed [M]	Triad distribution of copolymer						$H^{a)}$ [mol%]
		EEE	EEH	HEH	EHE	EHH	HHH	
1	0.15	0.672	0.086	0.087	0.130	0.001	0.024	16
1	0.45	0.217	0.033	0.248	0.161	0.206	0.135	50
1	0.75	0.169	0.017	0.242	0.160	0.179	0.233	57
1	1.5	0.172	0.000	0.232	0.125	0.215	0.256	60
2	0.15	0.644	0.050	0.128	0.126	0.052	0.000	18
2	0.45	0.208	0.097	0.228	0.147	0.260	0.060	47
2	0.75	0.096	0.120	0.184	0.145	0.197	0.258	60
2	1.5	0.000	0.182	0.162	0.111	0.286	0.259	66

$^{a)}$ 1-hexene in copolymer calculated by ^{13} C NMR

From Table II, it can be seen that the comonomer incorporation in all systems gave copolymers with similar triad distribution. The increase in comonomer concentration enhanced the comonomer incorporation for all of the catalyst systems. Based on the ^{13}C NMR results, the reactivity ratios of comonomer were calculated according to the following equation; [9]

$$r_E = 2[EE]/[EC]X, \qquad r_H = 2X[CC]/[EC] \qquad (1)$$

Where [EE], [EC] and [CC] are the diad distribution in copolymer , X is the mole ratio of ethylene (E) and comonomer (C) in feed at the low conversion (<10%).

In this work, the monomer reactivity ratios were estimated from ^{13}C NMR according to the Finemann-Ross [10] and Kelen-Tüdös method [11].

TABLE III
REACTIVITY RATIOS OF ETHYLENE/1-HEXENE COPOLYMERIZATION

Complex	^{13}C NMR method		Fineman-Ross		Kelen-Tüdös	
	r_E	r_H	r_E	r_H	r_E	r_H
1	3.11	0.35	3.27	0.43	2.07	0.21
2	2.27	0.33	3.09	0.47	2.30	0.32

As seen in Table III, it was found that the r_H values of ethylene/1-hexene copolymerization over complex 1 were higher than those of complex 2. It means that the higher steric hindrance caused by the presence of substituent make the difficult for 1-hexene to incorporate, resulting in the lower 1-hexene reactivity ratio. The r_H values are small, indicating the tendency to form long 1-hexene sequence are

small. Based on ^{13}C NMR result, it implies that 1-hexene coordination and insertion at the active site were strongly affected by the catalyst structure. In addition, it can be observed that the $r_E \cdot r_H$ values obtained from all titanium complexes are closed to 1, meaning a random copolymer were produced in these systems.

IV. CONCLUSION

In this study, the influence of catalyst structure on the catalytic activity and polymer properties were investigated. It indicates that the fluorenyl ring substitued by t-Bu groups showed higher catalytic activity and produced copolymer with higher molecular weight than the catalyst without substituent. Moreover, the substituent also affected the monomer reactivity ratio, confirming by ^{13}C NMR.

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