

# Ethylene-hexene copolymer derived from [t-butylfluorenylsilyl-amido] dimethyl titanium complex

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**Abstract.** The copolymers of ethylene and 1-hexene were prepared with half-metallocene titanium complex ([t-BuNSiMe<sub>2</sub>Flu]TiMe<sub>2</sub>) and modified methylaluminoxane (MMAO). The initial concentrations of 1-hexene were varied to investigate how the different amounts of comonomer affect on the catalytic activity of copolymerization system and microstructure of the copolymers. It has been found that this catalytic system was not active for hexene polymerization, however, it can be active when ethylene was introduced to perform ethylene-hexene copolymerization. As comonomer, 1-hexene provides positive comonomer effect on the system although very high concentration of 1-hexene was introduced. However, the microstructures of the obtained copolymers, which were examined by <sup>13</sup>C-NMR need to be improved because with highly alternating sequence distribution of comonomer causing them losing some essential specific thermal properties.

**Keywords:** polymer synthesis, molecular engineering, metallocene, copolymer, LLDPE

## 1. Introduction

It is generally presumed that crystallinity of polymer plays an important role in determining the polymer properties, such as mechanical and thermal properties [1, 2]. We have known that, in synthesis of linear low-density polyethylene (LLDPE) by copolymerization of ethylene with  $\alpha$ -olefins, the crystallinity depends mainly on the amount of  $\alpha$ -olefin (comonomer) content in copolymer [3]. So, if the comonomer content can be controlled, properties of copolymer can be also altered. Appropriate crystallinity or comonomer content is varied depending on the application of polymer. The high comonomer content of copolymer has been commercially produced, named plastomers [1]. The advantages of plastomers are low density, high elongation, and low haze in film form. In order to obtain the plastomer derived from the metallocene

catalysts, the open structure of metallocene catalyst is crucial. Half-metallocenes and/or constrained geometry catalysts (CGCs) are subset of general metallocene catalyst, which pose the open structure because they have just one cyclopentadienyl ring (or their family, such as, indenyl or fluorenyl rings) bonded with the group IV transition metal leaving the opposite side of that ring large enough space for comonomer incorporation with less hindrance [4]. Therefore, plastomers or LLDPE with high comonomer content can be obtained with this type of catalyst.

As mentioned, comonomer contents are sensitive to many factors, such as the structure of catalyst, type of catalyst activators and the initial concentration of comonomer in the system. When considering the initial concentration, it has been found that the initial comonomer concentration not only affects

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directly on the comonomer contents, but it also affects on the catalytic activity of system [5, 6]. Therefore, in this present study the effect of the initial comonomer concentration in ethylene-1-hexene copolymerization with half-metallocene is investigated to determine both the catalytic performance and the specification of the obtained copolymers.

## 2. Experimental

### 2.1. Materials

All operations were manipulated under an argon atmosphere using glove box and/or standard Schlenk techniques. The [t-BuNSiMe<sub>2</sub>Flu]TiMe<sub>2</sub> (Ti-complex) was synthesized according to the procedure described by Hagihara *et al.* [7]. Ethylene (polymerization grade) was obtained from the National Petrochemical Co. Ltd., Thailand. 1-Hexene ( $\geq 97\%$ ) was purchased from Aldrich Chemical Company, Thailand and further purified by distilling over CaH<sub>2</sub> for 6 h. Modified methyl aluminumoxane, MMAO [(Me–Al–O–)<sub>m</sub>–(i–Bu–Al–O–)<sub>n</sub>] having 1.86 M in toluene, was donated by Tosoh Akzo, Japan. Toluene (commercial grade) was donated by the Exxon Chemical, Thailand Co. Ltd. It was dried over dehydrated CaCl<sub>2</sub> and distilled over sodium/benzophenone.

### 2.2. Polymerization procedure

Ethylene/1-hexene copolymerization reaction was carried out in a 100 ml semibatch stainless steel autoclave reactor equipped with a magnetic stirrer. At first, the desired amounts of MMAO and the toluene were introduced into the reactor. The titanium complex in toluene (10  $\mu\text{mol}\cdot\text{ml}^{-1}$ ) was put into the reactor to make the  $[\text{Al}]_{\text{MMAO}}/[\text{Ti}]_{\text{cat}} = 400$ . Then, the reactor was immersed in liquid nitrogen. 1-hexene was added into the frozen reactor (to stop or prevent possible polymerization of 1-hexene). The reactor was heated up to the polymerization temperature at 343 K. The polymerization was started by feeding ethylene (0.018 moles) into the reactor. The ethylene pressure and reactor temperature were kept constant during the polymerization (pressure in reactor = 349 kPa (50 psi)). Due to the fixed ethylene consumption (at 0.018 moles), the polymerization time was defined as the time that all ethylene gas was totally consumed (the equivalent pressure drop of 42 kPa (6 psi) was observed). The

polymerization time was recorded to calculate the activity. The reaction was terminated by adding acidic methanol and the material was stirred for 30 min. After filtration, the copolymer obtained was washed with methanol and dried at room temperature.

### 2.3. <sup>13</sup>C-NMR spectroscopy

<sup>13</sup>C-NMR spectroscopy was used to determine the  $\alpha$ -olefin incorporation and copolymer microstructure. Chemical shifts were referenced internally to the CDCl<sub>3</sub> and calculated according to the method described by Randall [8]. Each sample solution was prepared by dissolving 50 mg of copolymer in 1,2,4-trichlorobenzene and CDCl<sub>3</sub>. <sup>13</sup>C-NMR spectra were taken at 333 K using a BRUKER AVANCE II 400 operating at 100 MHz with an acquisition time of 1.5 s and a delay time of 4 s.

### 2.4. Differential scanning calorimetry

The melting temperature of ethylene/1-octene copolymer products was determined with a Perkin-Elmer diamond DSC. The analyses were performed at the heating rate of 20°C/min in the temperature range of 50–150°C. The heating cycle was run twice. In the first scan, samples were heated, and then cooled to room temperature. In the second scan, samples were reheated at the same rate, but only the results of the second scan were reported because the first scan was influenced by the mechanical and thermal history of samples.

## 3. Results and discussion

### 3.1. Reactivity of (co)monomer to catalyst

The catalytic activities based on polymer product are shown in Table 1. It can be seen that there is no catalytic activity for system conducted with only 1-hexene as monomer (**entry 1**). The opposite occurred on **entry 2** for the system that used only ethylene as monomer. It suggests that this half-metallocene catalyst ([t-BuNSiMe<sub>2</sub>Flu]TiMe<sub>2</sub>) is active for ethylene polymerization, but not for 1-hexene polymerization. This result agreed with the finding of Intaragamjon *et al.* [9], who reported that this catalyst cannot proceed 1-hexene polymerization under the specified condition. It has been known that ethylene is the most reactive olefin

**Table 1.** Activities of system with various monomer concentrations

Entry	Ethylene <sup>a</sup> [mol/l]	1-Hexene [mol/l]	Time [s]	Weight [g]	Activity <sup>b</sup> (kg polymer/mol Ti .h)
1	0.0	0.6	475	–	–
2	0.6	0.0	475	0.2468	187
3	0.6	0.3	500	1.0596	763
4	0.6	0.6	248	1.4030	2037
5	0.6	1.2	326	1.9241	2125

<sup>a</sup>Ethylene addition into the system

<sup>b</sup>Copolymerization condition: Ti = 10 μmol, Al/Ti = 400, temperature = 343 K, 349 kPa (50 psi) of ethylene pressure was applied

[10], so it can react with itself for polymerization in the absence of any comonomer. Although 1-hexene was not reactive in its homopolymerization, it can be reacted in the system of copolymerization with ethylene (**entry 3–5**). Thus, this should be clarified in this finding that why 1-hexene was not active unless ethylene was introduced together in the system, even with the small amount of ethylene as seen for **entry 5**.

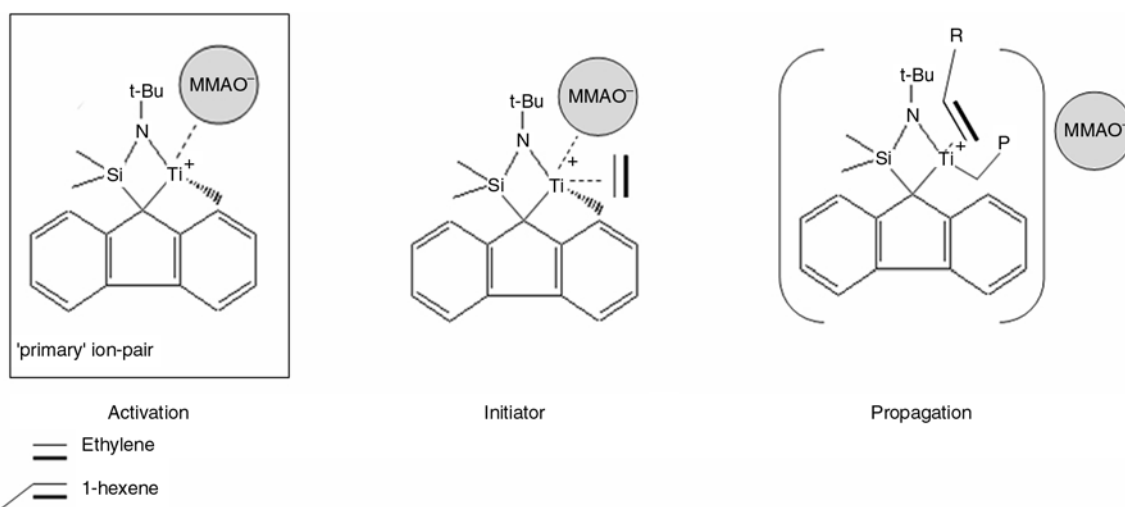
The mechanism of polymerization by metallocene catalyst system is reviewed here to explain the result. There are three main steps for completing the copolymerization (excluding chain transfer step), as shown in Figure 1 [10]. The first step is the ‘activation’ of metallocene catalyst typically achieving via contact with an appropriate cocatalyst species (MMAO in this case). The second is the ‘initiation’ of the polymerization occurring as a result of the displacement of the anion and coordination of the monomer in the primary complex. In our study, this step seems to be a problem for obtaining the 1-hexene polymerization, since the ion-pairs still stay in their coordinated tightly. Therefore, only the strong reactive monomer like ethylene is able to insert in this coordination, and

consequently displace the anion and make coordination with catalyst active site. This step can generate an available coordination site on the metal center, which provides high enough space for a large molecule, such as 1-hexene to coordinate with it in the next step. As the result, the final step that is the ‘propagation’ step will be the open competition between ethylene monomer and 1-hexene comonomer for insertion into the growing chain of polymer.

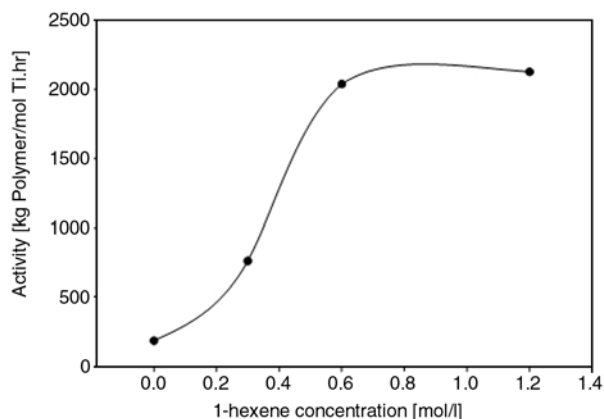
As describe above, for this catalytic system, if ethylene was not introduced into the system first, 1-hexene would not be reactive for this half-metallocene catalyst even open structure. However, in many cases, 1-hexene can perform polymerization by itself with some metallocenes such as *i*Pr(Cp)(Flu)ZrCl<sub>2</sub> and En(Ind)<sub>2</sub>ZrCl<sub>2</sub> [11] indicating that reactivities of α-olefin also depend on the catalyst structure [12].

### 3.2. Effect of the amount of 1-hexene on catalytic activity

In **entry 3–5**, introducing of 1-hexene into copolymerization enhanced catalytic activity higher than



**Figure 1.** Schematic representation of copolymerization mechanism



**Figure 2.** Activity profile with various 1-hexene concentrations

that of system without 1-hexene (**entry 2**). When the amounts of 1-hexene were increased, the catalytic activities were also increased. They increased pronouncedly when the amount of 1-hexene was raised from 0.3 to 0.6 mol/l. However, they gradually increased when the amount of 1-hexene was raised two times again from 0.6 to 1.2 mol/l. A comparison of activities is also shown in Figure 2. It can be explained that the first range of increasing is because of comonomer effect in copolymerization behavior [13]. The chain structure of 1-hexene can increase the gap between the cationic active species and counter anion more separately in propagation step (Figure 1). Then, the propagation rate of polymerization can be raised leading to enhancing the activity of copolymerization. However, at 1.2 mol/l of 1-hexene concentration (**entry 5**), the anticipated activity can not be attained. This is because high excess of 1-hexene obstructed active sites of catalyst from reacting with ethylene monomer, and consequently reduce rate of ethylene insertion into the chain of growing polymer. The explanation can be supported by polymerization time of **entry 5**, which was longer than that of **entry 4**. The longer polymerization time suggests that, in **entry 5**, the rate of ethylene consumption for polymerization was slower than that of **entry 4**.

Although the rate of ethylene consumption in **entry 4** was faster, activity or productivity of **entry 5** was higher. This is because initial concentration of 1-hexene of **entry 5** was higher then it can produce more product than **entry 4** did resulting in high catalytic activity for the system.

### 3.3. Effect of the amount of 1-hexene on microstructure of copolymers

As seen in Table 2, the comonomer incorporations apparently increased with increasing the amount of 1-hexene in copolymerization. In this copolymerization process, which fixed the amount of ethylene addition and kept ethylene pressure constant during copolymerization, the incorporation of 1-hexene can be increased by two primary reasons. One is that enhancing the reactivity of 1-hexene or two, diminishing the reactivity of ethylene. It can be seen from Table 2 that reactivities of ethylene decreased dramatically with increasing the concentration of 1-hexene in the system while reactivities of 1-hexene just slightly increased. So, it can be concluded that the initial concentrations of 1-hexene in the system have more effect on the reactivity of ethylene than itself. The increase of 1-hexene reactivity enables it to still incorporate continuously into the growing chain even at high concentration. The open structure of half-metallocene catalyst is one of the important factors that retains high reactivity of 1-hexene and encourages high comonomer incorporation. As compared with the works done by our group previously with normal metallocene, it has been found that with the same initial comonomer concentration in copolymerization, the obtained copolymer from those studies exhibited much lower comonomer incorporation than in this study [14, 15].

On account of the fact that the uniform comonomer incorporation is the key feature for producing low-density plastomer, which exhibited plastic and elas-

**Table 2.** Comonomer incorporation and the reactivity ratios

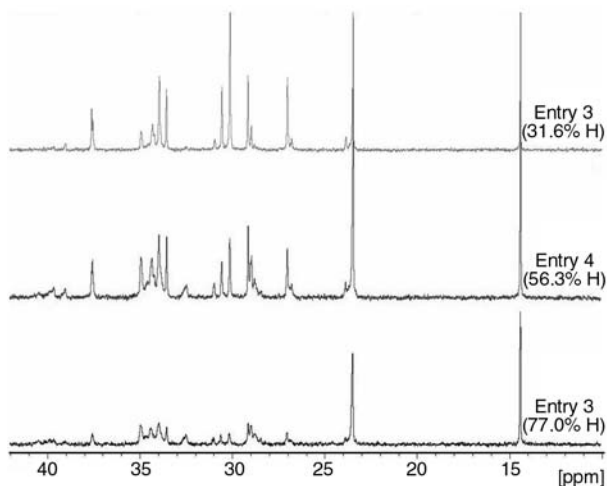
Entry	Ethylene [mol/l]	1-Hexene [mol/l]	Incorporation <sup>a</sup>		Reactivity <sup>b</sup>		
			E [mol%]	H [mol%]	r <sub>E</sub>	r <sub>H</sub>	r <sub>E</sub> r <sub>H</sub>
3	0.6	0.3	68.4	31.6	1.121	0.658	0.737
4	0.6	0.6	43.7	56.3	0.797	0.738	0.588
5	0.6	1.2	23.0	77.0	0.621	0.784	0.487

<sup>a</sup>Examined by <sup>13</sup>C-NMR by Randall method [8]

<sup>b</sup>Relative comonomer reactivities (r<sub>E</sub> for ethylene and r<sub>H</sub> for 1-hexene) calculated by  $r_E = 2[EE]/[EC]X$ ,  $r_H = 2X[CC]/[EC]$ ,  $[EE] = [EEE] + 0.5[CEE]$ ,  $[CC] = [CCC] + 0.5[ECC]$ ,  $[EC] = [CEC] + 0.5[CCE] + [ECE] + 0.5[ECC]$

**Table 3.** Triad distribution of copolymer obtained from  $^{13}\text{C}$ -NMR

Entry	Ethylene [mol/l]	1-Hexene [mol/l]	EEE	EEH	HEH	EHE	EHH	HHH
3	0.6	0.3	0.345	0.292	0.048	0.172	0.144	0.000
4	0.6	0.6	0.091	0.270	0.076	0.185	0.339	0.039
5	0.6	1.2	0.015	0.130	0.085	0.154	0.424	0.192

**Figure 3.**  $^{13}\text{C}$ -NMR spectra of copolymers

tomeric behavior [16], the distribution of comonomer in the copolymers needs to be concerned in order to obtain plastomers with desired specification. The triad distribution for all copolymers obtained from  $^{13}\text{C}$ -NMR is shown in Table 3. Triad block of comonomer (HHH) was detected in samples having 1-hexene incorporation above 31.6% (**entry 4, 5**). It was also noticed from Figure 3, which showed  $^{13}\text{C}$ -NMR spectrum of the copolymers that the peaks between 39.5 and 42 ppm (proportional to the HHH triad) occurred obviously in the copolymer from **entry 4** and **5**. Nevertheless, the number of HHH triad was not converted directly from the area under these peaks. There are other peaks, which are more pronounced in the calculation. Therefore, the larger area of these peaks of **entry 4** than **entry 5** did not mean that **entry 4** had more HHH triad than **entry 5**.

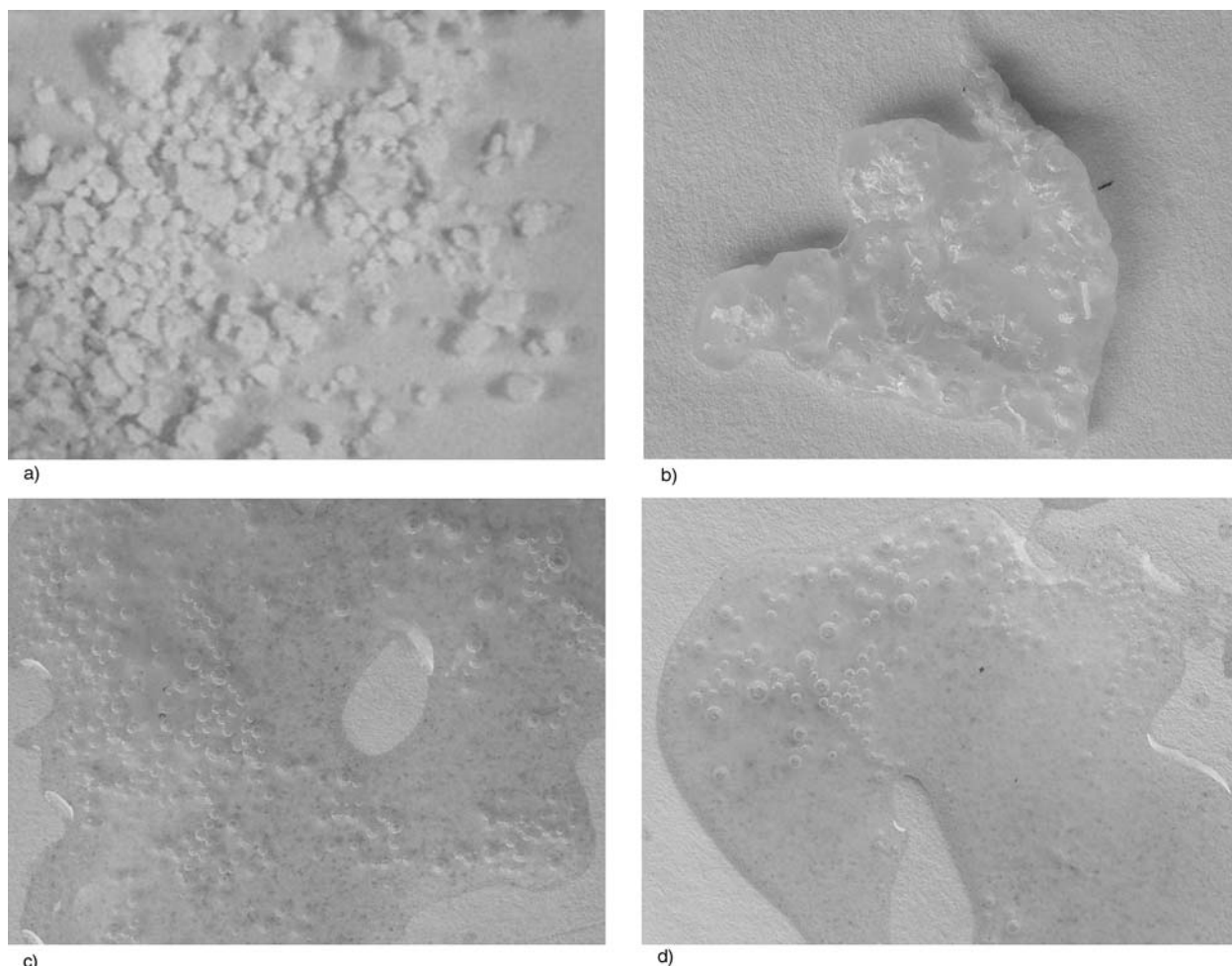
The presence of HHH triad can imply that the good distribution of comonomer throughout the copolymer chain was interrupted at high incorporation of comonomer. Although the copolymers with high 1-hexene incorporation contain the block of comonomer, they are still not the block copolymer. It can be observed from the product of reactivity ratio ( $r_{EH}$ ), which is one of the parameters that can identify types of copolymer. A value  $r_{EH} > 1$  indicates a block copolymer structure and  $r_{EH} < 1$

reveals an alternating copolymer structure. Therefore, all the obtained copolymers are alternating copolymers having the  $r_{EH}$  value being lower than 1. Once the alternating copolymers were obtained, it means the comonomers in their chain are distributed moderately well along the backbone, then shortening the average backbone sequence length for crystallization and therefore low crystallinity, including low density, would be gained. Thus, with these properties, the obtained copolymers are in closing proximity to be low-density plastomer. However, these copolymers might not meet all properties required for the use in plastic industry because they probably lost completely the thermal properties.

As a result of the fact that disadvantages of alternating copolymer, which have been found by Hung *et al.* [17] that the polymer with a highly alternating sequence distribution did not exhibit any melting behavior. Based on the result, when the incorporations of comonomers increased, the obtained polymer tended to exhibit more highly alternating copolymer structure ( $r_{EH} < 1$ ). Therefore, they might lose the melting behavior at high level of 1-hexene incorporation. To prove that, melting temperatures of the obtained polymers were investigated by differential scanning calorimetry (DSC). From the investigation, it was found that only the sample from **entry 2**, which is the polyethylene sample, has the melting temperature (130°C) and the remaining samples cannot be found the melting temperatures. Thus, the losses of thermal properties existed in all obtained copolymers even the one that had low comonomer content (**entry 3**, 31.6%).

Copolymers were formed the gel-like structure as seen in Figure 4 when the 1-hexene was introduced into the system, especially at the high level of incorporation. With this structure, it is obviously shown the character of amorphous material. Therefore, it accords with the results from  $^{13}\text{C}$ -NMR and DSC that the obtained copolymers should not have the melting temperature.





**Figure 4.** Digital photograph of copolymer with various 1-hexene contents a) 0%, b) 31.6%, c) 56.3% and d) 77.0%

#### 4. Conclusions

It was found that the positive comonomer effect occurred even though a very high concentration of 1-hexene that was introduced into the system. However, the microstructures of the obtained copolymer examined by  $^{13}\text{C}$ -NMR need to be improved because the highly alternating sequence distributions of copolymer cause the loss of essential specific thermal properties.

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