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Research Article

Facile Investigation of Ti^{3+} State in Ti-based Ziegler-Natta Catalyst with A Combination of Cocatalysts Using Electron Spin Resonance (ESR)

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Abstract

This study aims to investigate the influences of a combination of cocatalysts including triethylaluminum (TEA) and tri-n-octylaluminum (TnOA) for activation of a commercial Ti-based Ziegler-Natta catalyst during ethylene polymerization and ethylene/1-hexene copolymerization on the change in Ti^{3+} during polymerization. Thus, electron spin resonance (ESR) technique was performed to monitor the change in Ti^{3+} depending on the catalyst activation by a single and combination of cocatalyst. It revealed that the amount of Ti^{3+} played a crucial role on both ethylene polymerization and ethylene/1-hexene copolymerization. For ethylene polymerization, the activation with TEA apparently resulted in the highest catalytic activity. The activation with TEA+TnOA combination exhibited a moderate activity, whereas TnOA activation gave the lowest activity. In case of ethylene/1-hexene copolymerization, it revealed that the presence of 1-hexene decreased activity. The effect of different cocatalysts tended to be similar to the one in the absence of 1-hexene. The decrease of temperature from 80 to 70 °C in ethylene/1-hexene copolymerization tended to lower catalytic activity for TnOA and TEA+TnOA, whereas only slight effect was observed for TEA system. The effect of different cocatalyst activation on the change of Ti^{3+} state of catalyst was elucidated by ESR measurement. It appeared that the activation of catalyst with TEA+TnOA combination essentially inhibited the reduction of Ti^{3+} to Ti^{2+} leading to lower activity. Furthermore, the polymer properties such as morphology and crystallinity can be altered by different cocatalysts.

Keywords: Ethylene polymerization; Ziegler-Natta catalyst; Cocatalysts; Titanium oxidation state; Electron spin resonance

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1. Introduction

Currently, the demand of plastics leads to high productivity of polyolefins, especially films for bags, sheets, and the packaging industry. Plastics are made from different structure of polyolefins such as polyethylene (PE) and polypropylene (PP), but somehow those popularly produced from polyethylene are widely used [1,2]. Linear-low density polyethylene (LLDPE) as linear polymer with short branches is one of the most consumption of PE and importance in industries. LLDPE is produced by copolymeriza-

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tion of ethylene and higher olefins, such as: 1-butene, 1-hexene, 1-octene, etc. The insertion of olefins as comonomer can be obtained differently depending on various comonomer sizes, its content, its structure, catalysts and cocatalysts used, and condition of polymerization. It is well known that types of catalyst play important roles on improvement of polymerization process and activity. The productions of this copolymer normally undergo using supported metallocene catalyst or Ziegler-Natta catalysts (ZN) with proper cocatalysts [3-5]. In fact, the metallocene catalysts as single site catalyst produce polymers with narrow molecular weight distribution (MWD) and chemical composition distribution (CCD) including high insertion of comonomer. Conversely, the Ziegler-Natta catalysts generate polymers with broader MWD and CCD. Although metallocene catalyst is an effective catalyst, it only shows enhancement of 1-olefins insertion in polymer chain without increasing catalytic activity [6]. In industrial scale, the metallocene catalysts can be used in ethylene polymerization [7], but the polymerization system is more sensitive and it requires large amounts of cocatalyst, such as: methylalumoxane (MAO) [5,8,9]. It is necessary to rely on more suitable catalyst for improving properties of polymer and easy control of the catalytic system.

Ziegler-Natta catalyst is one of the most suitable choices of catalysts in the polyolefins industry used to control mechanical polymer properties having high catalytic activity. Furthermore, ZN catalysts still have low cost and less poison. This catalyst must have support for improving morphology, protecting fine particles, and fouling in reactor. Since these titanium catalysts cannot activate themselves, they are essential to use with cocatalyst in olefins polymerization. The cocatalysts or activators are mainly composed of alkyl aluminum compounds, which have been used in polymerization of olefin. Many industries use alkylaluminums such as triethylaluminum (TEA), trimethylaluminum (TMA), tri-iso-buthylaluminum (TiBA), tri-n-octylaluminum (TnOA), and diethyl aluminum chloride (DEAC) in polymerization processes [10-12]. The main function of these alkyl aluminum groups is to reduce the oxidation state of titanium (Ti) complex in catalyst into the suitable active forms for olefin polymerization. As known, ethylene polymerization can occur via both titanium (II) and titanium (III) species, whereas propylene polymerization needs only active titanium (III) ions [13]. Based on many researches, ZN catalyst is more popular for polymerization of ethylene due to its high activity. Thus, this research chose the commercial ZN catalyst for ethylene polymerization and ethylene/1-hexene copolymerization. As well known, LLDPE is produced using the commercial catalyst probably due to increased insertion of comonomer [14]. Hence, the suitable cocatalysts are preferred for reduction of Ti^{4+} to obtain high polymer yields. In addition, alkyl aluminums also scavenge impurities. In this reason, these activators are used in polymerization of ethylene and copolymerization of ethylene/1-olefins with Ziegler-Natta catalysts [14]. Previously, Hongmanee *et al.* revealed the effect of different reducing power of cocatalyst and Al/Ti molar ratios in synthesized ZN catalyst for ethylene polymerization. They showed that TEA exhibited the highest activity and the activity enhanced with increased Al/Ti molar ratios (from 2 to 5). They concluded that an increase in Al/Ti molar ratios can alter the catalytic activity [15]. Later, other researchers suggested that different activators likely increased the insertion of 1-hexene in polyethylene. Furthermore, using different types of single and combination of alkylaluminum compounds for suitable alkyl aluminum groups were investigated [16-18]. Commonly, TEA as activator having high reducing power is preferred. However, several cocatalysts have been also studied. For instance, TnOA was selected because it is also available and has octyl group, which can combine with other cocatalysts. This perhaps facilitate the insertion of 1-olefins and stability of Ti^{3+}. Since the catalyst and cocatalysts in this system are very sensitive to oxygen and moisture, it is a difficult task to characterize the change in catalyst properties under inert condition. Therefore, more powerful techniques are crucial to monitor the change in active sites during activation with cocatalyst and polymerization. One of the most powerful techniques is electron spin resonance (ESR) that can be used to observe the change in Ti^{3+} state in Ti-based ZN catalysts. Although the application of ESR is promising, only few studies [15,19] were used this technique to determine the change in active species in polymerization catalysts.

In this present work, effects of different cocatalyst activation on a commercial Ti-based ZN catalyst on the change of Ti^{3+} state were elucidated by means of ESR. The change in Ti^{3+} state essentially plays an important role on the behaviors of ethylene polymerization and ethylene and 1-hexene copolymerization.

2. Materials and Methods

2.1 Materials

A commercial ZN catalyst (Cat-A) containing ca. 4 wt% of Ti was used. Triethylaluminum (TEA), tri-n-octyl-aluminum (TnOA), and n-hexane for polymerization grade were donated from Thai Polyethylene Co. Ltd. Ethylene gas, hydrogen, and nitrogen were supplied from Linde (Thailand) Ltd. The 1-hexene (1-C_6H_{12}) was purchased from Sigma Aldrich and dehydrated with the 3 Å molecular sieve. All chemicals were prepared under argon atmosphere with glove box and 1-hexene was handled with Schlenk technique under nitrogen atmosphere.

2.2 Polymerization Procedure

The slurry ethylene polymerization and ethylene/1-hexene copolymerization were operated in 2L-autoclave reactor linked with the purified nitrogen, hydrogen, and ethylene gases line and directly connected with purified n-hexane as solvent line. First, all equipment as the reactor and all feed lines were evacuated and purged with nitrogen gas to purify system many times at 70 °C. Then, purging nitrogen gas to fill in for 50 minutes. Next, the reactor was cooled down to 40 °C and 1 L of n-hexane as solvent was filled into the reactor. In case of ethylene/1-hexene copolymerization, 20 mL of 1-hexene as comonomer was injected into the reactor at constant stirring. Cocatalysts [TEA, TnOA and TEA+TnOA (1:1)] were added into the system, followed by injection of desired amount of slurry catalyst at Al/Ti molar ratio equal to 140 and heated up to 70 °C. Then, nitrogen gas was released until steady at 1 bar of nitrogen and pressurized with 3.5 bars of hydrogen gas followed by total pressure of ethylene gas at 8 bars. Polymerization was started at 75 °C and continued for 1 h at 80 °C. Finally, the polymerization was terminated by diluting hydrochloric and methanol. The obtained polymer was dried. The polymer nomenclatures are given as listed in Table 1.

2.3 Measurement of Ti^{3+} State by Electron Spin Resonance (ESR)

Intensity of Ti^{3+} oxidation state was analyzed by electron spin resonance (ESR) technique. The slurry catalyst in n-hexane was prepared and activated by activators as TEA, TnOA, and mixed cocatalysts (TEA+TnOA, 1:1) in glove box. To collect the ESR spectra, the microwave frequency (9.419 GHz) was measured by Bruker Elexys 500 model under *in situ* condition. A typical microwave power 2.005 mW was chosen in ESR method. The ESR tubes were heated to 70 °C and held for 90 minutes. And then, the ESR spectra were captured for each 15 minutes until 90 minutes.

2.4 Characterization of Polymer

The polymer morphology at x50 and x1k micrographs was observed by SEM. Melting temperature of polymer and % crystallinity were analyzed by differential scanning calorimetry (DSC). These measurements were operated in the temperature range from room temperature to 300 °C and heating rate of 10 °C/min. Moreover, calculation of % crystallinity of polymer was conducted based on this following equation as shown in Equation (1). The crystalline phase of obtained polymer was determined with XRD using Bruker of D8 advance model. Diffraction patterns were examined in diffraction angle range of 2θ = 10-80 degree with scan size of 0.02 and scan speed of 0.3 sec/step. ^{13}Carbon Nuclear Magnetic Resonance (^{13}C NMR) using

Table 1. Given polymer nomenclatures depending on different polymerization systems.

Polymer Samples	Nomenclatures		
	Monomer	Activator	Polymerization Temperature (°C)
PE/TEA/80	Ethylene	TEA	80
PE/TnOA/80	Ethylene	TnOA	80
PE/TEA+TnOA/80	Ethylene	TEA+TnOA	80
CoPE/TEA/80	Ethylene/1-hexene	TEA	80
CoPE/TnOA/80	Ethylene/1-hexene	TnOA	80
CoPE/TEA+TnOA/80	Ethylene/1-hexene	TEA+TnOA	80
CoPE/TEA/70	Ethylene/1-hexene	TEA	70
CoPE/TnOA/70	Ethylene/1-hexene	TnOA	70
CoPE/TEA+TnOA/70	Ethylene/1-hexene	TEA+TnOA	70

a high-solution ^{13}C NMR Bruker DRX 500 spectrometer was performed to determine the comonomer incorporation. The samples were measured in benzene-D6 at 125 °C. The ^{13}C NMR was operated pulse angle 90° and pulse interval 12 sec.

$$\%\text{crystallinity}\left(X_c\right) = \Delta H_f \times \frac{100}{291.7\ \text{J/g}} \qquad (1)$$

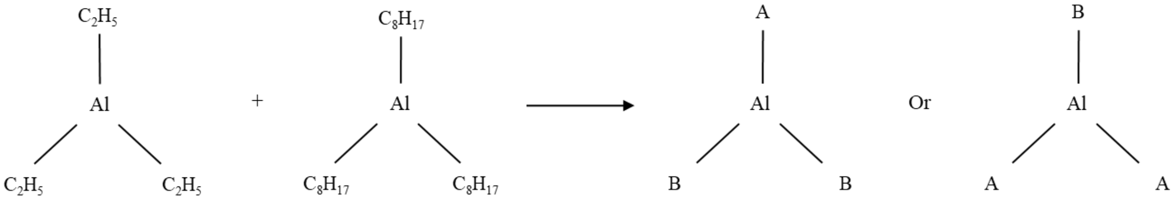
ΔH_f is heat of fusion of polyethylene.

3. Results and Discussion

3.1. Catalytic Activity

Ethylene polymerization and ethylene/1-hexene copolymerization activity data are shown in Table 2. There are four variables studied including bulkiness size of cocatalyst types (TEA and TnOA), a single (TEA or TnOA) and combination (TEA+TnOA) of cocatalysts, polymerization types (homo- or copolymerization) and polymerization temperatures (70 or 80 °C in copolymerization). First, when considered the ethylene polymerization (Runs 1-3), it appeared that TEA (Run 1, PE/TEA/80) exhibited the highest catalytic activity among other cocatalysts including TnOA and TEA+TnOA (Runs 2 and 3). It is known that the larger size of activator group diffuses slower than small one. Thus, the bulkiness of cocatalysts responds to the diffusion of activator through titanium active site, and then catalytic activity. On the other words, the less bulkiness of cocatalysts exhibit high reducing power (TEA > TnOA). Considering in the case of TEA+TnOA, the polymerization activity was in between both activators. It was not surprising since the combination of cocatalysts may result in the random insertion of different alkyl groups from each cocatalyst to form new cocatalyst having mixed alkyl groups as shown in Scheme 1. It is presumable that the reducing power of the mixed cocatalyst should be in the average value, and then giving the average polymerization activity.

In case of ethylene/1-hexene copolymerization (Runs 4-6), the catalytic activity tended to be similar as seen from the homopolymerization system (TEA > TEA+TnOA > TnOA). However, it seemed that the catalytic activities



Scheme 1. The possible new alkyl aluminum to produce suitable activators (A and B refer to randomly -C_2H_5 or – C_8H_{17}).

Table 2. Catalytic activity of ethylene polymerization and ethylene/1-hexene copolymerization under different activator[a]

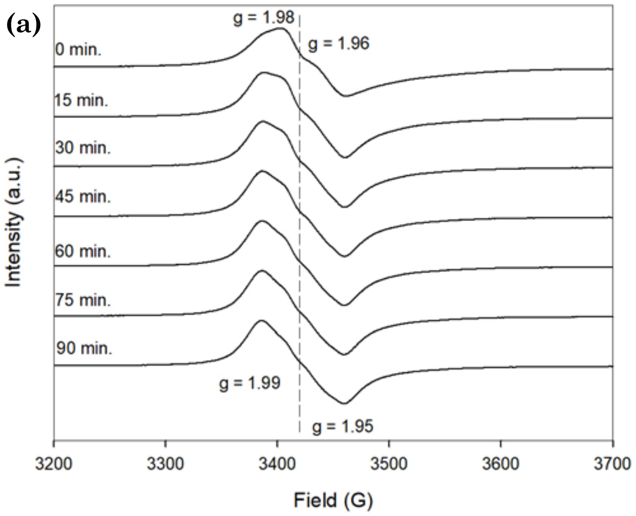
Run number	Polymer Samples	PE yield (g)	Catalytic Activity (kg PE/g Ti.h)
1	PE/TEA/80	297	776
2	PE/TnOA/80	109	285
3	PE/TEA+TnOA/80	185	483
4	CoPE/TEA/80	185	484
5	CoPE/TnOA/80	96	250
6	CoPE/TEA+TnOA/80	167	437
7	CoPE/TEA/70	184	480
8	CoPE/TnOA/70	38	100
9	CoPE/TEA+TnOA/70	133	348

[a] Polymerization condition: 2-L autoclave reactor, catalyst 0.008 mmol Ti, solvent = n-hexane, total pressure = 8 bars, H_2 = 3.5 bars, Al/Ti molar ratio = 140, polymerization time = 1 h, ICP_Ti = 3.99%

for the copolymerization system was lower than those obtained from the homogeneous system for all cocatalysts. It should be mentioned that with the use of TEA (Runs 1 and 4), the catalytic activity of copolymerization system (Run 4) remarkably decreased (from 776 to 484 kg PE/g Ti.h) when compared to the homopolymerization system (Run 1), whereas only slight decrease in catalytic activities of copolymerization system using TnOA (Run 5) and TEA+TnOA (Run 6) was observed. It indicated that the change in active Ti species activated by TEA played a key role on different catalytic activity for both homo- and copolymerization in this specified condition. To study the temperature effect on copolymerization system, the polymerization temperature was lower from 80 to 70 °C (Runs 7 to 9). It revealed that activity decreased with decreasing polymerization temperature for TnOA and TEA+TnOA, whereas it did not affect in case of TEA. It suggested that the use of TnOA was more sensitive to polymerization temperature.

In order to elucidate the change of active Ti species depending on different cocatalysts, the electron spin resonance (ESR), which is one of the most powerful techniques, was performed. It is known that in ethylene polymerization or ethylene/1-hexene copolymerization, $TiCl_4$ (Ti^{4+}) as catalyst was reduced to bulk $TiCl_3$ (Ti^{3+}) by cocatalysts. In this investigation, the *in situ* ESR was conducted at 70 °C after activation of catalyst with different cocatalysts for 90 minutes. The ESR spectra of catalyst activated with various activators are shown in Figure 1 (a) to (c). In fact, the change in Ti^{3+} oxidation state, which was reduced from $TiCl_4$ [20] can be monitored. The major peaks of Ti^{3+} were observed at the g-factor value of 1.95, 1.96, 1.98, and 1.99 in Figure 1 (a) for TEA activation, 1.95, 1.97, 1.98, and 1.99 in Figure 1 (b) for TnOA activation, and 1.94, 1.95, 1.96, 1.97, 1.98, and 2.00 in Figure 1 (c) for TEA+TnOA activation. In the absence of interaction between the catalyst and cocatalyst, peaks at g-factor of 1.98, 1.95, and small peak at g = 1.96 were assigned to tetrahedral Ti^{3+} species, probably lowest Ti/Mg ratios, and interaction between Ti^{3+} and electron donor, respectively. [21] The peak at 1.95 tended to increase with time indicating the transformation of Ti^{4+} to Ti^{3+}. The generation of a new signal at g-value of 1.99 can be assigned to the lowest Ti/Mg stoichiometry. However, addition of TEA results in the disappearance of peaks at g-factor of 1.96 and 1.98 [22,23]. In recent work, more

(a)



(b) (c)

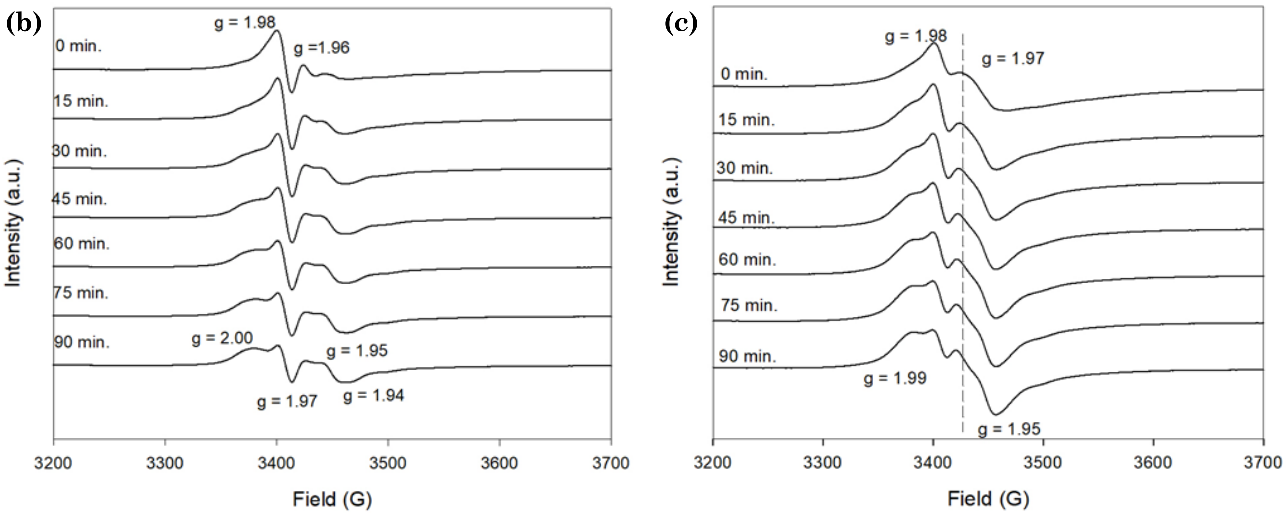


Figure 1. The *in situ* ESR spectra of catalyst activated with different cocatalysts; (a) TEA, (b) TnOA, and (c) TEA+TnOA.

complex EPR spectrum of titanium- magnesium catalysts are commonly observed for signals with wide ranges between 1.89 and 1.99. Figure 1 (b) shows a broad peak with g = 1.99 indicating the lowest Ti to Mg molar ratio and increased signal of g-factor at 1.97 in the ESR spectrum [23,24]. Moreover, the g value at 1.94 refers to six-coordinated Ti^{3+} dissolved in $MgCl_2$ and isolated octahedral Ti^{3+} ions [24,25]. From other researches, ESR spectra of $TiCl_3$ were observed with g = 1.94 along with a new g-factor of 1.97 corresponding to alkylated Ti^{3+} on surface [22,26]. After activation of the catalyst with TEA+TnOA as shown in Figure 1 (c), the appearance of peak at g = 1.98 also assigned to tetrahedral Ti^{3+} and a small signal g value of 1.97 was observed showing the alkylated Ti^{3+} on surface. In addition, the g-value of 1.95 appeared to increase with the activation time indicating the presence of Ti^{3+} ions.

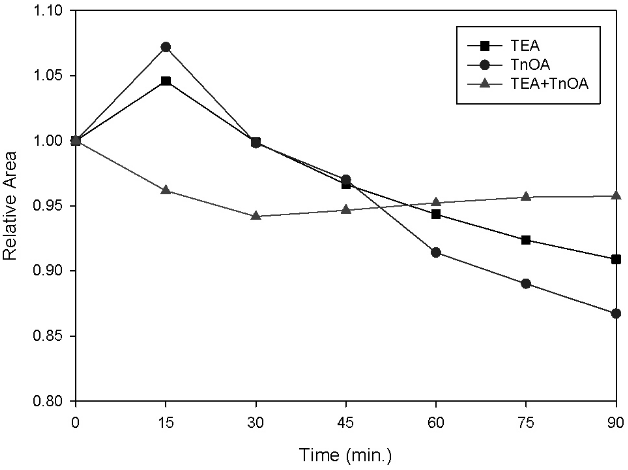


Figure 2. Stability of Ti^{3+} in the catalyst activated with different cocatalysts at 70 °C for 90 min.

For quantitative analysis of Ti^{3+} species, ESR peak area relating to the relative amounts with activation time of Ti^{3+} species was calculated by double integration [15]. In addition, the ESR results obtained from Figure 1 were further calculated by double integration technique and normalized peak areas of interval time to compare with the data at initial time (no activation) to obtain the plot of relative area (corresponding to the amount of changes in Ti^{3+}) with time in Figure 2. In Figure 2, it shows the Ti^{3+} intensity change (relative area) in catalyst and cocatalyst system with time at 70°C. The relative peak area corresponding to the amounts of Ti^{3+} species and activation time are plotted as shown in Figure 2. It was found that the Ti^{3+} amounts of TEA activation tended to abruptly increase within 15 min, and then consistently decrease. Similarly, for TnOA activation, the relative area Ti^{3+} reached the maximum within the first 15 min, and then consistently declined with time. It is worth noting that the Ti^{3+} amounts for TEA+TnOA activation tended to slightly decrease within first 30 min, and then being quite constant with time. On the other words, the Ti^{3+} can be stabilized with the combination of TEA+TnOA. Moreover, all cocatalysts also reduced titanium state from Ti^{4+} to Ti^{3+} and then to Ti^{2+} differently. For TEA activation, it showed the highest catalytic activity in ethylene polymerization because

Table 3. Properties of homopolymer and copolymer with different cocatalysts types and polymerization temperature[a]

Run number	Polymer Samples	T_m [a] (°C)	Heat reaction (J/g)	%Crystallinity[b]	1-hexene insertion[c] (%mol)
1	PE/TEA/80	135.62	210.9	72.3	-
2	PE/TnOA/80	135.15	221.2	75.8	-
3	PE/TEA+TnOA/80	134.60	218.4	74.9	-
4	CoPE/TEA/80	128.63	164.8	56.5	0.67
5	CoPE/TnOA/80	130.61	183.3	62.8	0.38
6	CoPE/TEA+TnOA/80	128.27	172.8	59.2	0.59
7	CoPE/TEA/70	129.86	171.9	58.9	0.40
8	CoPE/TnOA/70	132.73	167.5	57.4	0.29
9	CoPE/TEA+TnOA/70	130.00	179.2	61.4	0.35

[a] Melting temperature (T_m) was analyzed by DSC.

[b] %crystallinity $(X_c) = \Delta H_f \times \frac{100}{291.7\ \text{J/g}}$

[c] analyzed by ^{13}C NMR

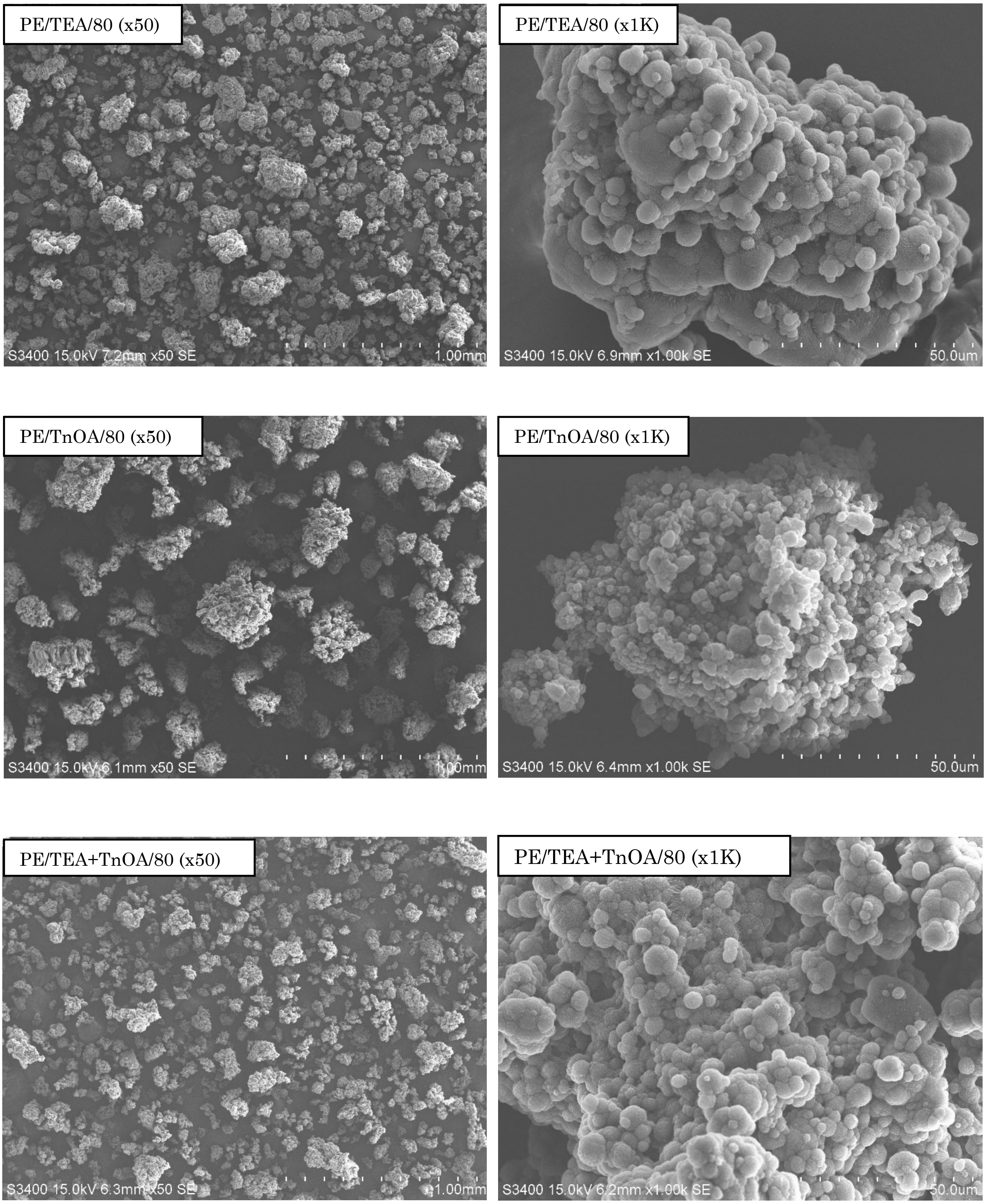


Figure 3. SEM micrographs of the obtained polymer samples

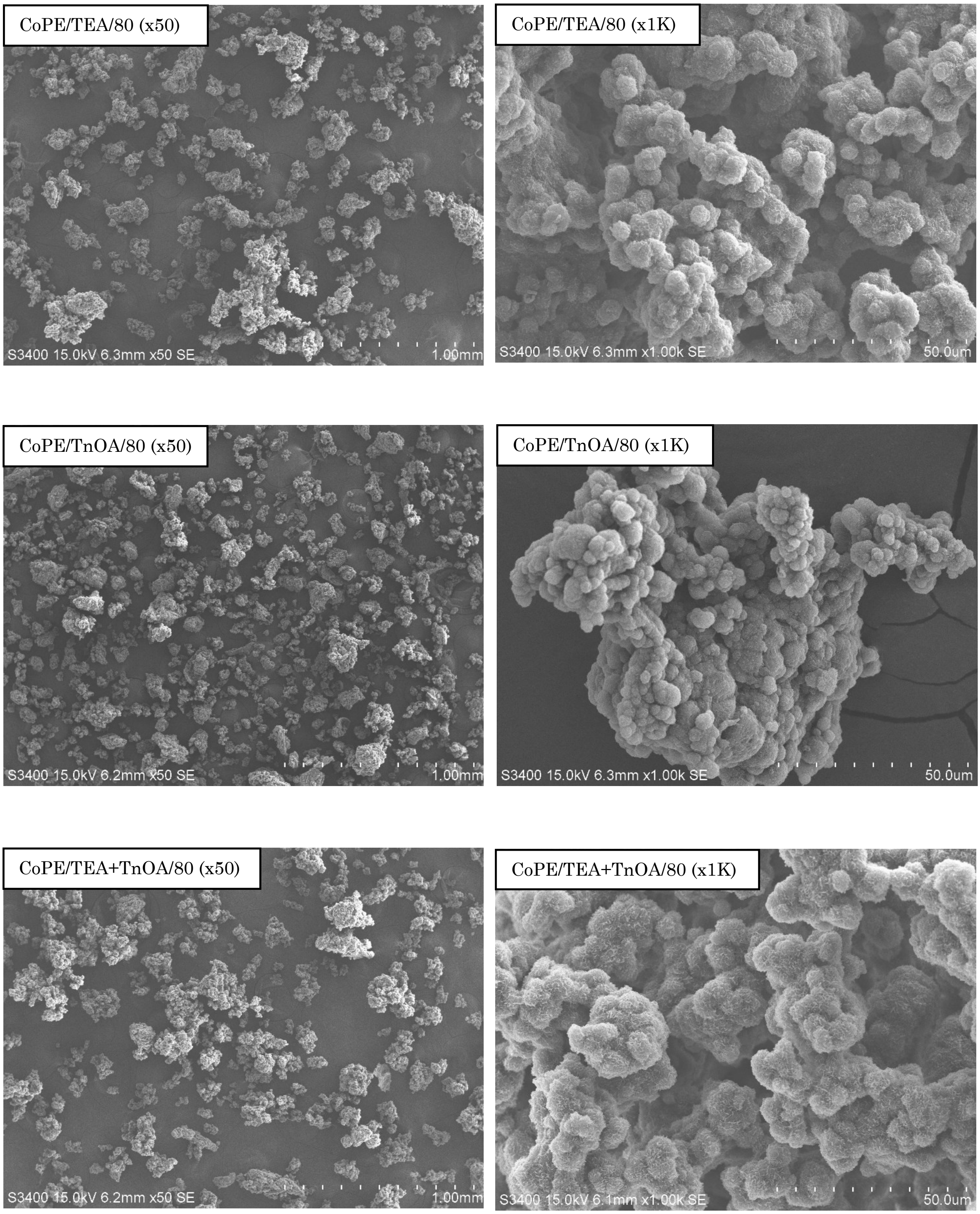


Figure 4. SEM micrographs of the obtained copolymers

ethylene polymerization is active both Ti^{3+} and Ti^{2+}, but Ti^{2+} is recognized to be more active than Ti^{3+} [27,28]. In case of TnOA activation, the catalytic activity was found to be the lowest relating to the lowest relative area of Ti^{3+} because it is too bulky resulting in low reducing power.

3.2. Polymer properties

Morphology of polymers was observed as seen in Figures 3 and 4. The shapes of polymer obtained with different cocatalysts were highly porous and had both small and large spheroidal lump. When compared the polymer samples in Figures 3 and 4, it revealed that no significant differences in morphology of polymers and copolymer obtained from different cocatalysts. The XRD technique was used to ensure the characteristics of polyethylene obtained. The crystal structure of homopolymer and copolymer under ambient condition was confirmed using XRD measurement as shown in Figure 5. All homopolymer and copolymer samples exhibited the two sharp peaks at 2θ degree of ca. 21.6° and 23.8° attributed (110) and (200) plane of polyethylene. Previously, Kageyama *et al.* [29] also confirmed the XRD peaks of polyethylene located at 21.6° and 23.8°. In addition, the intensity of XRD peaks may relate to the degree of crystallinity in polymer obtained from DSC technique under thermal condition. Thus, in this study, we used DSC technique to determine the melting temperature (T_m) and crystallinity of polymer as reported in Table 3. Based on DSC results, %crystallinity of polymer was calculated from heat of fusion and the typical DSC spectra for polymer samples are also shown in Figure 6. However, different types of cocatalysts and variety of polymerization temperature may not affect crystallinity of polyethylene. It is known that increased comonomer insertion would result in decreased crystallinity degree. The decrease in melting temperature perhaps suggests a higher degree of comonomer insertion. It is obvious that T_m of homopolymers (134-135 °C) was higher than that of copolymers (128 to 132 °C). The ^{13}C NMR analysis is one of the most powerful techniques used to determine the degree of comonomer insertion. The % insertion of 1-hexene is also listed in Table 3. The incorporation of 1-hexene into polyethylene slightly improved in the order of TEA > TEA+TnOA > TnOA. However, changing the temperature of polymerization did not have significant effect on the polymer properties.

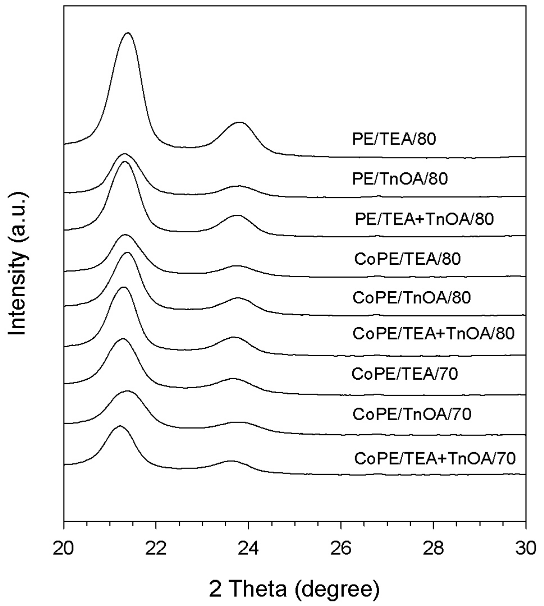


Figure 5. XRD patterns of the obtained polymer samples

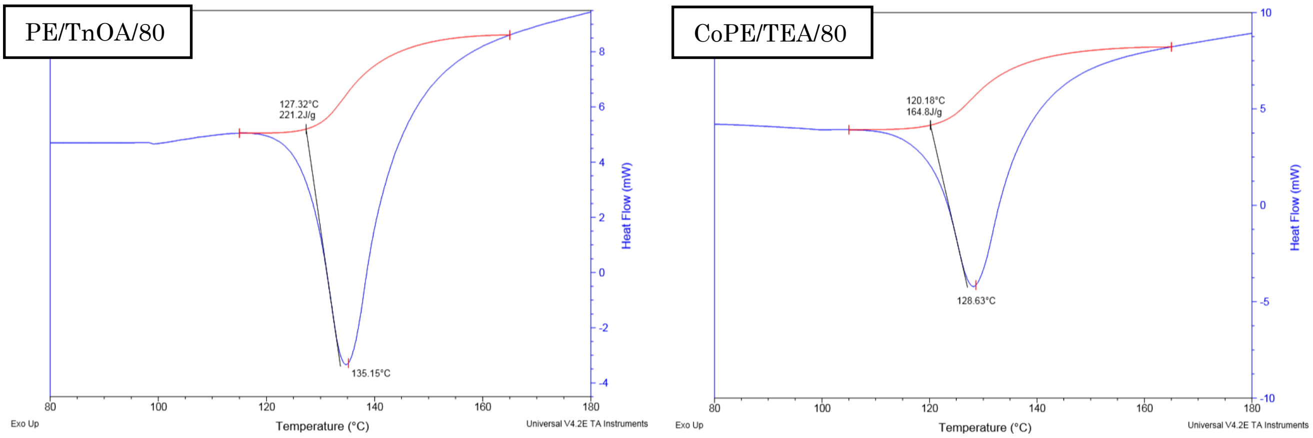


Figure 6. Typical DSC spectra of polyethylene and ethylene/1-hexene copolymers.

4. Conclusions

In summary, the TEA activation exhibited the highest catalytic activity in both ethylene polymerization and ethylene/1-hexene copolymerization. From ESR measurement, it revealed that TEA has high reducing power having more Ti^{2+}, which is highly active for ethylene polymerization. The TnOA activation resulted in the lowest activity due to its lowest reducing power. It was surprising that the use of TEA+TnOA combination to activate ZN catalyst led to increase the stability of Ti^{3+} species, even though it exhibited lower activity in ethylene polymerization. In most case, different cocatalysts did not have significant effect on polymer properties.

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