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Temperature effect on propylene polymerization behavior over Ziegler-Natta catalyst with different cocatalyst systems

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Abstract
This study focused on the effect of temperature in propylene polymerization behaviors up on different cocatalysts employed. It revealed that triethylaluminum (TEA) exhibited higher activity than tri-n-octylaluminum (TnOA) with the optimal temperature of 60 °C, whereas the over reduction of catalyst occurred at 70 °C. However, at low temperature (ca. 50 °C), the mixed cocatalysts (TEA + TnOA) gave the highest activity among the sole cocatalyst. This can be attributed to the occurrence and stabilization of proper Ti oxidation state (Ti3+) form as proven by the electron spin resonance (ESR) with the combination of cocatalysts. In addition, temperatures and types of cocatalyst did not have significant effects on morphology and crystallinity of polymer.

1. Introduction
Titanium-based Ziegler-Natta (ZN) catalyst is widely used in industrial olefins polymerization. Majority of titanium-based catalyst is employed in ethylene polymerization and highly active [1–3]. For ethylene polymerization, this produces more active sites of titanium for both divalent (Ti2+) and trivalent (Ti3+). Hence, these valences are the key to improve catalytic activity in polymerization of ethylene. Besides, the synthesis of this catalyst is not complicated. Therefore, catalysts for ethylene polymerization are usually employed in propylene polymerization with a slight adjustment. For propylene polymerization, it can be catalyzed by only titanium state of oxidation at trivalent [4]. Therefore, the stabilization of Ti3+ is very crucial for this reaction and types of cocatalyst play important roles on this. In the activation process, the catalyst must react with cocatalyst or alkyl aluminum compounds to transform the inactive titanium (Ti4+) into active form (Ti3+). In general, cocatalysts such as triethylaluminum (TEA), tri-iso-butyl aluminum (TIBA), and tri-octyl aluminum (TnOA) are used widely [5–7]. Each cocatalyst or activator has different reducing power depending on the steric hindrance. Thus, the suitable cocatalyst must be chosen in order to stabilize the active form of Ti state [8–10].

Besides types of cocatalyst, polymerization temperature strongly affects the polymerization behaviors. This is because a change in temperature can essentially alter the activation and stabilization of active form of Ti state. In previous study, effect of temperature in propylene polymerization with metallocene catalysts was investigated to produce isotactic polypropylene [11–13]. Based on researches, various temperatures were manipulated and found to differently produce isotactic and syndiotactic polypropylene [14]. These results reveal that both temperature effect and types of cocatalyst play a key role to alter the polymerization behaviors, especially for the stabilization of active Ti species.

Therefore, the present study aims to investigate the effects of polymerization temperature along with different types of cocatalyst on propylene polymerization behaviors using titanium-based ZN catalyst. The polymerization temperature was varied from 50 to 70 °C, whereas TEA, TnOA and mixed TEA + TnOA as cocatalyst were used for each temperature. Moreover, the real time of Ti3+ present during activation of catalyst was monitored using electron spin resonance (ESR). The effects of polymerization temperature up on variation of cocatalyst types can be elucidated by the stabilization of Ti3+ in each catalytic system.
2. Experimental

2.1. Materials
All materials and steps in operation were conducted under oxygen and moisture free system in nitrogen and argon atmospheres using glove box. Polymerization grade of propylene gas (99.9%) and purified nitrogen gas were supplied from Linde Co., Ltd. The commercial titanium–magnesium catalyst (TMC) (ca. 4 wt% of titanium) for propylene polymerization, n-hexane, triethylaluminum (TEA), and tri-n-octylaluminum (TnOA) were donated from Thai polyethylene Co., Ltd.

2.2. Polymerization procedure
The polymerization of propylene was operated in 100 ml semi-batch stainless steel autoclave reactor with magnetic stirrer. All chemicals such as catalyst, cocatalysts (TEA, TnOA, and TEA + TnOA mixtures), and n-hexane as solvent were prepared in glove box. The purification of reactor was evacuated and purged with propylene gas for many times. First, the designed amount of cocatalyst and catalyst was injected into the reactor, consecutively. The Al/Ti molar ratio of 140 was used in this study. Then, 30 ml of n-hexane was introduced under argon atmosphere into the reactor. The polymerization was started by pressurizing with propylene gas to 5 bars. The polymerization time was kept for 15 min at each run and polymerization temperatures were varied at 50, 60, and 70 °C. Then, polymerization was terminated by addition of acidic methanol (HCl in excess methanol). Finally, the precipitated polymer powder was filtered and vacuum dried. The nomenclature of polymers obtained was given as follows;

\[
PP - X - Y
\]

Where;
- **PP** refers to polypropylene
- **X** refers to polymerization temperature in °C (50, 60, and 70)
- **Y** refers to cocatalyst types (A is TEA, B is TnOA, and AB is TEA + TnOA)

2.3. Characterization of catalyst
The commercial Ziegler–Natta catalyst (TMC) was chosen. The catalyst components mainly consist of titanium and magnesium–based compounds. The alkylaluminums such as TEA, TnOA, and mixed TEA + TnOA were used as cocatalyst or activator to obtain proper oxidation state of Ti\(^{3+}\) for propylene polymerization. Besides high catalytic activity, the stabilization of titanium states is crucial for this reaction. It is known that the polymerization temperatures up on different cocatalysts play important roles in polymerization behavior due to the stabilization of titanium active species. Thus, it is captivating to determine the temperature effect with different cocatalysts in this present study. Moreover, the electron spin resonance (ESR) is one of the most powerful techniques used for studying unpaired electrons. In this study, ESR was used to observe the trivalent titanium state (Ti\(^{3+}\)) intensity during the activation of TMC with different cocatalyst system under specified temperature. The Bruker Elexys 500 model of ESR instrument with magnetic frequency of 9.419 GHz was used for this analysis. ESR was performed to elucidate the different activation behaviors regarding to different cocatalyst systems at 50 °C. It was conducted under three different cocatalyst systems including TMC with TEA, TMC with TnOA, and TMC with TEA + TnOA using Al/Ti molar ratio of 140 as being used in polymerization. Besides, ESR was also used to track the change of Ti\(^{3+}\) with time. For each measurement, it was operated at 50 °C for 90 min. The relative amount of Ti\(^{3+}\) as a function of time for each measurement was calculated and compared [15].

2.4. Characterization of polymer
Polymeric crystalline structure of polypropylene and the degree of crystallinity were determined by x-ray diffraction (XRD) analysis. The XRD measurement was performed using Bruker D8 advance model, operating Cu K\(_\alpha\) radiation with step time of 0.3 s and 0.02° of scan size in range of 2θ equals to between 10° and 60°. Differential scanning calorimeter (DSC) was carried out to determine melting temperature of polymer and percentage of polypropylene crystalline. The heat of fusion value obtained from DSC is used to calculate the crystallinity of polymer. This analysis was conducted using TA instruments SDT Q600 V8.1 Build 99 with a heating rate of 10 °C min\(^{-1}\). The range of temperature was scanned from room temperature to 200 °C. % crystallinity (X\(_c\)) can be calculated from equation below [16, 17]

\[
X_c = \frac{\text{heat of fusion of polypropylene} (\Delta H_f)}{100} \times \frac{207 \text{ J }/ \text{g}}{207 \text{ J }/ \text{g}}
\]

Scanning electron microscope (SEM) with JEOL S-3400N of Hitachi mode was used to scan over polymer morphology to obtain SEM micrographs at 20× magnification. The isotactic index (I.I.) of polypropylene was
measured using Soxhlet extraction (Kumagawa extractors). It was performed using 1 g of polymer in 250 ml of boiling n-heptane as extraction solvent for 6 h. The obtained heptane-insoluble residue (as isotactic PP portion) was dried at 70 °C for 16 h, and then weighted.

3. Results and discussion

3.1. Catalytic activity

Table 1 shows the polymerization activity under different temperatures and cocatalysts. Considering polymerized at 70 °C (high temperature) up on different cocatalyst types (Run 1–3), the TnOA (PP-70-B) exhibited the highest catalytic activity followed by TEA (PP-70-A) and mixed cocatalysts (PP-70-AB). It is well known that TEA has higher reducing power than TnOA due to its less steric hindrance. Thus, it would have higher activity than that obtained from TnOA. However, in propylene polymerization, the active site is Ti3+, while Ti2+ is inactive form [4]. Therefore, the over reduction of Ti3+ to Ti2+ was likely occurred with TEA activation at 70 °C resulting in lower activity compared to the system with TnOA activation. The mixed cocatalysts rendered the lowest activity at 70 °C. As we mentioned earlier, the high activity found it at 60 °C apparently led to over reduction of Ti3+ resulting in lower activity compared to the system with TnOA activation. The mixed cocatalysts rendered the lowest activity at 70 °C. When the polymerization temperature was lower down to 60 °C (Run 4–6), the polymerization behavior is quite different. As expected, the TEA activation system exhibited the highest activity (1486 gPP/gTi.h.) among other systems (PP-60-A > PP-60-B > PP-60-AB). This can be attributed to the optimal temperature to activate the catalyst for each cocatalyst system. Moreover, the polymerization temperature at 50 °C (Run 7–9) was also studied. Surprisingly, at this low temperature, it can be observed that the mixed cocatalyst system (PP-50-AB) gave the highest activity (1242 gPP/gTi.h.). It was suggested that the stabilization of Ti3+ at this temperature was suitable for the activation of this catalyst with mixed TEA + TnOA cocatalysts. In order to better understand the temperature effect up on different cocatalyst types, the summarized result is illustrated in figure 1. It can be concluded that for a single cocatalyst system including TEA and TnOA, the optimal temperature for polymerization is 60 °C due to both cocatalysts exhibited high activity. Increased temperature to 70 °C apparently led to over reduction of Ti3+ to Ti2+ resulting in low activity. However, when this polymerization was performed at 50 °C, it is quite interesting that the mixed TEA + TnOA cocatalyst system render the highest activity. As we mentioned earlier, the high activity found it at this low temperature should be related to the stabilization of Ti3+.

The ESR technique detects only unpaired spin of the radicals such as trivalent Ti (Ti3+). In case of Ti-based Ziegler–Natta catalyst, Ti has oxidation state of 4+ at the beginning, and then it is reduced to Ti3+ by cocatalyst in the activation process. However, polymerization of propylene can be energetic with Ti4+ and Ti3+ species. It is attested that active species as Ti3+ of catalyst can be measured from this technique. The obtained ESR raw data between field wavelength (G) and intensity values were captured in every 15 min until 90 min and computed to double integration. Therefore, these data were resulted in normalized peak with no reaction time. Thus, a change of Ti3+ amount with time was plotted in relative area form as seen in figure 2. Figure 2 shows ESR spectra at 50 °C for the catalyst during activation with three different cocatalyst types over a period of 90 min. The relative area of all cocatalysts tended to significantly rise with increased time. For TnOA activation, the relative area of Ti3+ was the lowest and slightly increased at the beginning, and then it was rather constant throughout the measurement. When compared to TnOA, the TEA activation rendered higher relative area of Ti3+ indicating that TEA system exhibited higher activity due to higher amount of Ti3+. This result is in accordance with that as seen from table 1. Moreover, it was found that for the mixed cocatalyst system, the relative area of Ti3+ is the
highest suggesting that this system exhibited the highest activity as also confirmed by the results from table 1. Thus, results from ESR measurement are in agreement with those seen from Run 7–9 in table 1.

It is likely that the mixed cocatalysts generate new active site formation as shown in Scheme 1. From previous theories and literatures, propylene polymerization is active for both 4+ and 3+ of titanium site, but bivalence of the catalyst was not active in reaction. Thus, new active center formation was possibly produced, and then more active centers can stabilize the Ti oxidation state [18–21]. Moreover, it indicated that Ti-based Ziegler-Natta catalyst slowly decomposed or the active centers moderately deactivated. In agreement with at low reaction

Figure 1. Catalytic activity to effect of temperature of propylene polymerization compared with difference activators at Al/Ti = 140.

Figure 2. Relative area correlated with reaction time in effect of cocatalyst types at Al/Ti = 140 and T = 50 °C.
temperature directly replied on propylene chain-transfer because of new cocatalysts model and mainly saved thermal energy. It is surprising that combination of cocatalyst impacts on the increment in the catalytic activity with decreased temperature of reaction. In consequence of new formation model of cocatalysts, it may be due to more stabilization of trivalent titanium can facilitate the yield of polymer \[22-25\]. Hence, it is interesting that stability of \(\text{Ti}^{3+}\) for combination of activators at 50 °C can powerfully confirm from ESR technique.

### 3.2. Polymer characteristics

Morphologies of polymer obtained using different cocatalyst types at reaction temperature of 50 °C were typically displayed as shown in figure 3. All polypropylenes obtained exhibited similar shape. The PP-50-A had characteristic of fluffy pellet, whereas PP-50-B exhibited mostly inflexible fiber. As expected, the PP-50-AB was present as the combination of both PP-50-A and PP-50-B morphologies. The crystalline structure under ambient condition of polymer is simply determined using x-ray diffraction (XRD). The XRD patterns of polypropylene with different cocatalyst types, and polymerization temperature are displayed in figure 4. Typically, it showed two diffraction sharp peaks located at \(2\theta\) angles of 14.2° and 17.2° indicating isotactic PP in (110) and (040) planes, respectively. Moreover, there were also two peaks at \(2\theta\) degree of 18.6° and 21.6° for isotactic PP at planes (130) and (111) reflection \[26, 27\]. At 50 °C, the XRD peaks were sharper than those obtained at 60 and 70 °C. The crystallinity and melting temperature are shown in table 1. It revealed that PP-50-AB exhibited high crystallinity at ca. 40%. The other PPs gave almost similar crystalline value. Based on DSC measurement, polypropylenes have melting temperature about 152 °C–156 °C \[28\]. It can predict that high melting point is related to more isotactic since its better tendency to crystal formation. In addition, isotacticity index (I.I.) indicated the formation of stereoregularities of polypropylene. Combination of cocatalyst also presented more isotacticity polymer than that obtained from a single activator. On the contrary, TnOA activators exhibited the lowest isotactic index because alkyl group of activators maybe blocked to chain-transfer and interaction of propylene. Furthermore, isotacticity also directly affected stereoregularity, and then a stereoregulated adsorption of catalyst active sites \[29-31\]. It is possible that different cocatalyst types attached dissimilar alkyl group around aluminum reported that selectively stereospecific sites to more isotactic. In case of polypropylene, it is possible that catalytic centers had \(\alpha\)-TiCl\(_3\) on surface (random), but \(\beta\)-TiCl\(_3\) surface (linear) appeared to be covered with polymer. Thus, \(\alpha\) and \(\beta\) having arrangements of \(\text{Ti}^{3+}\) state was different. It should be noted that the variation of Ti oxidation state can alter the polymer structure and can be confirmed as also seen from figure 2.
4. Conclusions

Among effects of polymerization temperature (ca. 50, 60 and 70 °C) for three cocatalyst systems, TEA exhibited the highest activity at 60 °C (PP-60-A) for propylene polymerization. At 70 °C, the catalyst seemed to be over reduction to Ti^{2+} leading to decreased activity for each cocatalyst system. When the polymerization temperature was lower to 50 °C, the mixed cocatalyst system rather gave the highest activity. This can be attributed to the stabilization of Ti^{3+} throughout polymerization as proven by ESR measurement. Moreover, isotactic polypropylene obtained can be confirmed from melting temperature around 152 °C–156 °C and XRD patterns.

Figure 3. Typical morphologies of polypropylene in variation of cocatalyst at 50 °C.
indicating the characteristic peaks at 14.2°, 17.2°, 18.6° and 21.6°. It revealed that no significant effect was observed on the polymer properties regarding to the changes of polymerization temperature and types of cocatalysts.

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