

CHAPTER V

RESULTS & DISCUSSIONS

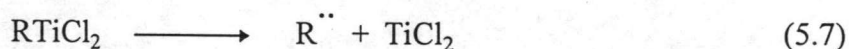
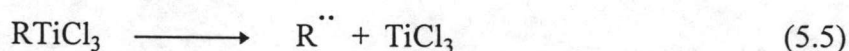
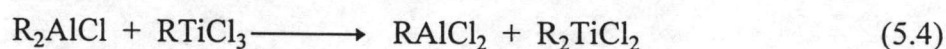
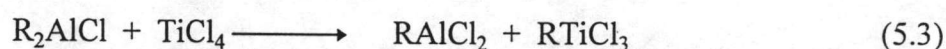
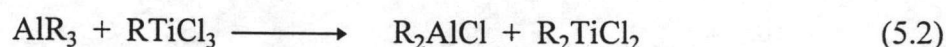
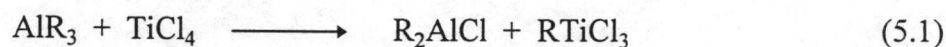
In this thesis, the experiment was successful in preparing supported Ziegler-Natta catalyst for propylene polymerization. This catalyst had higher activity and isotacticity than unsupported catalyst which was studied by Banglap [114].

This study was divided into two parts. To determine the suitable polymerization condition with catalyst, firstly the experiments were done in various mole ratio of catalyst composition, ratio of gas component, total pressure, and polymerization temperature. The external electron donors modified Ziegler-Natta catalyst system were investigated. Finally, the best activity of electron donor was varied in concentrations.

5.1 THE EFFECT OF Al/Ti RATIOS

Catalyst of Ziegler-Natta type composed of two main components, transition metal salt (TiCl_4), and aluminium alkyl (AlEt_3). It is generally believed that the catalyst is a complex of both components [111] and that this complex is in equilibrium with its components [112]. Thus, catalyst ratio could influence polymerization rate and polymerization activity [113]. The specific activity reaches a maximum value and then decreases with increasing ratio for the

system [8,113]. This behavior can be described by the mechanism that were proposed by Lenz [109] and Kirk-Othmer [110]. Alkylation and reduction occurred between both components to form active species for polymerization.



From mechanism above, this reduction involves the alkylation of TiCl_4 with aluminium alkyl molecules followed by a dealkylation reduction to trivalent state, the most active state [8]. Under drastic conditions, TiCl_3 can be similarly reduced to TiCl_2 which is an inactive state. The equations above only suggest the basic step which occur, the actual mechanistic process is very complex and not well understood [40].

From Figure 5.1a, the Al/Ti molar ratio which gave the maximum activity was found to be 170. This ratio is very high compared with unsupported catalyst [114] in Figure 5.1b. The supported catalyst also gave a very high activity as compared to the unsupported catalyst. This high activity is due to a high degree of isolated centers on the supported catalyst [7].

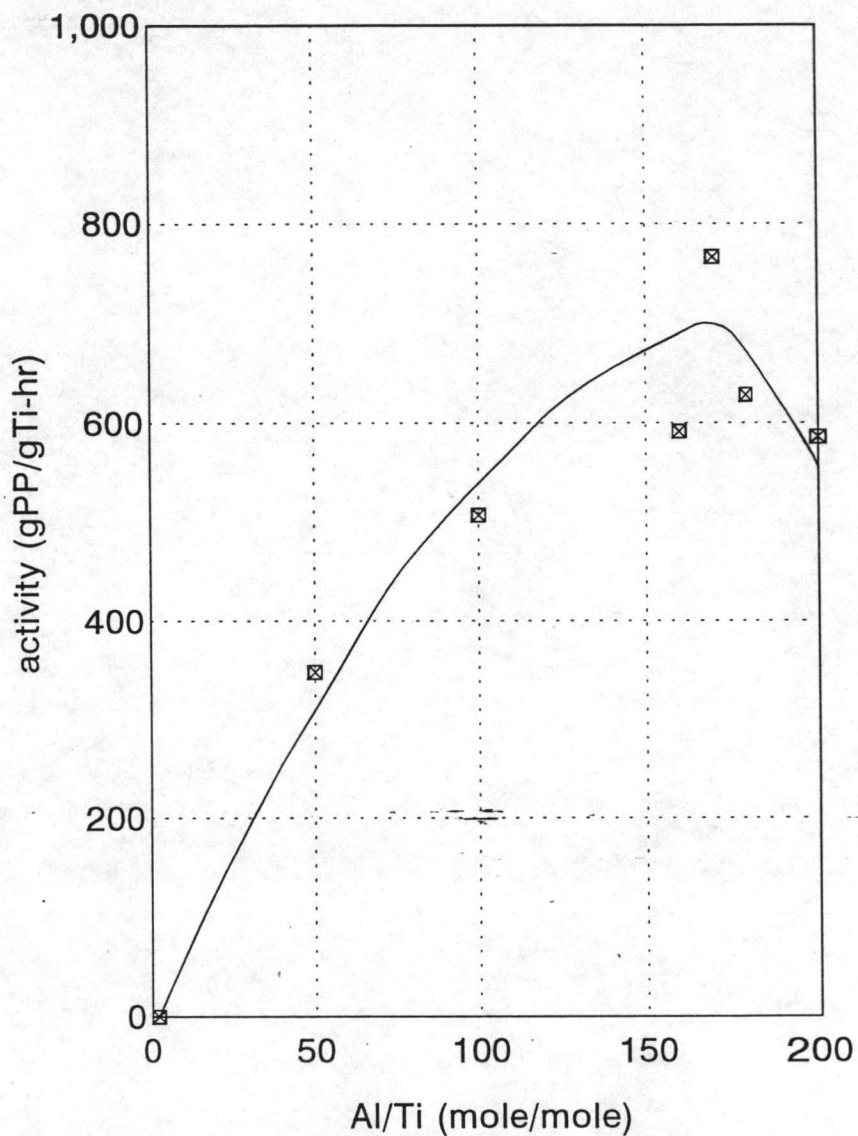


Figure 5.1a Effect of catalyst ratio on activity of supported catalyst
Polymerization condition; [Ti] = 8.936 mmol/l,
Temperature = 90 ° C,
Pressure of propylene = 75 psi,
Pressure of hydrogen = 25 psi,
Polymerization time = 1.5 hr.

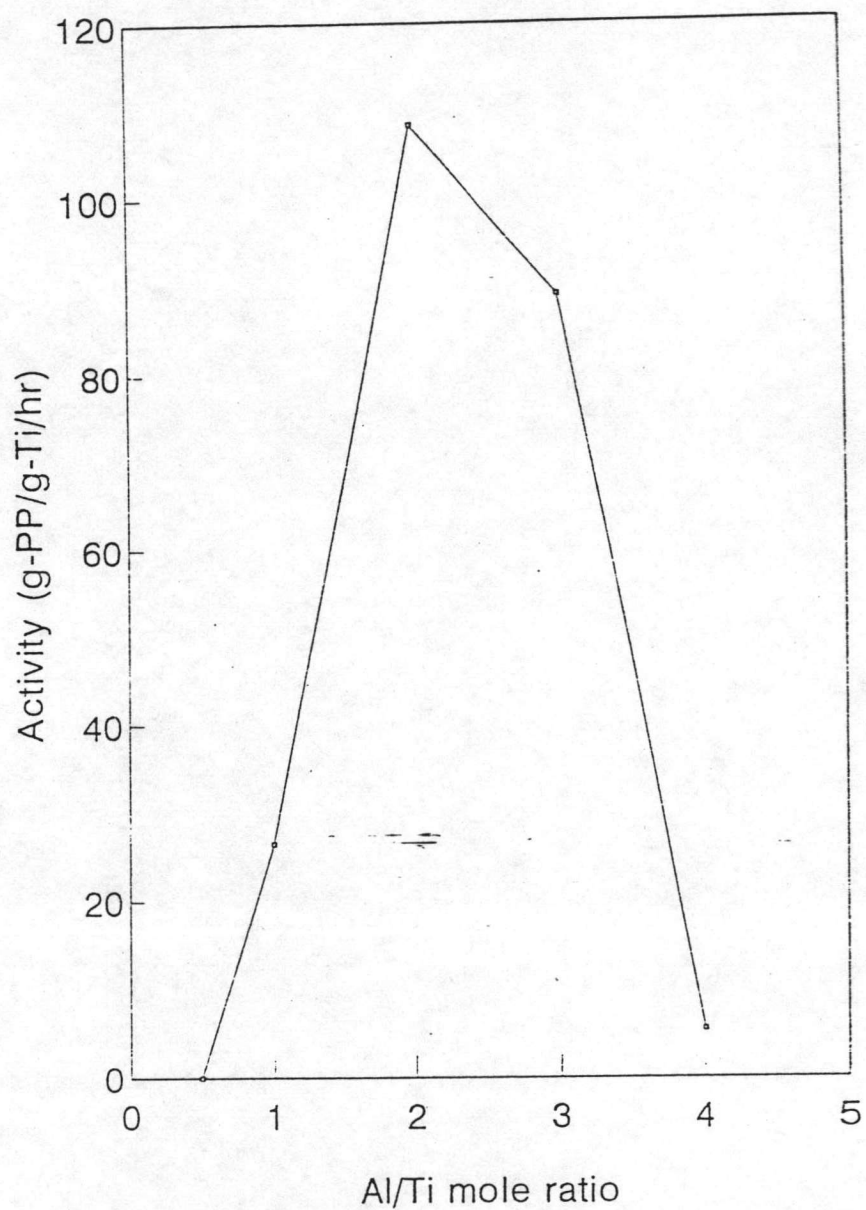


Figure 5.1b Effect of catalyst ratio on activity of unsupported catalyst [114]
Polymerization condition; [Ti] = 8.936 mmol/l,
Temperature = 70 ° C,
Pressure of propylene = 3 bar,
Pressure of hydrogen = 1 bar,
Polymerization time = 1.5 hr.

5.2 THE EFFECT OF HYDROGEN RATIO

Since the use of molecular hydrogen as a chain transfer agent was first described by Vandenberg [5], Ettore and Lucino [6] and Natta [58], it has been widely used to lower molecular weight of polymers synthesized with Ziegler-Natta catalyst.

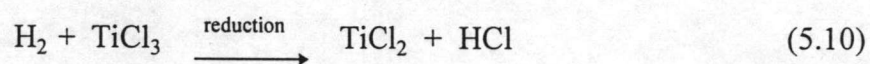
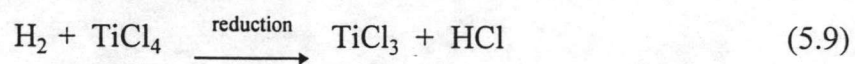
As a terminating agent, molecular hydrogen is most attractive because it does not simultaneously kill reaction centers [58]. Molecular hydrogen also functions as the activator in the catalyst system. The activation effect by hydrogen may be due to either an increase in propagation rate constant or an increase in the number of active centers in the system [5].

Figure 5.2 shows the effect of H_2 to propylene pressure ratios on supported and unsupported [114] catalysts at constant total pressure. For supported catalyst at ratio 0.1 the activity was highest and decreased at higher ratio. This behavior was found in unsupported catalyst also [114].

When hydrogen had diffused into n-hexane and absorbed on the supported catalyst surface, it dissociated into 2 atoms according to Eq. 5.8.



The proper amount of absorbed hydrogen atoms reduced the titanium supported atom to active center as in Eq. 5.9. But at higher amount of H₂, it would over-reduced Ti as shown in Eq. 5.10.



Above H₂/Propylene ratio of 0.1, the over-reduction of Ti occurred. Consequently, catalytic activity was decreased.

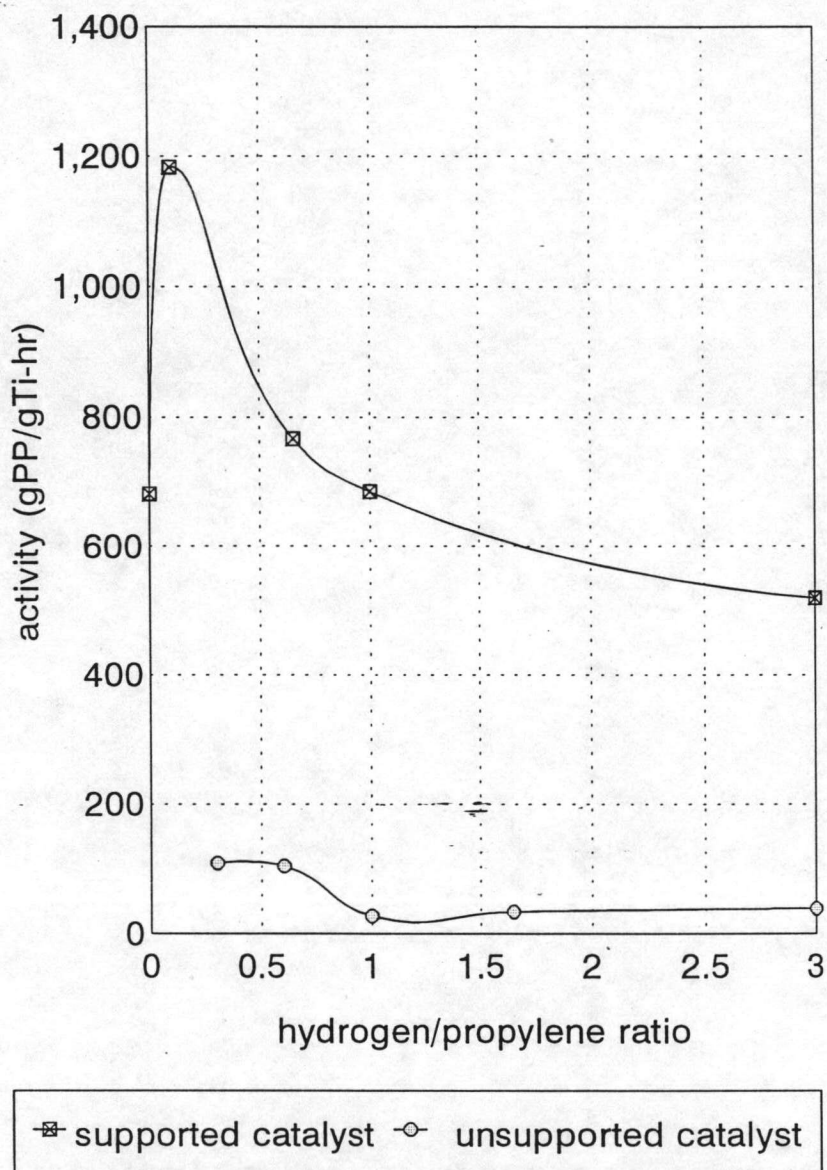


Figure 5.2 Catalyst activity at various ratio of hydrogen/propylene

Polymerization condition;

Catalyst	supported	unsupported [114]
[Ti] (mmol/l)	8.936	8.936
Al/Ti (mol/mol)	170	2
Temperature (°C)	90	70
Total pressure (psi)	100	58
Polymerization time (hr.)	1.5	1.5

5.3 THE EFFECT OF TOTAL PRESSURE

Propylene polymerization was carried out at various total pressure from 70 to 100 psi.

From Figure 5.3, the activity of supported catalyst was increased as the pressure of propylene increased. This behavior was described by Chien [24]. The rate of polymerization by the $MgCl_2$ ground supported catalyst (CW catalyst) for propylene and ethylene have been found to be

$$R_p = k_p[Ti^*][M] \quad (5.11)$$

From this equation propagation rate of polymerization (R_p) is increased by increasing pressure (monomer concentration $[M]$). Thus, within the scope of this work, the highest pressure 100 psi is found to be the best condition for this experiment.

This behavior is different from unsupported catalyst [114]. The activity of unsupported catalyst was increased rapidly at low total pressure and gradually increased at high total pressure following Langmuir-Hinshelwood mechanism [24].

$$R_p = \frac{k_p k_m [Ti^*][M]}{(1 + k_m[M])^2} \quad (5.12)$$

In unsupported catalyst, adsorption and hindrance of monomer have more effects on propagation rate than supported catalyst because active centers of supported catalyst are more isolated [7].

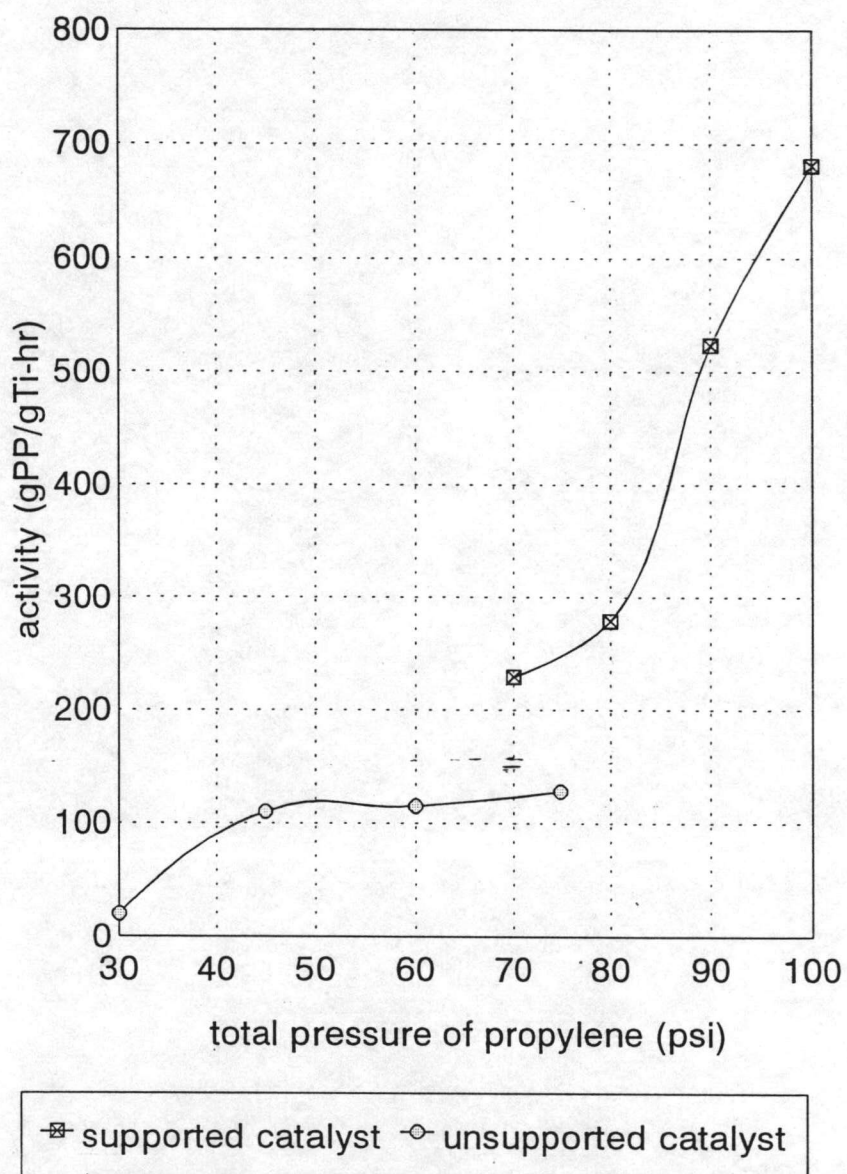


Figure 5.3 Effect of total pressure on catalyst activity

Polymerization condition;

Catalyst	supported	unsupported [114]
[Ti] (mmol/l)	8.936	8.936
Al/Ti (mol/mol)	170	2
H ₂ /Propylene (mol/mol)	0	3
Temperature (°C)	90	70
Polymerization time (hr.)	1.5	1.5

5.4 THE EFFECT OF TEMPERATURE

These experiments were carried out to observe the influence of temperature on catalyst activity. The effect of temperature on supported and unsupported catalyst [114] are shown in Figure 5.4.

Temperature has a strong influence on the catalyst activity. From Figure 5.4, the activity of both catalyst systems increase with the rise in temperature. This could be due to a higher number of active centers was formed and the propagation rate constant increased at higher temperature [115,123] following Arrhenius type relationship [123].

$$k_p = Ae^{-\frac{E}{RT}} \quad (5.13)$$

A = collision frequency factor
 E = Arrhenius activation energy
 T = temperature

Natta [116] determined the number of active centers in the catalyst systems, α -TiCl₃-AlEt₃ and α -TiCl₃-AlEt₂Cl, which were utilized for the polymerization of propylene. In order to determine the number of active centers resulting from the adsorption of aluminium alkyls on the α -TiCl₃, the latter was treated at given temperature with a solution of aluminium alkyl containing radioactive ¹⁴C followed by filtration and repeated washing of the resulting solid at a given temperature with anhydrous benzene until the filtrate was no longer

radioactive. The TiCl_3 so obtained liberated C_2H_4 and C_2H_6 upon treatment with acid, indicating that during the treatment of the TiCl_3 with aluminium alkyls, complex formation occurred on the surface of the crystalline substrate that was at least partially irreversible. The degree of reversibility was found to depend on the temperature at which adsorption of the aluminium alkyl was allowed to occur. Below 60°C , the number of alkyl(ethyl) groups found in the polymer was lower than the total number of ethyl groups adsorbed on the TiCl_3 (as measured by gas evolution). However, at 70°C and above, the number of ethyl groups in the polymer corresponded closely to the total number adsorbed on the TiCl_3 and it was therefore assumed that at these latter temperatures the ethyl groups found in the polymer correspond to the number of active sites initially present on the TiCl_3 surface. Hence, the work of Natta [116] showed that the number of active sites increased with increasing temperature. And catalyst activity increased with increasing number of active sites. Therefore, work of Natta [116] was another evidence which showed that the catalyst activity increases with increasing temperature.

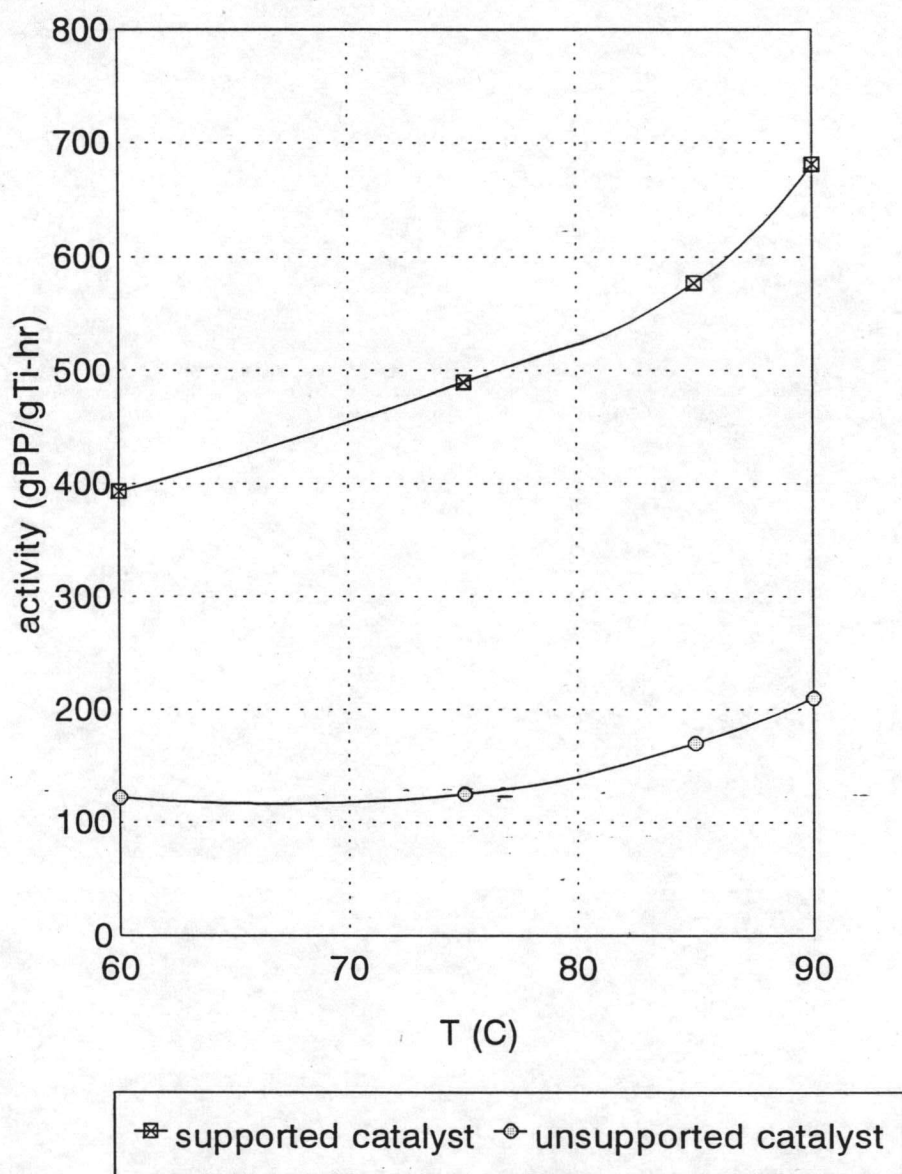


Figure 5.4 Effect of temperature on catalyst activity

Polymerization condition;

Catalyst	supported	unsupported[114]
[Ti] (mmol/l)	8.936	8.936
Al/Ti (mol/mol)	170	2
H ₂ /Propylene (mol/mol)	0	3
Total pressure (psi)	100	98
Polymerization time (hr.)	1.5	1.5

5.5 THE EFFECT OF EXTERNAL ELECTRON DONORS

Considerable information about alkoxysilane donors of various structure can be found in the patent literature [117,118], but scientific studies on the relationship between their structures and polymerization behavior are few.

Alkyl alkoxy silane donors in this study were investigated by varying the alkoxy group in ligand of Si. The alkoxy group in ligand of Si may effect to propylene polymerization. Electron donors used in this study were :

tetraethoxysilane ($\text{Si}(\text{OEt})_4$, TES)

methyltriethoxysilane ($\text{MeSi}(\text{OEt})_3$, MTES)

dimethyldiethoxysilane ($\text{Me}_2\text{Si}(\text{OEt})_2$, DMDDES)

trimethylethoxysilane ($\text{Me}_3\text{Si}(\text{OEt})$, TMES)

phenyltriethoxysilane ($\text{C}_6\text{H}_5\text{Si}(\text{OEt})_3$, PTES)

The structure of electron donors were shown in Figure 5.5.

Because AlEt_3 had a strong tendency to form dimer to each other as shown in Figure 5.6 [40], it caused the electron deficiency in the aluminium atom of AlEt_3 which has coordination number 3. This structure was stable and inactive. Each electron donors were added in the system to prevent this behavior by forming the complexes with AlEt_3 [40,121]. In studies on the complexation of different alkoxysilane with AlEt_3 , Iiskola et al. [121] found that, at room

temperature, AlEt_3 and alkoxysilane instantly form 1:1 complex independent of the number of alkoxy groups in the silane.

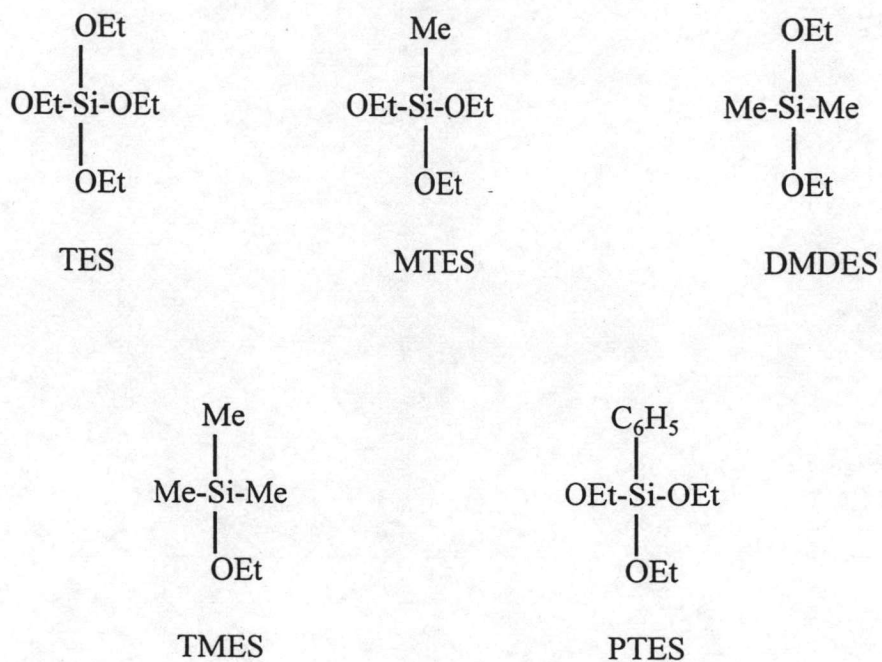


Figure 5.5 Alkylalkoxysilanes studied in this experiment

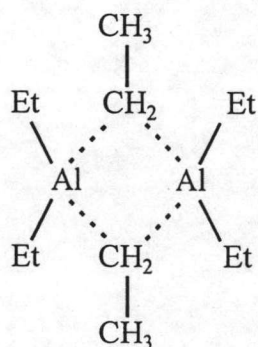


Figure 5.6 Dimer of AlEt_3 [40]

Guyot et al. [119] and Sacchi et al.[120] have suggested that this kind of complexes increased the isotactic activity by activating Ti sites to be isotactic centers.

From Figure 5.7a, It was found that the activity was decreased in order :



When increased the number of alkoxy groups, activity was decreased. This behavior was described by Iiskola et al. [121]. AlEt_3 and alkoxy silane form a complex via the aluminium atom in AlEt_3 and the oxygen atom in one alkoxy group of the silane. If the silane had originally more than one alkoxy group, there remain the other alkoxy groups uncoordinated in the AlEt_3 /donor complex.

Seppälä and Härkönen [29] suggested that uncoordinated alkoxy groups in the complex were able to deactivate the active centers at the catalyst. In case of unsupported catalyst [114], from-Figure 5.7b, effect of number of alkoxy groups was not clear. However, TMES had highest activity.

Effect of size of alkyl ligand of Si in triethoxysilane was also shown in Figure 5.7a. It was found that PTES showed the higher activity (Figure 5.7a) and lower isotacticity (Figure 5.8) than MTES because it had larger hydrocarbon group. This could be due to the steric hindrance that PTES could not reach active site [29].

Effect of electron donors on isotacticity was shown in Figure 5.8. From this study , isotacticity of the catalyst was increased by increasing the number of ethoxy groups because more ethoxy groups could give more electron to the

catalyst system [29]. But this observation was not actually confirmed because TMES showed higher isotacticity than DMDES.

Because TMES showed high isotacticity relative to its activity as shown in Figure 5.9 and in order to compare the result of this work with the data of TMES in unsupported catalyst as reported by Banglap [114], the TMES was then selected as the external electron donor to study further. The influence of TMES on the performance of the catalyst system was further studied at various TMES/Al mole ratio. The effect of donor/Al ratio on activity and isotactic index of supported and unsupported catalyst [114] was shown in Figure 5.10 and 5.11, respectively.

Figure 5.10 showed that the catalyst activity decreased as donor/Al ratio increased and were in agreement with many previous papers [25,26,29] because electron donor could block active sites of catalyst [26]. Figure 5.11 showed that isospecificity of catalyst was improved by the use of electron donor but at ratio higher than 0.1 external electron donor had deactivating effect for both isospecific and aspecific titanium sites [26].

From Figure 5.10 and 5.11, when electron donor concentration was increased, the rate of decreasing of activity and increasing of isotacticity of supported catalyst were higher than unsupported catalyst because active sites of supported catalyst had less steric hindrance due to more isolated centers of supported catalyst that were easier for electron donor to access [7,40].

From all results discussed in this chapter so far, it was found that the properties of supported catalyst was similar to unsupported catalyst but it had more isolated sites that caused higher activity and made it more sensitive to the change of monomer and electron donor concentrations.

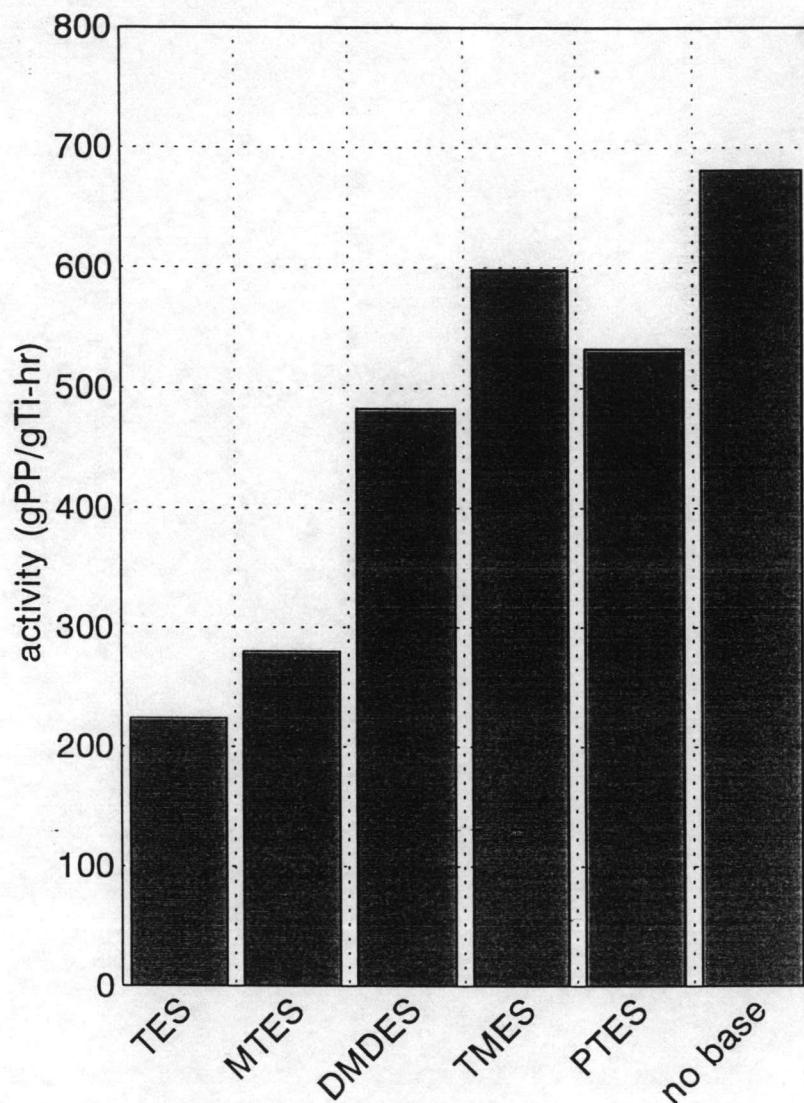


Figure 5.7a Effect of external electron donors on activity of supported catalyst

Polymerization condition; $[Ti] = 8.936 \text{ mmol/l}$,

$Al/Ti = 170$,

Hydrogen/Propylene ratio = 0,

Base/Al ratio = 0.05,

Total pressure = 100 psi.,

Temperature = 90 °C,

Polymerization time = 1.5 hr.

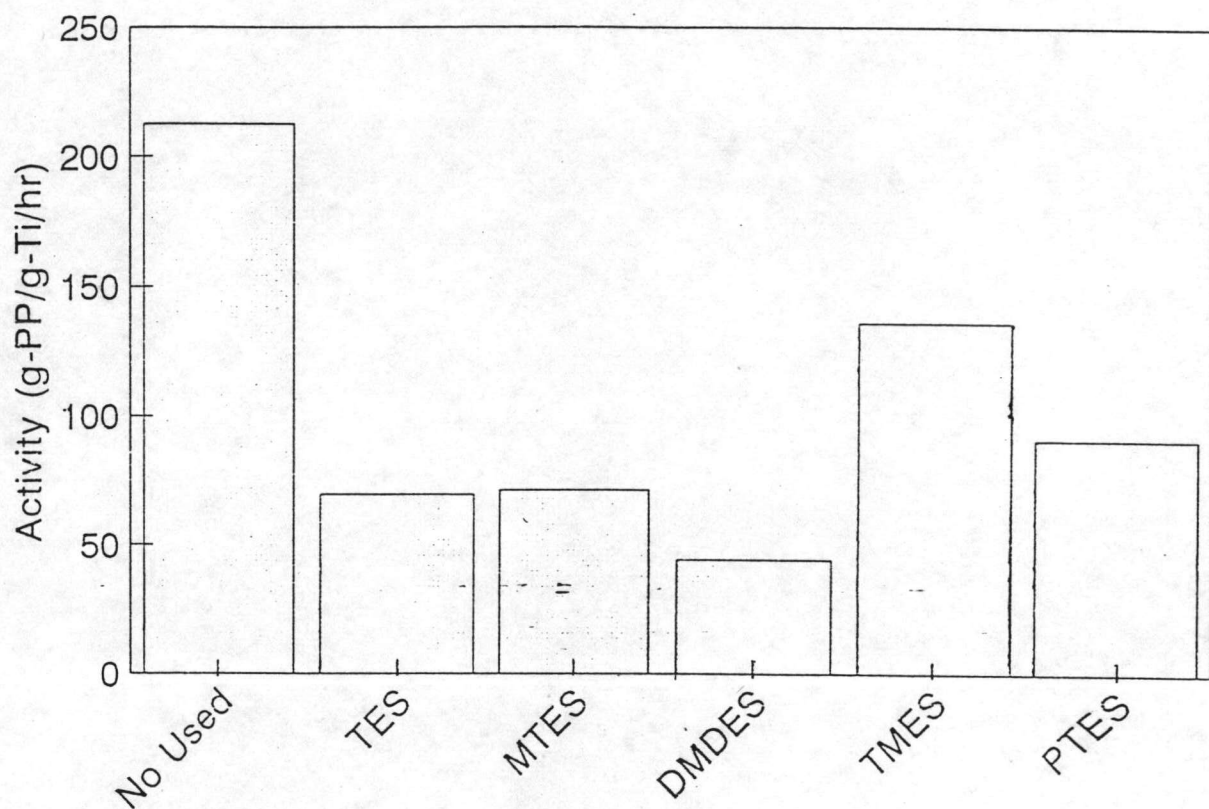


Figure 5.7b Effect of external electron donor on activity of unsupported catalyst [114]

Polymerization condition; $[\text{Ti}] = 8.936 \text{ mmol/l}$,

$\text{Al/Ti} = 2$,

Hydrogen/Propylene ratio = 3,

Base/Ti ratio = 0.05,

Total pressure = 98 psi.,

Temperature = 90°C

Polymerization time = 1.5 hr.

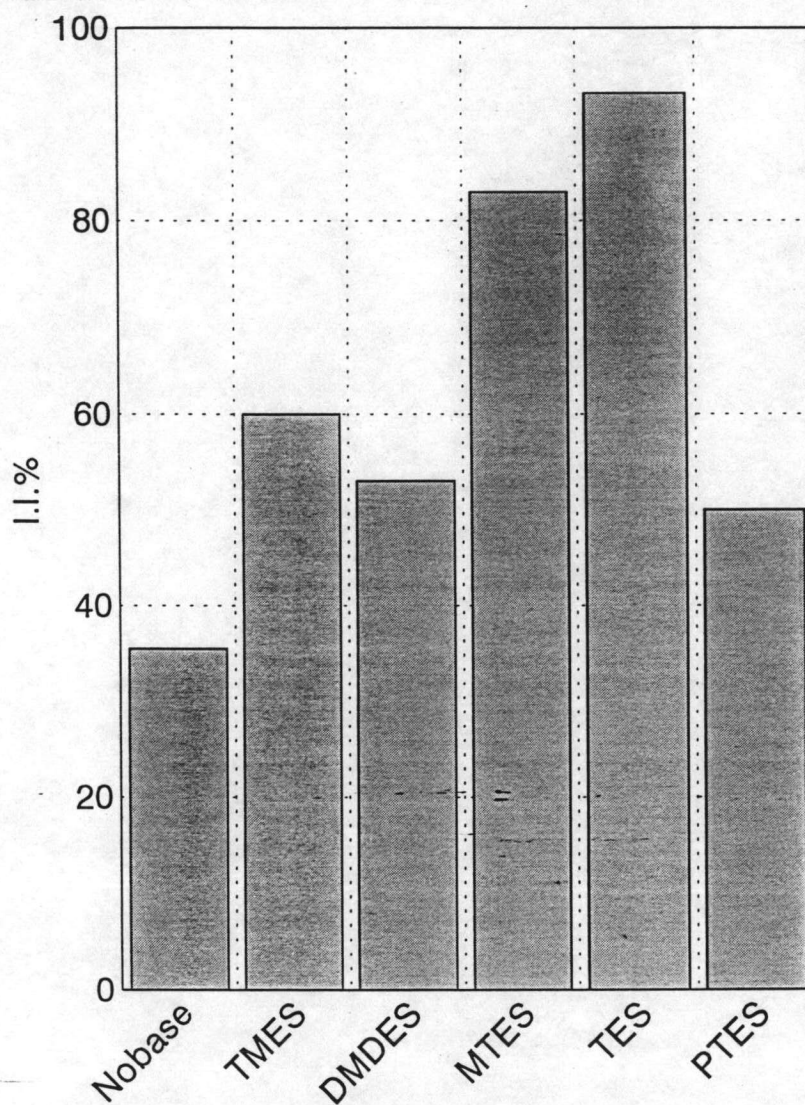


Figure 5.8 Effect of external electron donors on catalyst isotacticity

Polymerization condition; [Ti] = 8.936 mmol/l,

Al/Ti = 170,

Hydrogen/Propylene ratio = 0,

Base/Al ratio = 0.05,

Total pressure = 100 psi.,

Temperature = 90 °C,

Polymerization time = 1.5 hr.

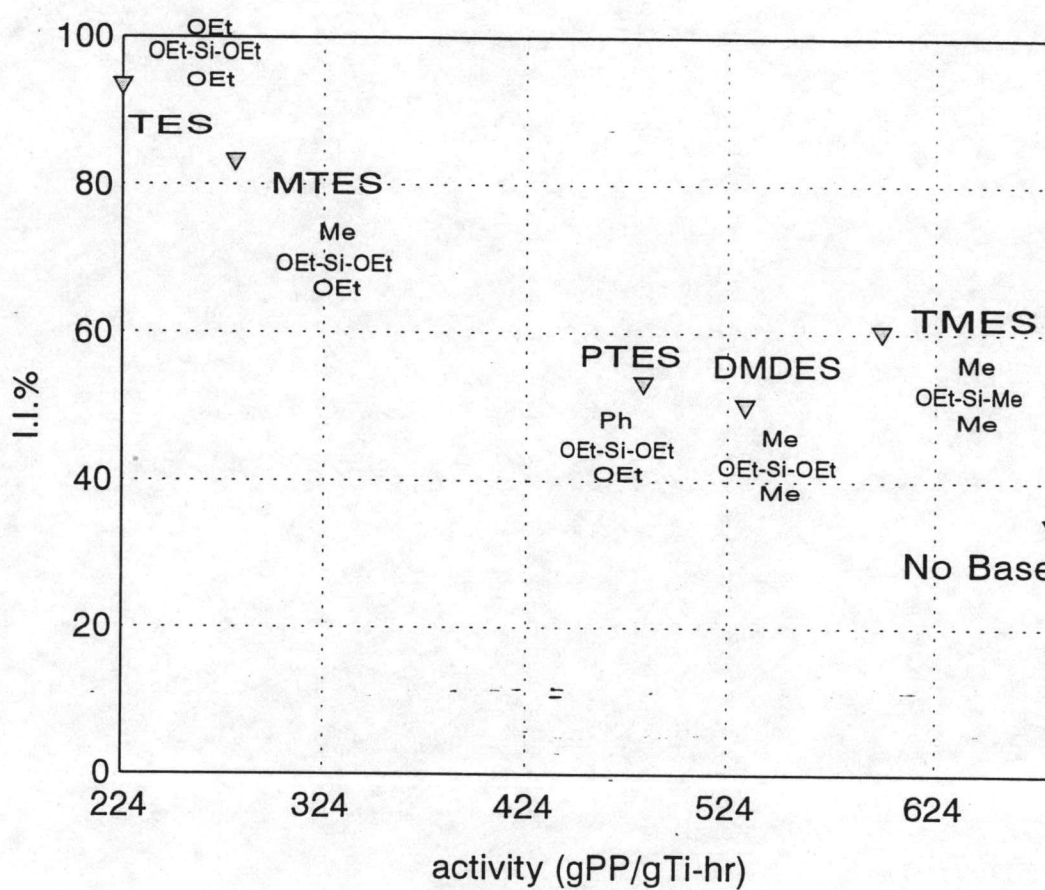


Figure 5.9 Relationship between activity and isotacticity of various electron donors
 Polymerization condition; $[Ti] = 8.936 \text{ mmol/l}$,
 $Al/Ti = 170$,
 Hydrogen/Propylene ratio = 0,
 Base/Al ratio = 0.05,
 Total pressure = 100 psi.,
 Temperature = $90 \text{ }^\circ\text{C}$,
 Polymerization time = 1.5 hr.

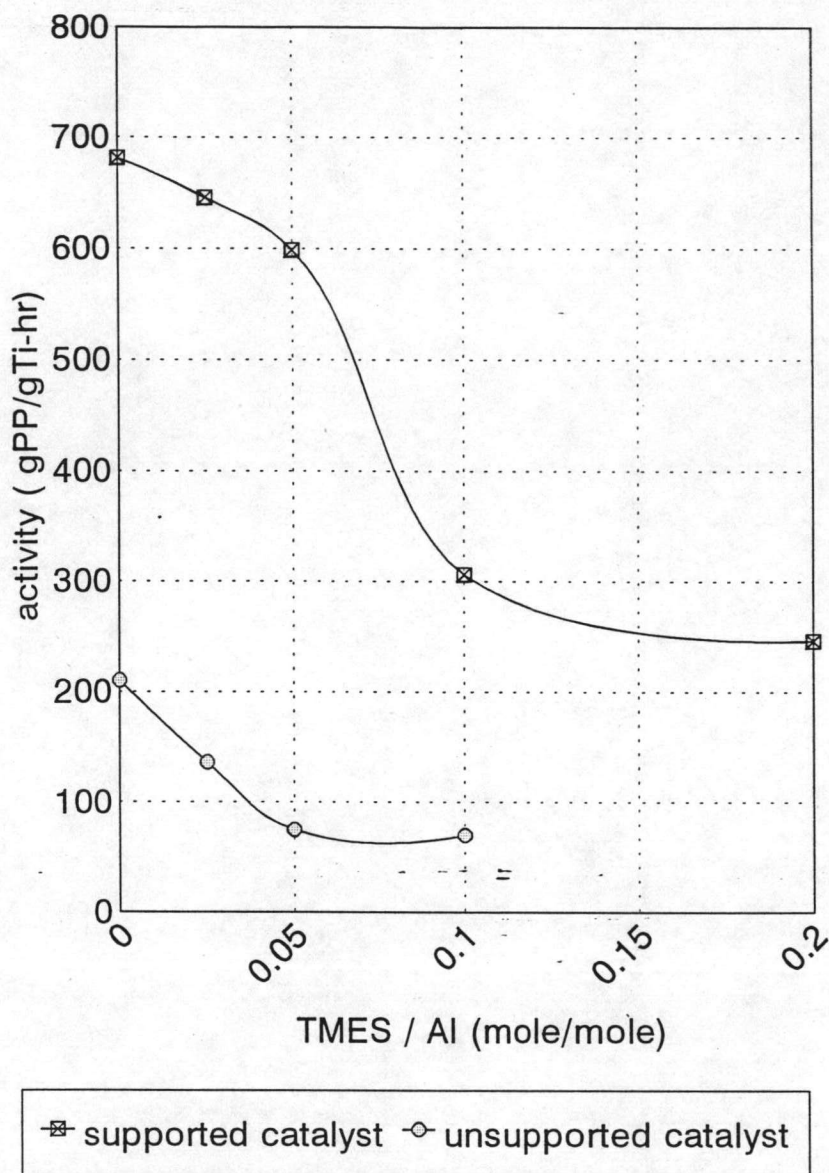


Figure 5.10 Effect of TMES/Al mole ratio on catalyst activity
Polymerization condition;

Catalyst	supported	unsupported [114]
[Ti] (mmol/l)	8.936	8.936
Al/Ti (mol/mol)	170	2
H ₂ /Propylene (mol/mol)	0	3
Total pressure (psi)	100	98
Temperature	90	90
Polymerization time (hr.)	1.5	1.5

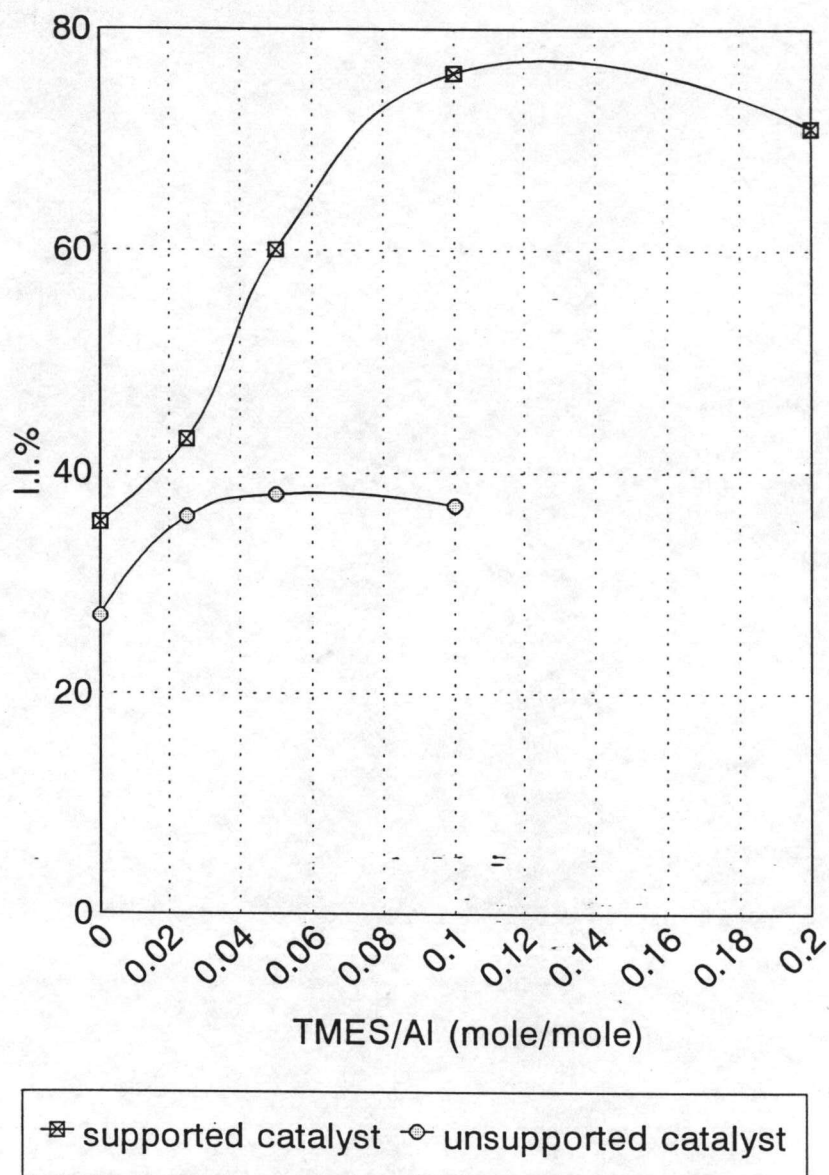


Figure 5.11 Effect of TMES/Al mole ratio on catalyst isotacticity
Polymerization condition;

Catalyst	supported	unsupported [114]
[Ti] (mmol/l)	8.936	8.936
Al/Ti (mol/mol)	170	2
H ₂ /Propylene (mol/mol)	0	3
Total pressure (psi)	100	98
Temperature	90	90
Polymerization time (hr.)	1.5	1.5

5.6 CHARACTERIZATION OF POLYPROPYLENE

The polypropylene obtained from catalyst at mole ratio of TMES/Al 0.1 and 0.2 and no TMES were subjected to scanning electron microscope at enlargement of 2000 times as show in Figure 5.12-5.14.

Polymer obtained from no base catalyst had lamellar structure. This lamellar form was gradually decreased by increasing base concentration. At TMES:Al ratio 0.2 globule structure appeared. This behavior could be described by Guttman and Guillet [122]. They proposed model on the basis of observations made when propylene was subjected to a vapor phase polymerization with $\text{AlMe}_3/\alpha\text{-TiCl}_3$ catalyst. According to their view, the rate of polymerization is initially more rapid than the rate of crystallization, resulting in a initial structure having the shape of a hemispherical mass of amorphous polymer. As the size of this globule increases, the rate of polymerization decreases and, at this time, crystallization occurs at the apex of the globule in the form of folded chain lamellae. From our results it could be concluded that electron donor had an effect on decreasing the growth of polymer chain that prevented forming of lamellar structure.



Figure 5.12 Electron micrograph of polypropylene without external electron donor
Polymerization condition; [Ti] = 8.936 mmol/l,
Al/Ti = 170,
Hydrogen/Propylene ratio = 0,
Base/Al ratio = 0,
Total pressure = 100 psi.,
Temperature = 90 °C,
Polymerization time = 1.5 hr.

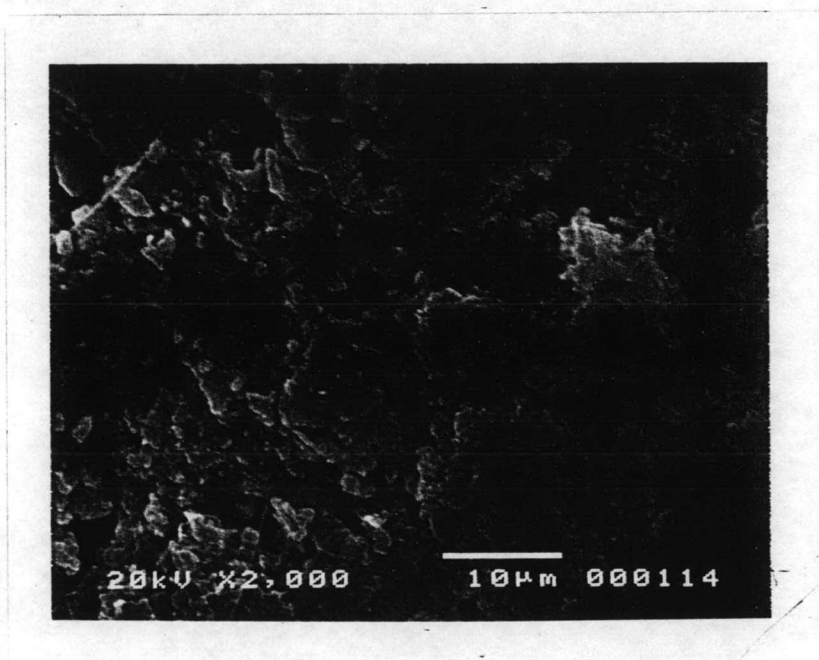


Figure 5.13 Electron micrograph of polypropylene at TMES/Al mole ratio 0.1
Polymerization condition; [Ti] = 8.936 mmol/l,
Al/Ti = 170,
Hydrogen/Propylene ratio = 0,
Base/Al ratio = 0.1,
Total pressure = 100 psi.,
Temperature = 90 °C,
Polymerization time = 1.5 hr.

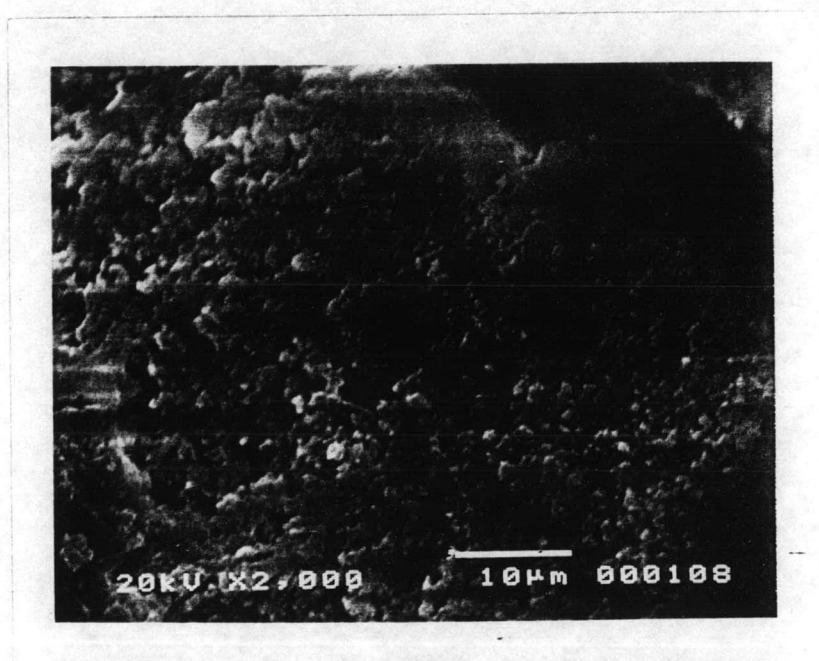


Figure 5.14 Electron micrograph of polypropylene at TMES/Al mole ratio 0.2
Polymerization condition; [Ti] = 8.936 mmol/l,
Al/Ti = 170,
Hydrogen/Propylene ratio = 0,
Base/Al ratio = 0.2,
Total pressure = 100 psi.,
Temperature = 90 °C,