CHAPTER V

RESULTS & DISCUSSIONS

Ziegler-Natta Catalysts for the polymerization of propylene is a multicomponent catalyst, the composition of which may vary over wide limits, and the catalyst activity is known to depend on the inherent activity of each component in the catalyst system In this work a titanium-based catalyst system of titanium tetrachloride and triethylaluminum was investigated.

Since the commercial Ziegler-Natta polymerization process of propylene based on titanium trichloride and triethylaluminum used in slurry polymerization. But the structure of polypropylene product is low isotactic contents. So the conventional Ziegler-Natta catalyst was modified by using suitable combinations of Lewis bases as donor [1]. The internal Lewis base is used for the preparation of solid catalyst and the external Lewis base is added in conjunction with aluminum alkyls to the solution containing catalyst [2]. This thesis , some alkoxy silane compounds were used as third components or Lewis bases. In this study was divided into two parts. To specify the suitable condition, firstly the experiments were done in various mole ratio of catalyst composition, ratio of gas components , total pressure , and polymerization temperature. Suitable polymerization conditions were selected for study of the effect of the external electron donors in propylene polymerization. Finally the electron donor that showed the best activity was varied in concentrations for determined the suitable quantity of electron donor in the polymerization system.

5.1 EFFECT OF CATALYST RATIO

With regard to dependence upon the inherent activity of each components of Ziegler-Natta catalyst, this has led to the first attention being focused on catalyst preparation. If assumptions were correct that the catalyst is a complex of both components [99] and that this complex is in equilibrium with its components [100], then the activity of the catalyst mixture should increase whereas the titanium tetrachloride concentration was kept constant and the mole ratio of Al/Ti rises.
The experimental curve of activity versus Al/Ti mole ratio as shown in Figure 5.1 was indicated to show a maximum activity at Al/Ti mole ratio of 2. (The term of

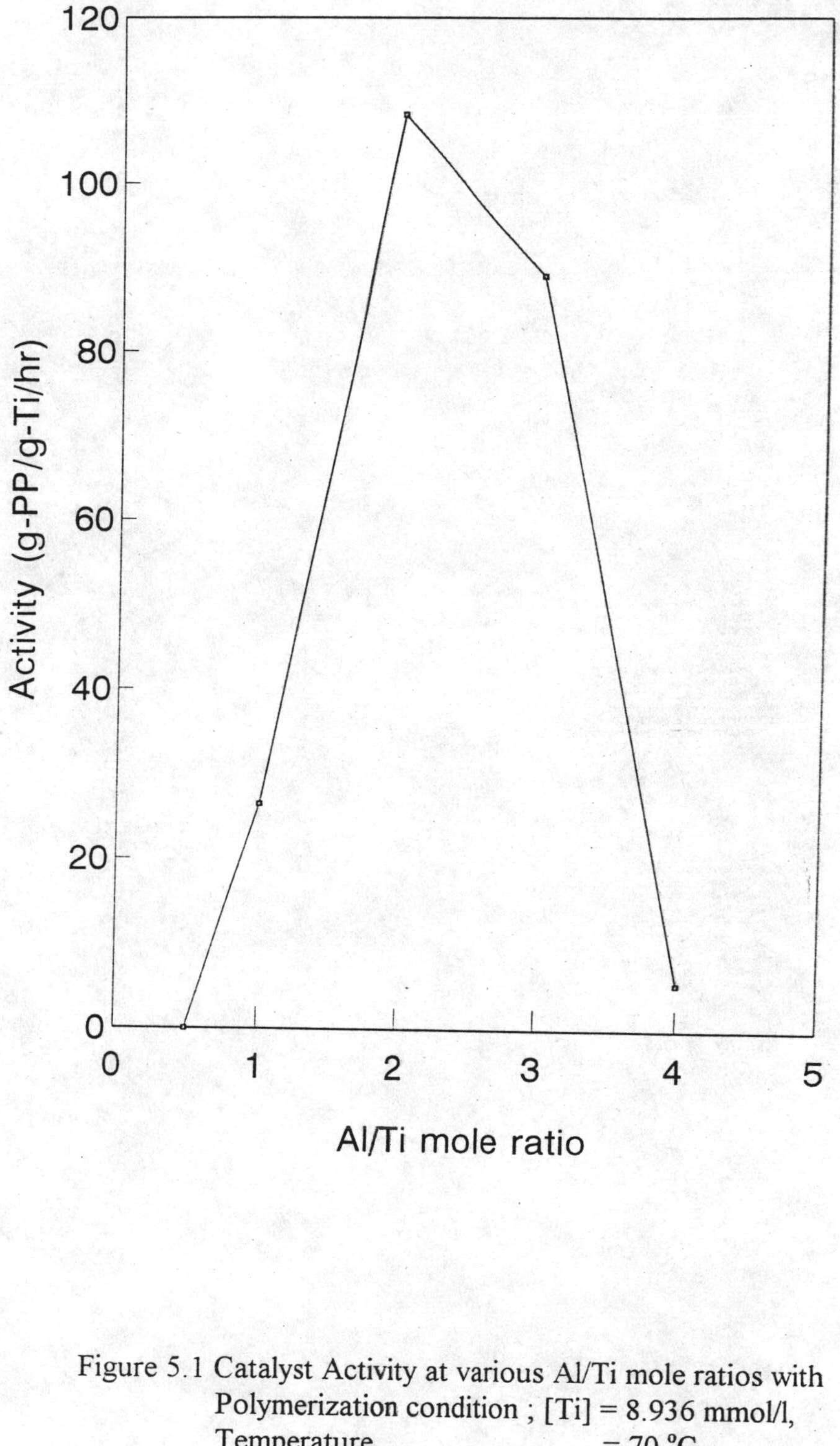


Figure 5.1 Catalyst Activity at various Al/Ti mole ratios with
Polymerization condition ; [Ti] = 8.936 mmol/l,
Temperature = 70 °C,
Partial pressure of propylene = 3 bar,
Parial pressure of hydrogen = 1 bar,
Polymerization time = 1.5 hr.

activity referred to gram of polypropylene produced by 1 gram-atom of titanium during 90 minutes of polymerization time)

Lenz [127]reported the reaction between titanium tetrachloride and aluminum alkyls in the following reaction.

$TiCl_4 + AlR_3 \longrightarrow RTiCl_3 + R_2AlCl$ (Eq.5.1)
$TiCl_4 + R_2AlCl \longrightarrow RTiCl_3 + RAlCl_2$ (Eq.5.2)
$TiCl_4 + RAlCl_2 \longrightarrow RTiCl_3 + AlCl_3$(slowly at 23 °C) (Eq.5.3)
$RTiCl_3 \longrightarrow TiCl_3 + R$ (Eq.5.4)
Cl
$TiCl_4{*}Al(C_2H5)_3 \longrightarrow TiCl_3{*}(C_2H_5)Al(C_2H_4{*}) + C_2H_6$ (Eq.5.5)
$2(C_2H_5)TiCl_3 \longrightarrow 2TiCl_3 + C_2H_4 + C_2H_6$ (Eq.5.6)
$TiCl_3 + AlR_3 \longrightarrow RTiCl_2{*}R_2AlCl$ (Eq.5.7)
$RTiCl_2 \longrightarrow R{*} + TiCl_2$ (Eq.5.8)
$R{*} + TiCl_4 \longrightarrow TiCl_3 + RCl$ (Eq.5.9)

where R denot ethyl group in this thesis

From Figure 5.1, at Al/Ti mole ratio was less than value 2, the oxidation state of Ti was +4 which is inactive in polymerization. At Al/Ti mole ratio of 2 showed a maximum activity and the oxidation state of Ti was +3 which was active in polymerization as shown in Eq.5.4 and Eq.5.9 [3-6]. When this ratio was higher than value 2, the over-reduction of Ti was occurred from the valence state +4 to +2 which is inactive in propylene polymerization as shown in Eq.5.8.

And at Al/Ti mole ratio was higher than 2. The activity showed decreasing value. Because the excess $AlEt_3$ competed with propylene monomer for adsorption on the acitve catalyst surface and also began to cover the surface. According to Lagmuir-Hinshelwood mechanism.

$$R_p = \frac{K_P K_M K_A [M][A][S]}{(1+K_M[M] + K_A[A])^2} \qquad \text{(Eq.5.10)}$$

where Rp : rate of polymerization

K_P : propagation rate constant

K_M : equilibrium constant of adsorption of monomer

K_A : equilibrium constant of adsorption of aluminum

[M] : concentration of monomer

[A] : concentration of aluminum

[S] : concentration of active center

At Al/Ti mole ratio less than 2, this competed effect was not occurred since aluminum alkyl was alkylated to titanium atom as in Eq.5.1

5.2 EFFECT OF PROPYLENE TO HYDROGEN RATIO

Besides from the catalyst ratio, propylene-hydrogen ratio influences to polymerization process. Molecular hydrogen functions as the activator and chain transfer in the catalyst system. The activation effect by the influence of hydrogen may be due either to an increase in the propagation rate constant or to an increase in the number of active centers in the system. Rishina et al.[126]reported that the activation effect is the result of increasing in number of active centers rather than the propagation rate constant. The higher activation of the system is achieved at a higher monomer concentration and there is a limiting value of activation. Vandenberg[111] reported that hydrogen was effective for lowering molecular weights of polypropylene using $TiCl_4$-containing catalyst by $AlEt_3$ was used as co-catalyst. So, if there was more hydrogen in the system, molecular weight of polymer would be shorten.

Figure 5.2 shows the effect of propylene to hydrogen ratios at constant total pressure. At propylene to hydrogen ratio of 0.5, the activity was high and decreasing to the ratio of 1. Because at high partial pressure hydrogen gas (low propylene to hydrogen ratio) caused the reaction to terminate faster than that at low partial pressure of hydrogen gas. Whereas the surplus adsorbing hydrogen atoms remained on the surface, its function was the effective chain transfer agent to terminate poymer chains to obtain the lower molecular weight of polypropylene [78]. At low partial pressure of hydrogen, it could activate the titanium atoms to polymerize the propylene.

When hydrogen molecules had diffused into n-hexane and adsorbed on the catalyst surface; it dissociated into 2 atoms on the surface of the surface of the catalyst as in Eq.5.11.

$$H_2 \xrightarrow{\text{dissociation}} 2H \qquad \text{(Eq.5.11)}$$

The proper amount of adsorbed hydrogen atoms would reduced the titanium atom to the active centersas in Eq.5.12. But the hydrogen atoms may propably furhter reduced the titanium atoms to the lower oxidation state. This lower oxidation state of titanium atom did not possess a high acivity as that of the Ti +3. The over-reduction mechanisms of hydrogen atom could be established as the following Eq.5.13.

$$H + TiCl_4 \xrightarrow{\text{reduction}} TiCl_3 + HCl \qquad \text{(Eq.5.12)}$$

$$H + TiCl_3 \xrightarrow{\text{reduction}} TiCl_2 + HCl \qquad \text{(Eq.5.13)}$$

Hydrogen is also known, among the research involving in the Ziegler-Natta catalytic polymerization, as the effective chain transfer in propylene polymerization. The possible Eq.5.14 of the termination reaction by hydrogen is [80]

$$\text{M-(chain)} + H_2 \longrightarrow \text{M-H} + \text{(chain)-H} \qquad \text{(Eq.5.14)}$$

Then it could propagate to the next propation sites. So molecular weight of polymer was shorten by molecular hydrogen. Molecular weight of polypropylene products was shown in Table 5.1 which correspods to that possible mechanism.

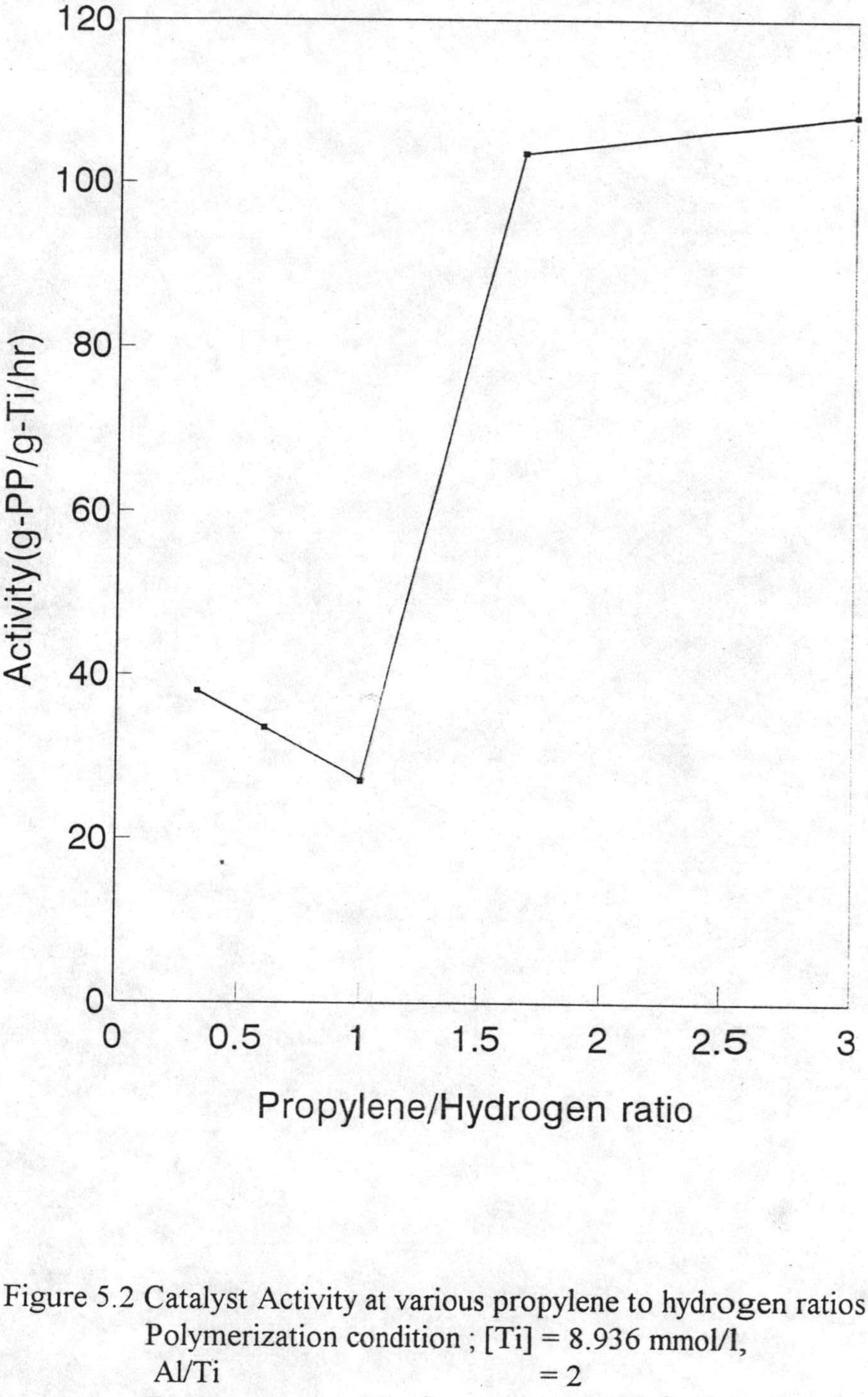


Figure 5.2 Catalyst Activity at various propylene to hydrogen ratios with,
Polymerization condition ; [Ti] = 8.936 mmol/l,
Al/Ti = 2
Temperature = 70 °C,
Total pressure = 4 bar,
Polymerization time = 1.5 hr.

Table 5.1 show molecular weight of polypropylene product from $TiCl_4/AlEt_3$ catalyst at total pressure of 4 bar , temperature 70 °C.

Propylene to hydrogen ratio	Activity (gPP/gTi-hr)	Molecular weight (Mv)
0.33	38.55	390
0.60	33.56	400
1.00	27.06	410
1.67	103.52	4154
3.0	108.26	5064

From Figure 5.1 when the propylene to hydrogen ratio value higher than 1, the activity sharply increased. Because high propylene monomer could adsorb on the catalyst surface according to Langmuir-Hinshelwook mechanism Eq.5.10.

When the propylene to hydrogen ratio value higher than 1.6, the activity gradually increased. Because the polymerization rate was limitted by mass transfer of propylene monomer to the propagation site. The decreasing dued to the encapsulation of the active sites by the previous polymer chains entanglement. Therefore, the polymer chains that occurred at the active sites formed film to hamper the new molecule of propylene monomer to polymerize effectively [103]

The propylene to hydrogen ratio was not continuely increased because the limitted of reactor used in this study.

5.3 EFFECT OF VARIOUS TOTAL PRESSURE

On the assumption that both alkyl aluminum compound and monomer are adsorbed on the surface of $TiCl_3$ lattice, a maximum increase in the rate of polymerization can occur at the amount of both components adsorbed. The rate of polymerization is expressed in Eq.5.10.

From the kinetic view-point, propylene polymerization with $AlEt_3$-$TiCl_4$ catalyst system is observed to be closely related to the assumption of Langmuir-Hinshelwood mechanism. It appears that the activity of catalyst depends upon $AlEt_3$ concentration as previously observed and so depends upon the monomer concentration too. The characteristic curves of activity versus propylene pressure shown in Figure 5.3

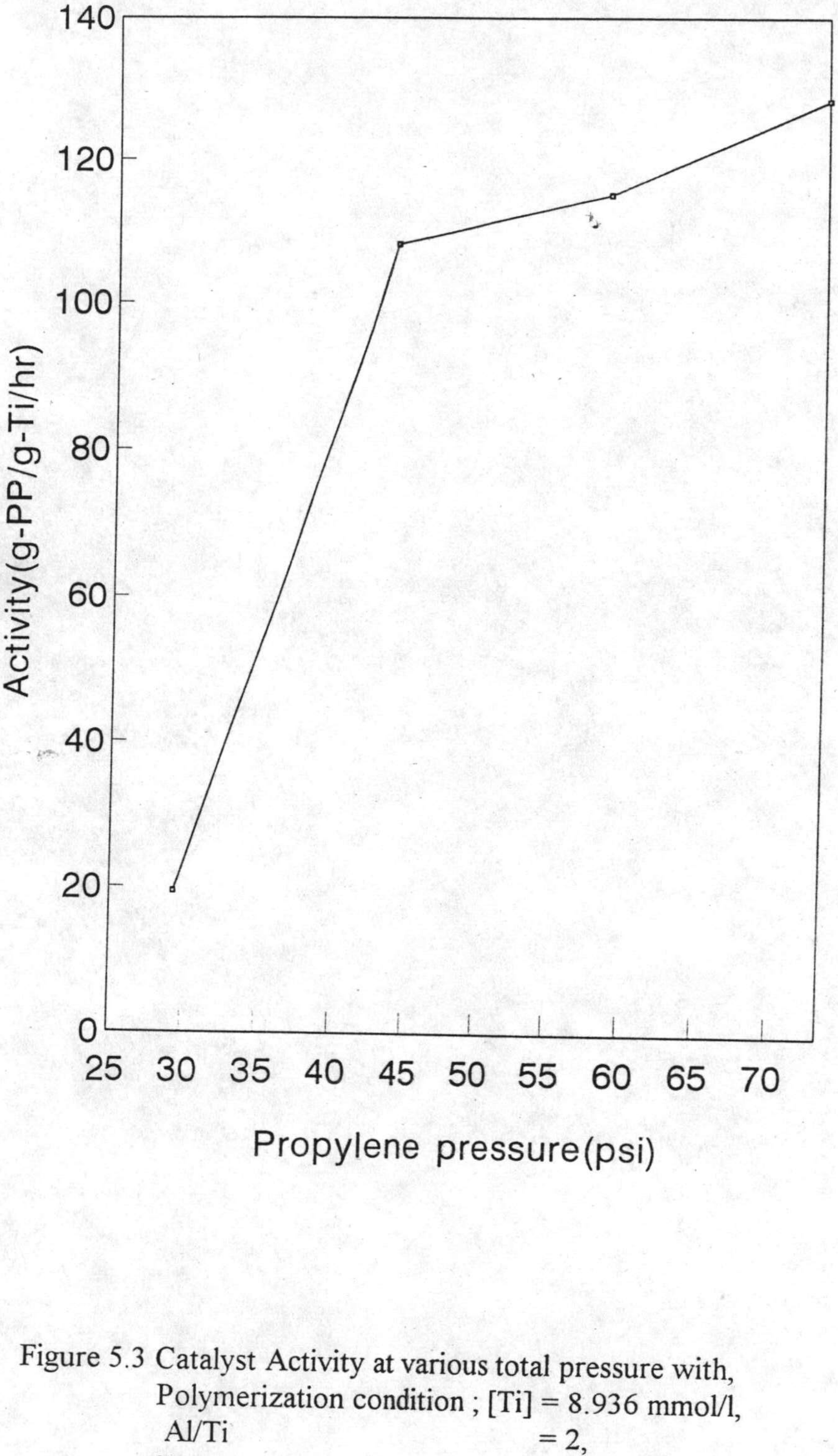


Figure 5.3 Catalyst Activity at various total pressure with,
Polymerization condition ; [Ti] = 8.936 mmol/l,
Al/Ti = 2,
Temperature = 70 °C,
Propylene to hydrogen ratio = 3,
Polymerization time = 1.5 hr

At low pressure of propylene , the activity of catalyst increased as the pressure of propylene increase following Langmuir-Hinshelwood mechanism. The activity gradually increased again at high propylene pressure at which the activity of catalyst became independent of monomer concentration. Such an explanation could apply in the case of heat and mass transfer effects [103]. In general, polymerization of olefin with $TiCl_3$ catalyst showed a rapid increase in molecular weight in the first few minutes of reaction [10]. The shapes of curves are governed by the relative speeds of the chain growth and chain transfer processes, and any changes that may occur in the catalyst itself [11]. Because the polymerization is an exothermic reaction, the rapid increase in growth rate induces the high temperature that can make the reaction run away. In this point of views, good heat transfer operation was necessary. The more rapid growth of polymer took place the less diffusion of monomer to attach the propagation site became. Hence, the polymerization rate or activity was limited by the mass transfer process in the early duration then an initial decline in rate was mostly observed in the case of higher pressure employed.

From a practical point of view, the condition of 73.5, 24.5 psi partial pressure of propylene and hydrogen, respectively was in investigated for further experiments because it showed the highest activity.

5.4 EFFECT OF TEMPERATURE

These experiments were carried out to observe the influence of temperature on catalyst activity. Four different temperatures (60, 70, 80, and 90°C) were used. The temperature of 70 °C was used in all previous parts because Coutinho et al. [ ] showed that the rate of polymerization showed high activity at this temperature. And the temperature was increased to 90 °C since the propylene polymerization showed high activity at 80-90 °C in industry. The results of effects of temperature are shown in Figure 5.4 . Temperature had a strong influence on the catalyst activity. The activity of $TiCl_4/AlEt_3$ catalyst system increase with the rise in temperature. This could be due to a higher number of active centers was formed and the propagation rate increased at higher temperature [12].

Natta [84] determined the number of active centers in the catalyst systems, α-$TiCl_3$-$AlEt_3$ and α-$TiCl_3$-$AlEt_2Cl$, which were utilized for the polymerization of propylene. In order to determine the number of active centers resulting from the adsorption of aluminum alkyls on the α-$TiCl_3$, the latter was treated at given

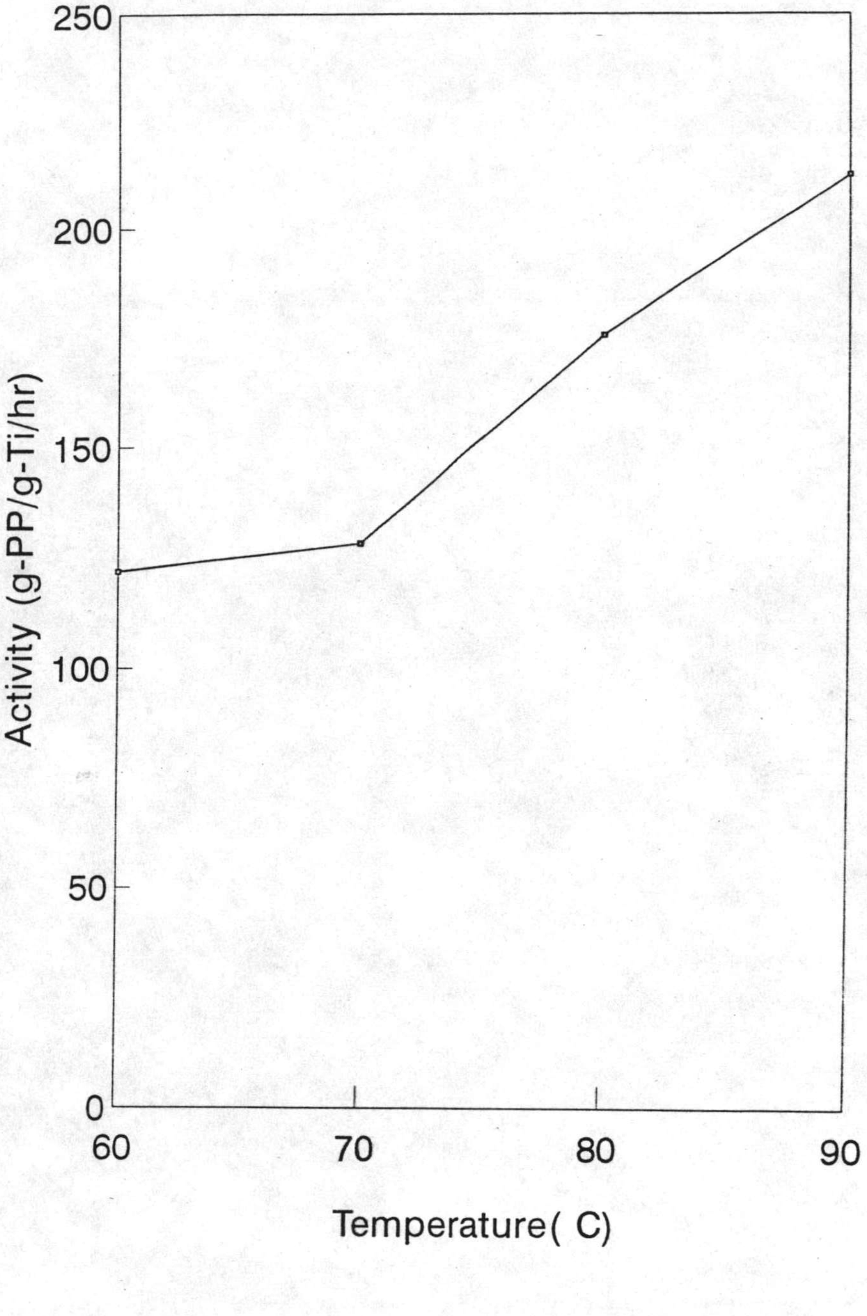


Figure 5.4 Catalyst Activity at various temperature with,
Polymerization condition ; [Ti] = 8.936 mmol/l,
Al/Ti = 2,
Propylene to hydrogen ratio = 3,
Total pressure = 98.0 psi,
Polymerization time = 1.5 hr

temperature with a solution of aluminum alkyl containing radioactive ^{14}C 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 aluminum 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 upon the temperature at which adsorption of the aluminum alkyl was allowed to occur. Below 60 ^{o}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 ^{o}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 site initially present on the $TiCl_3$ surface.

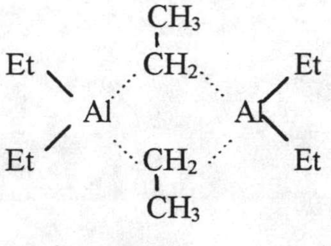
5.5 EFFECT OF EXTERNAL ELECTRON DONOR

Polymerization investigation was done on the highest selected activity from the previous work as mole ratio of $TiCl_4$:$AlEt_3$ of 8.936 : 4.463 mmol/l : mmol/l (2:1), mole ratio of propylene : hydrogen of 73.5 : 24.5 psi : psi, temperature of 90 ^{o}C and polymerization time 90 minutes for further study on the effects of external electron donor or external Lewis base as third component on the Ziegler-Natta polymerization of propylene.

External electron donors were used in this study which were alkyl alkoxy silane compounds by varying the alkyl group in ligand of Si. The alkyl group in ligand of Si may effect to propylene polymerization. Electron donors used in this study were:-

tetraethoxysilane($Si(OC_2H_5)_4$
methyltriethoxysilane($CH_3Si(OC_2H_5)_3$)
dimethyldiethoxysilane(($(CH_3)_2Si(OC_2H_5)_2$))
trimethylethoxysilane(($(CH_3)_3Si(OC_2H_5)$))
phenyltriethoxysilane($C_6H_5Si(OC_2H5)_3$)

Each of electron donors was added to the triethylaluminum solution. Because triethylaluminum had a strong tendency to associate into dimers [1]. This strong tendency to associate was attributed to the electron deficiency of the aluminum atom in triethylaluminum with coordination number 3. as shown below



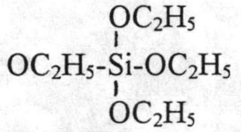
(Eq.5.15)

This structure was stable and it could be seperated by addition of electron donor as shown in Eq.5.16.

$$(AlEt_3)_2 + 2ED \rightleftharpoons 2(AlEt_3)*ED \qquad \text{(Eq.5.16)}$$

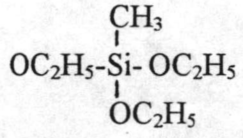
When ED denote electron donor.

The structure of electron donors used in this study were shown in Eq. 5.17



$$\begin{array}{c} OC_2H_5 \\ | \\ OC_2H_5\text{-}Si\text{-}OC_2H_5 \\ | \\ OC_2H_5 \end{array}$$

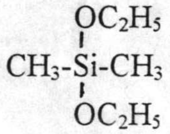
Tetraethoxysilane(TES)



$$\begin{array}{c} CH_3 \\ | \\ OC_2H_5\text{-}Si\text{-}OC_2H_5 \\ | \\ OC_2H_5 \end{array}$$

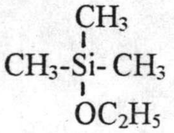
Methyltrimethylethoxysilane(MTES)

(Eq.5.17)



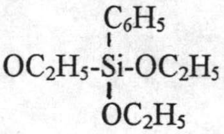
$$\begin{array}{c} OC_2H_5 \\ | \\ CH_3\text{-}Si\text{-}CH_3 \\ | \\ OC_2H_5 \end{array}$$

Dimethyldiethoxysilane(DMDES)



$$\begin{array}{c} CH_3 \\ | \\ CH_3\text{-}Si\text{-}CH_3 \\ | \\ OC_2H_5 \end{array}$$

Trimethylethoxysilane(TMES)



$$\begin{array}{c} C_6H_5 \\ | \\ OC_2H_5\text{-}Si\text{-}OC_2H_5 \\ | \\ OC_2H_5 \end{array}$$

Phenyltriethoxysilane(PTES)

From Table 5.2 found that TMES showed the highest activity. The possible reason may be the effect of methyl ligand of Si. When methyl ligand increased, the activity ought to decrease. Because methyl group transfer electron to oxygen atom in ethoxy group. So oxygen atom in ethoxy group of TMES had much electron and it could complex with titanium atom in catalyst surface better than oxygen atom in other silane compounds which titanium atom at catalyst surface was electron-deficient which it was active in polymerization [1]. But this proposal was not actually because TES showed activity higher than DMDES.

The size of alkyl ligand of Si in triethoxysilane was compared the activity from methyltriehtoxysilane and phenyltriethoxysilane. It found that PTES showed the activity higher than MTES which did not correspond the proposal. Because PTES had phenyl group which the size was larger than methyl group in MTES that phenyl group could give electron better than methyl group. So this proposal was not reliably.

Because TMES showed the highest value as shown in Figure 5.5. The influence influence of TMES on the performance of $TiCl_4/AlEt_3$ catalyst system was further studied at various TMES/Ti molar ratios. The effect of mole ratios of TMES/Ti to catalyst activity and % Isotactic Index of polypropylene were shown in Figure 5.6-5.7, respectively.

The curve indicated that the decrease of activity at TMES/Ti ratio of 0.05 increased isotactic index of polypropylene. Further increasement of the ratio depressed the polymer yield without affecting the isotactic index as shown in Figure 5.7. These results demonstrated that, at the optimum TMES/Ti ratio of 0.05 based on the scope of this work, the isospecificity of the catalyst system was considerably improved and the polymer yield was marginally decreased. These data indicated that the addition of trimethylethoxysilane in conjunction with triethylaluminum to $TiCl_4$ catalyst had activating effect at low ratios of TMES/Ti for isospecific titanium centers. At higher ratios, the external Lewis base had deactivating effects for both isospecific and nonspecific titanium sites that was in agreement with Gupta's results [14]. Thus, TMES/Ti mol ratio of 0.05 was the most interesting.

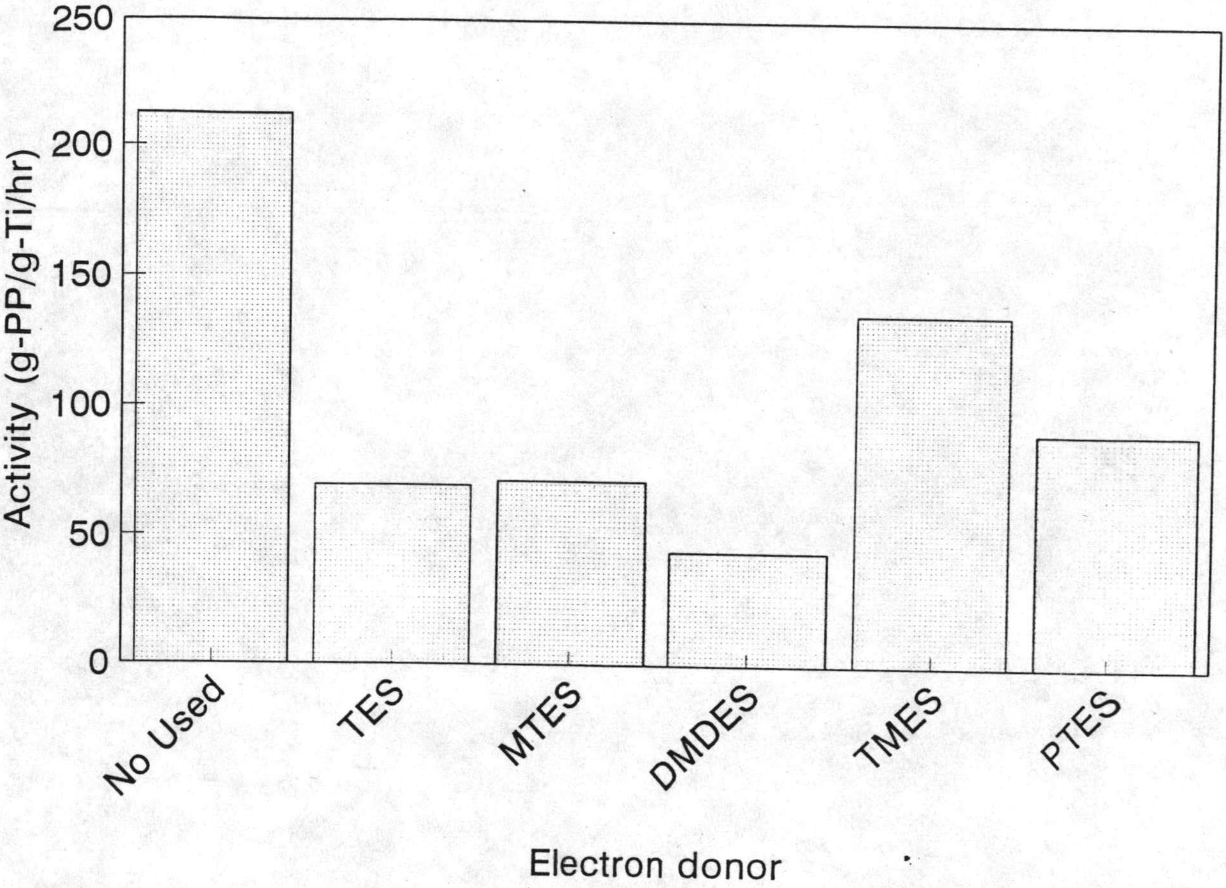


Figure 5.5 Catalyst Activity at various external electron donor (EED) with,
Polymerization condition ; [Ti] = 8.936 mmol/l,
Al/Ti = 2,
Propylene to hydrogen ratio = 3,
Total pressure = 98.0 psi,
EED/Ti ratio = 0.05,
Polymerization time = 1.5 hr

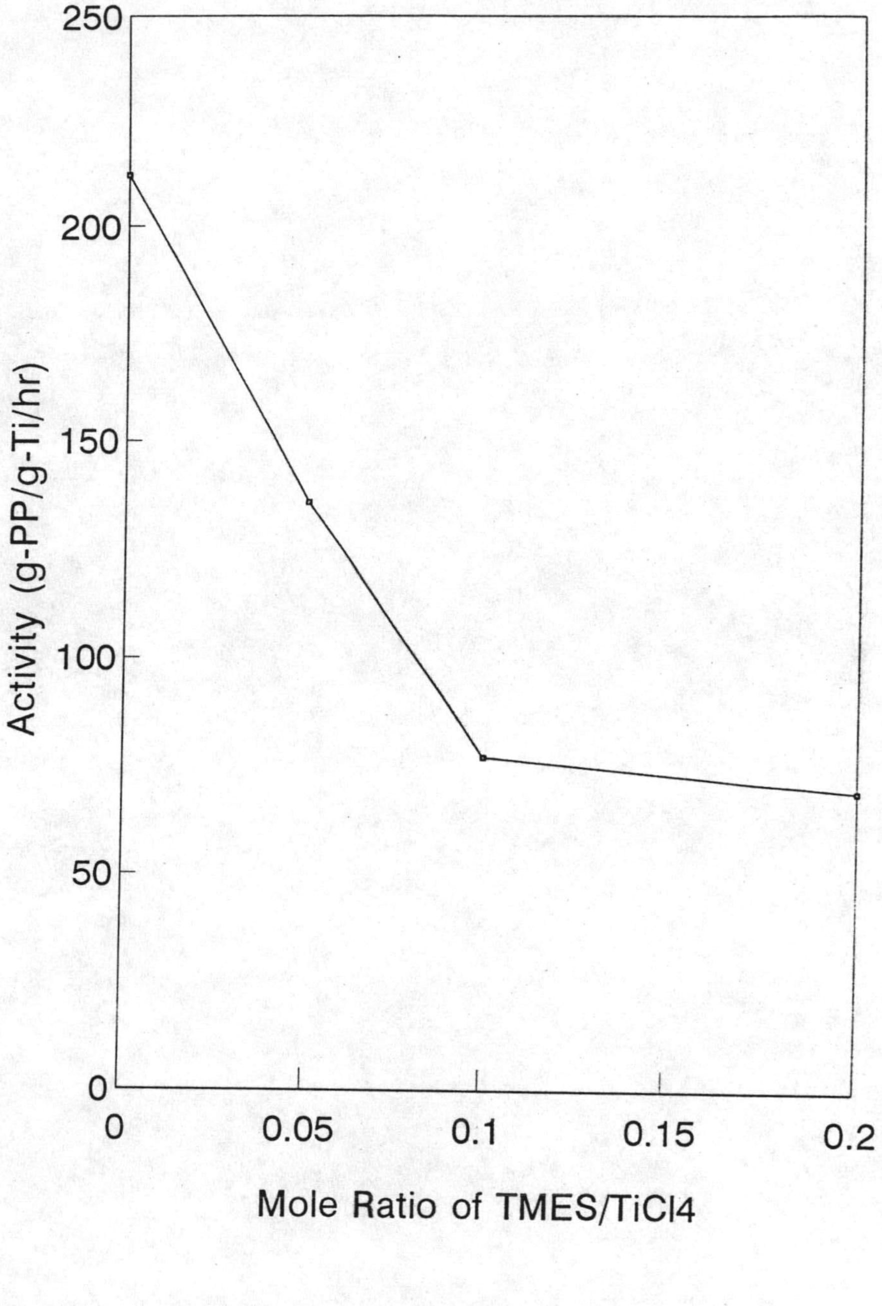


Figure 5.6 Catalyst Activity at various concentration of TMES with,
Polymerization condition ; [Ti] = 8.936 mmol/l,
Al/Ti = 2,
Propylene to hydrogen ratio = 3,
Total pressure = 98.0 psi,
Polymerization time = 1.5 hr

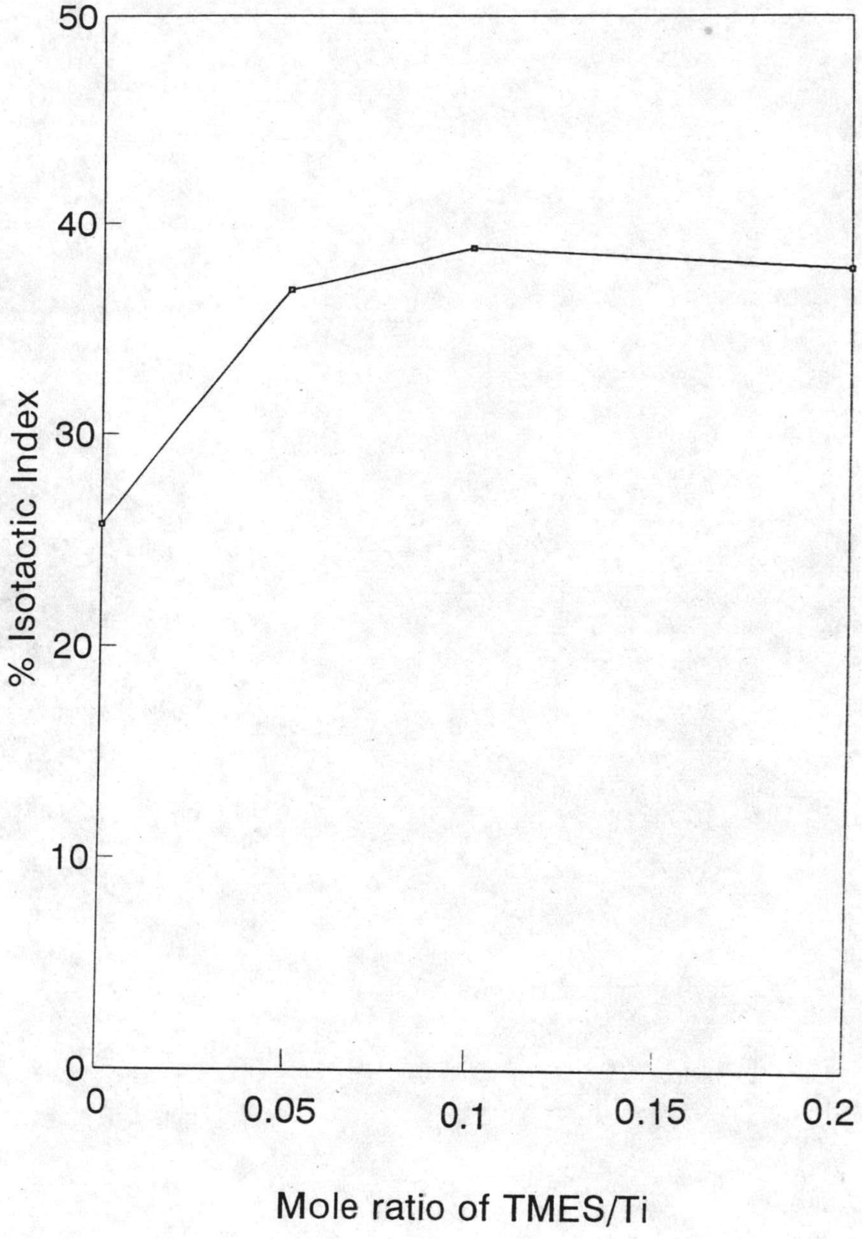


Figure 5.7 % Isotactic Index of polypropylene at various mole ratio of TMES/Ti with,

Polymerization condition ; [Ti] = 8.936 mmol/l,
Al/Ti = 2,
Propylene to hydrogen ratio = 3,
Total pressure = 98.0 psi,
Polymerization time = 1.5 hr

Table 5.2 Effect of external electron donors on polypropylene synthesis.

Electron donor*	Activity (gPP/gTi-hr)	% Isotactic Index (% I.I) **
No Use	212.69	25.73
TES	69.50	25.00
MTES	71.30	35.20
DMDES	44.22	36.40
TMES	136.06	36.82
PTES	90.81	37.00

* Mole ratio of Electron donor to Ti of 0.05

** % I.I. was determined from % insoluble weight of polypropylene in boiling heptane

Characterization of polypropylene

The polypropylene products were subjected to Scanning Electron Microscope at enlargement of 1500 times. Morphology meaned the size and shape of polypropylene. Polypropylene fibrils form $TiCl_4/AlEt_3$ system without external electron donor were shown in Figure 5.8 a. Since the rate of polymerization was initially more rapid than the rate of crystallization as proposed by Guttman and Guillet [78]. They proposed a model on the basis of observations made when propylene was subjected to a vapor phase polymerization with the $AlMe_3{*}\alpha\text{-}TiCl_3$. According to their view, the rate of polymerization was initially more rapid than the rate of crystallization, resulting in an initial structrure having the shape of a hemicpherical mass of amorphous polymer. As the size of this globule increases the rate orf polymerization decreases, and at this time, crystallization occurs at the apex of the globule in the form of floded chain lamellae.

Figure 5.8 b showed polypropylene particles from the same system which suspended in hexane. Their morphologies were same morphologies in Figure 5.8 a. Chanzy and co-workers [76] proposed that at high temperature (90 °C in this study), there was an opportunity for the polymer to dissolve in n-hexane solvent and then recrystallize.

Figure 5.8 c and Figure 5.8 d were scanning electron micrographs of polypropylene which were synthesized by adding TMES as external electron donor at ratio of TMES/Ti of 0.05. Figure 5.8 c was the polypropylene with fibrous shape when it was in the reactor. When it was enlarged by scanning electron microscope, it found that the microstructure was powder like as Figure 5.8 d. Figure 5.8 d was suspended polypropylene in n-hexane.

Figure 5.8 e and Figure 5.8 f were scanning electron micrographs of polypropylene which were synthesized by adding TMES at ratio of TMES/Ti of 0.1 and 0.2, respectively. It found that the fibrous structure of polymer was gradually disappeared. This result was in agreement with Lenz [127] but the real reason was unknown. It may be possible that TMES slow down the initial rate of polymerization as proposed by Wrister [79]. Because electron donor was the third component in the catalyst system which competed to adsord on the catalyst surface according to Langmuir-Hinshelwood mechanism (5.10)

Wrister proposed that the degree of order of polymer were : polymer coil (d = 6.4 A°), fibril (400 A°) which consisted of filaments and lamellae (100 A° thick), fibers (d = 5000 A°), subparticles 20 to 70 μm, and particle (60 to 500 μm) as shown in Figure 5.2

If TMES increase the initial rate of polymerization, the activity must be higher than the catalyst system without TMES according toWrister's proposal. But the activity was less than the catalyst system without TMES. So it may be possible that TMES slow down the initial rate of polymerization.

The other proposal for the fibrous structure of polymer disappeared was that TMES functioned as chain transfer as shown Eq. 5.18

$$[\mathrm{Cat}]\text{-}\mathrm{Pn} + \mathrm{CH_3Si(OC_2H_5)_3} \longrightarrow [\mathrm{Cat}]\text{-}\mathrm{CH_3} + \mathrm{PnSi(OC_2H_5)_3} \quad \text{(Eq. 5.18)}$$

From the result of the addition of TMES as external electron donor was found that the suitable of ratio of TMES/Ti was 0.05. (based on the scope of this work)

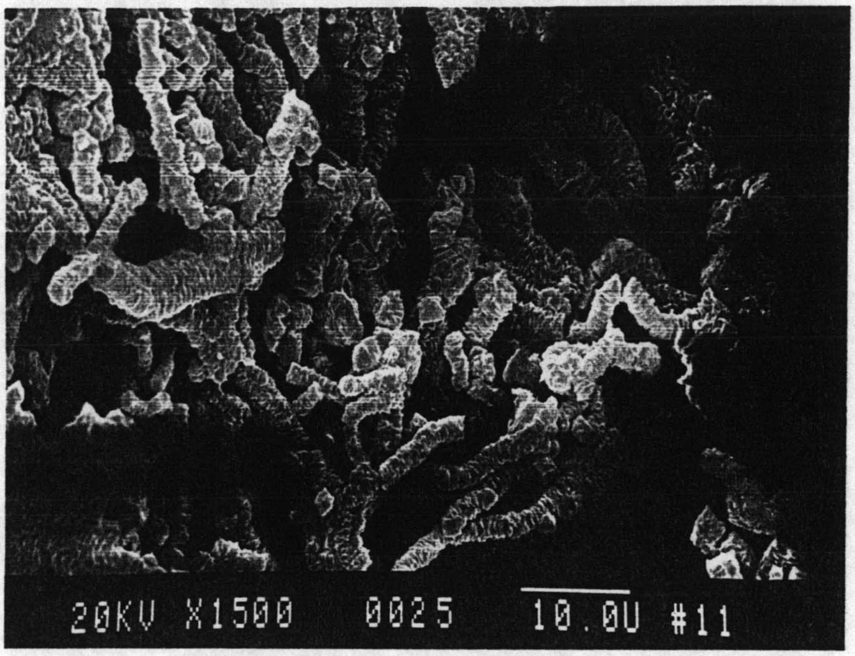


Figure 5.8 a Scanning electron micrograph of polypropylene fibril with,
Polymerization condition ; [Ti] = 8.936 mmol/l,
Al/Ti = 2,
Propylene to hydrogen ratio = 3,
Total pressure = 98.0 psi,
Polymerization time = 1.5 hr
No TMES used

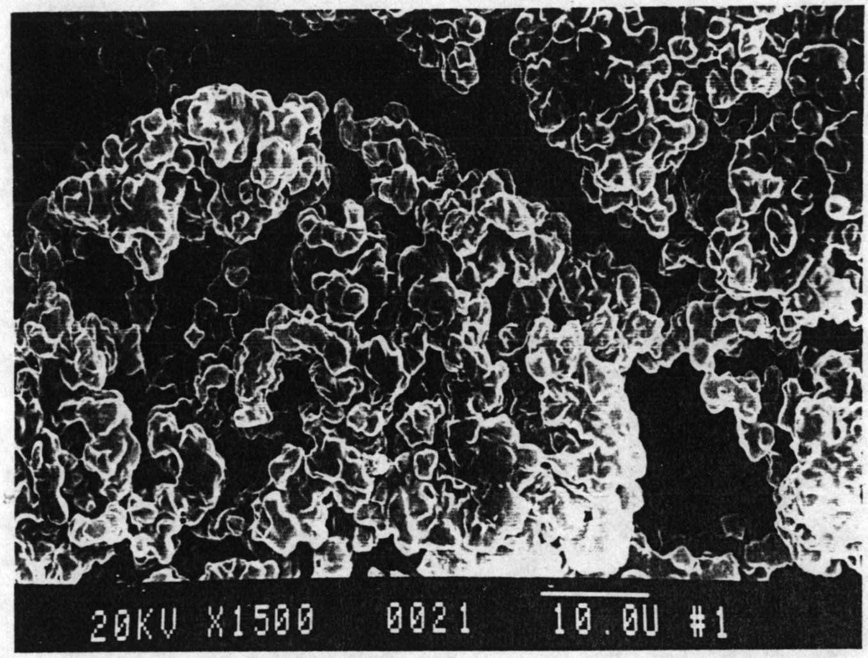


Figure 5.8 b Scanning electron micrograph of polypropylene which suspend in hexane with,
Polymerization condition ; [Ti] = 8.936 mmol/l,
Al/Ti = 2,
Propylene to hydrogen ratio = 3,
Total pressure = 98.0 psi,
Polymerization time = 1.5 hr
No TMES used

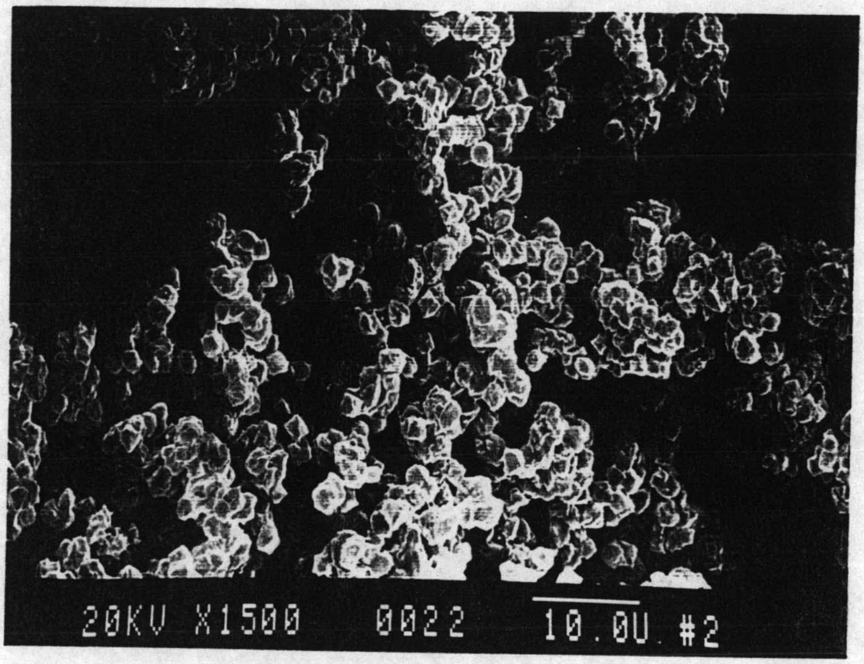


Figure 5.8 c Scanning electron micrograph of polypropylene fibril with,

Polymerization condition ; [Ti] = 8.936 mmol/l,
Al/Ti = 2,
Propylene to hydrogen ratio = 3,
Total pressure = 98.0 psi,
Polymerization time = 1.5 hr
TMES/Ti = 0.05

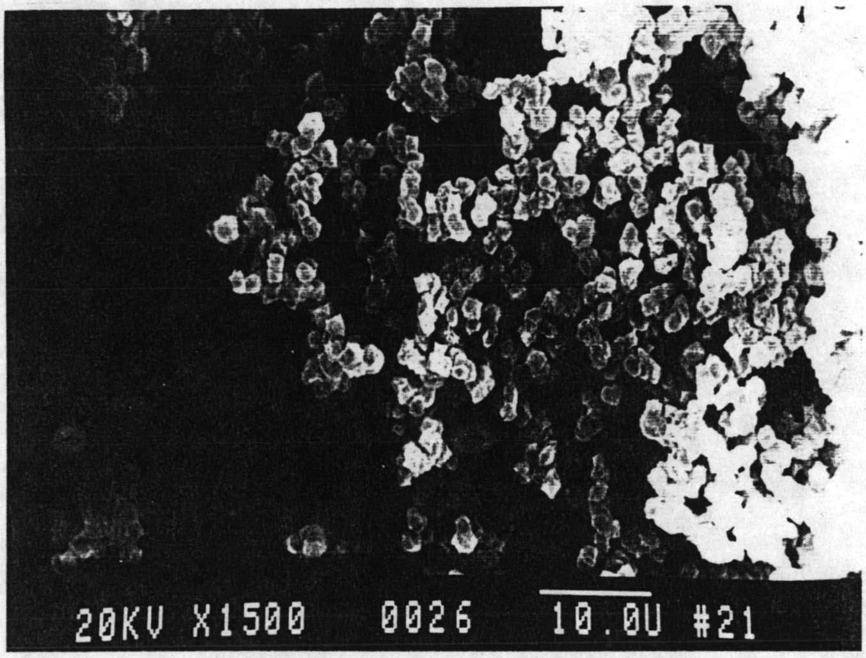


Figure 5.8 d Scanning electron micrograph of polypropylene which suspend in hexane with,

Polymerization condition ; [Ti] = 8.936 mmol/l,
Al/Ti = 2,
Propylene to hydrogen ratio = 3,
Total pressure = 98.0 psi,
Polymerization time = 1.5 hr
TMES/Ti = 0.05

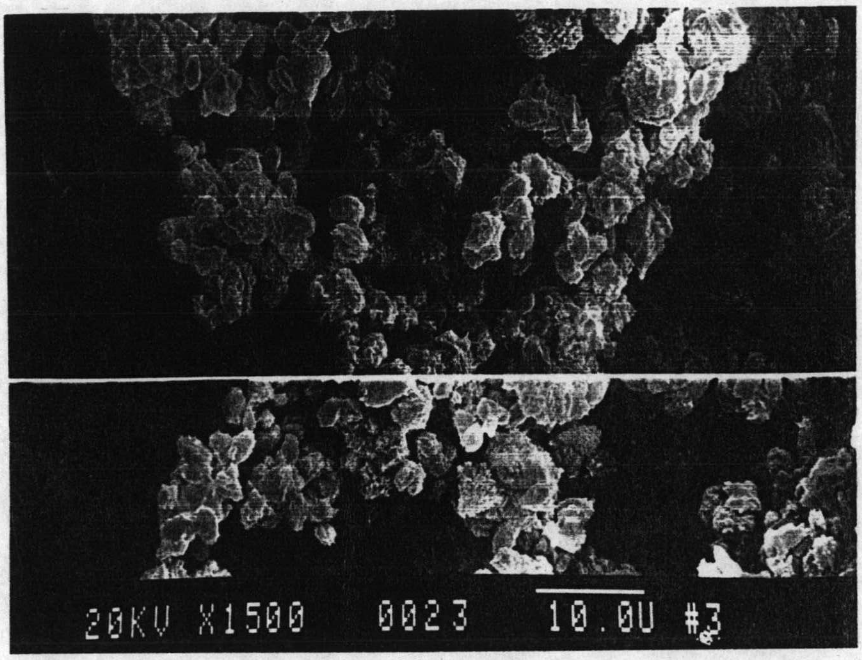


Figure 5.8 e Scanning electron micrograph of polypropylene which suspend in hexane with,

Polymerization condition ; [Ti] = 8.936 mmol/l,
Al/Ti = 2,
Propylene to hydrogen ratio = 3,
Total pressure = 98.0 psi,
Polymerization time = 1.5 hr
TMES/Ti = 0.10

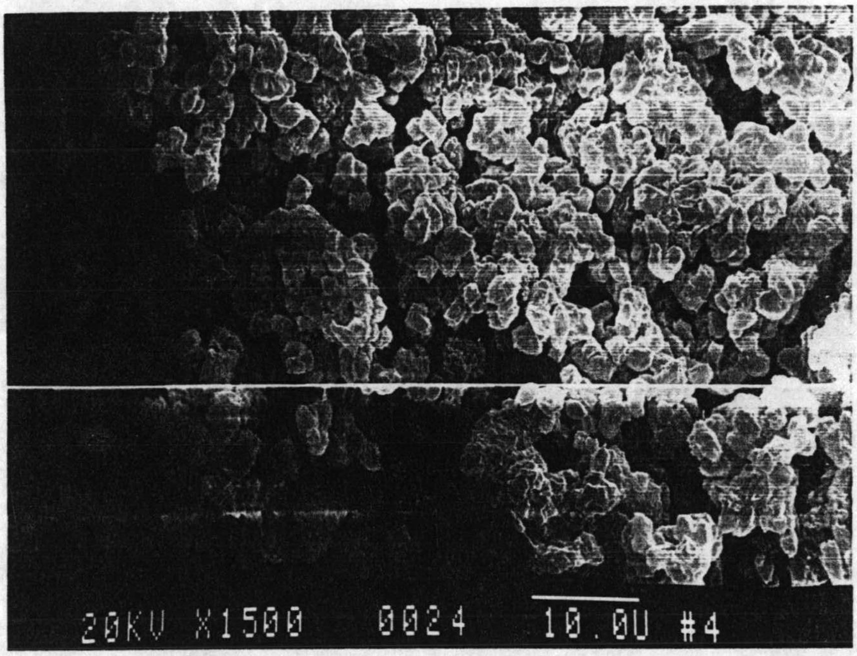


Figure 5.8 f Scanning electron micrograph of polypropylene which suspend in hexane with,
Polymerization condition ; [Ti] = 8.936 mmol/l,
Al/Ti = 2,
Propylene to hydrogen ratio = 3,
Total pressure = 98.0 psi,
Polymerization time = 1.5 hr
TMES/Ti = 0.20