

## CHAPTER V

### RESULTS & DISCUSSION

#### 5.1 CHARACTERIZATION OF THE PREPARED CATALYST

##### 5.1.1 Chemical Composition

The chemical analysis of each batch of the prepared Ziegler-Natta catalyst was carried out using inductively couple plasma emission spectrometer and atomic absorption spectrometer. The amount of titanium and magnesium in the catalyst are 1.53-2.22 % by weight and 16.1-20.5 % by weight, respectively as shown in Table 5.1. The results are in the expected range as reported in literature [49].

Table 5.1 The amount of titanium and magnesium in the prepared supported Ziegler-Natta catalysts

Sample Number	Amount of Ti (% by wt.)	Amount of Mg (% by wt.)
1	2.22	20.5
2	1.53	16.1
3	1.78	18.9

##### 5.1.2 Surface Area Measurement

Surface area of the prepared Ziegler-Natta catalyst was measured by BET method using  $N_2$  at  $-195\text{ }^\circ\text{C}$ . BET surface area of the catalyst was compared to those of the starting material magnesium chloride and intermediates as shown in Table 5.2.

Table 5.2 Surface area of the materials in each step of the catalyst preparation

Materials	BET surface area(m <sup>2</sup> /g)
MgCl <sub>2</sub>	1.5951
MgCl <sub>2</sub> /2EHA/PA/TiCl <sub>4</sub>	148.1734
MgCl <sub>2</sub> /2EHA/PA/TiCl <sub>4</sub> /DEP	159.4849
Ziegler-Natta catalyst	166.0676

After recrystallization of commercial magnesium chloride and addition of 2-ethyl hexanol, phthalic anhydride and titanium tetrachloride, the surface area of the material becomes much larger than that of magnesium chloride itself. Subsequent addition of diethyl phthalate and double treatment with titanium tetrachloride causes little increase in surface area. Eventually, the obtained catalyst presents the highest surface area comparing to other materials in the catalyst preparation process.

Increment of surface area indicates that the catalyst exists in small crystals not aggregates. This is from the influence of the internal electron donor diethyl phthalate which prevents reagglomeration of small particles [11].

From the results of surface area prepared above, it can elucidate that the catalysts prepared by this method may have high activity. This could be described by higher surface area making higher amount of Ti to be supported on. The supported Ziegler-Natta catalyst prepared by Sakdejyont [114] using no internal electron donor and ball-milled of MgCl<sub>2</sub> had specific surface area of only 16 m<sup>2</sup>/g in contrast to the supported Ziegler-Natta catalyst prepared in this work using internal electron donor and recrystallized MgCl<sub>2</sub> which has specific surface area of about 166 m<sup>2</sup>/g. The surface area of the latter is about 10 fold improved. This implies that the amount of Ti supported on the catalyst may be upto 10 fold also. Subsequent expectation is the improvement of the catalyst activity due to the increase of surface area.

### 5.1.3 X-ray Diffraction (XRD)

The x-ray diffraction patterns of chemically treated magnesium chloride loaded with titanium tetrachloride are shown in Figure 5.1. Crystalline structure of  $\text{MgCl}_2$  disappeared after the chemical modification of  $\text{MgCl}_2$  to  $\text{MgCl}_2 / 2\text{EHA} / \text{PA} / \text{TiCl}_4$  and  $\text{MgCl}_2 / 2\text{EHA} / \text{PA} / \text{TiCl}_4 / \text{DEP}$ . This may be due to the formation of a new complex from chemical treatment. Only amorphous was found with treatment of 2-ethyl-hexanol (EHA), phthalic anhydride (PA),  $\text{TiCl}_4$  and even with diethyl phthalate (DEP). The x-ray diffraction pattern of the Ziegler-Natta catalyst in this work and that prepared by You Liang Hu are shown in Figure 5.2. From this figure it was found that a new crystalline phase was formed after second loading with  $\text{TiCl}_4$  in the last step. This shows that it is the product from  $\text{TiCl}_4$  reacted with the treated surface of  $\text{MgCl}_2$  or the amount of  $\text{TiCl}_4$  at the first loading is not enough to form the crystalline product. The new crystalline phase may be a combinatorial compound comprising of two phases at least, and similar to the catalyst prepared by You Liang Hu and Chien [121]. However, it had a little second phase above the 60 degree of  $2\theta$  in the prepared catalyst from this work.

### 5.1.4 Active Sites Measurements

As shown in Table 5.3, the active sites of the Ziegler-Natta catalyst with different external electron donors have a trend to decrease when increasing number of ethoxy group in external electron donors like a trend of activities.

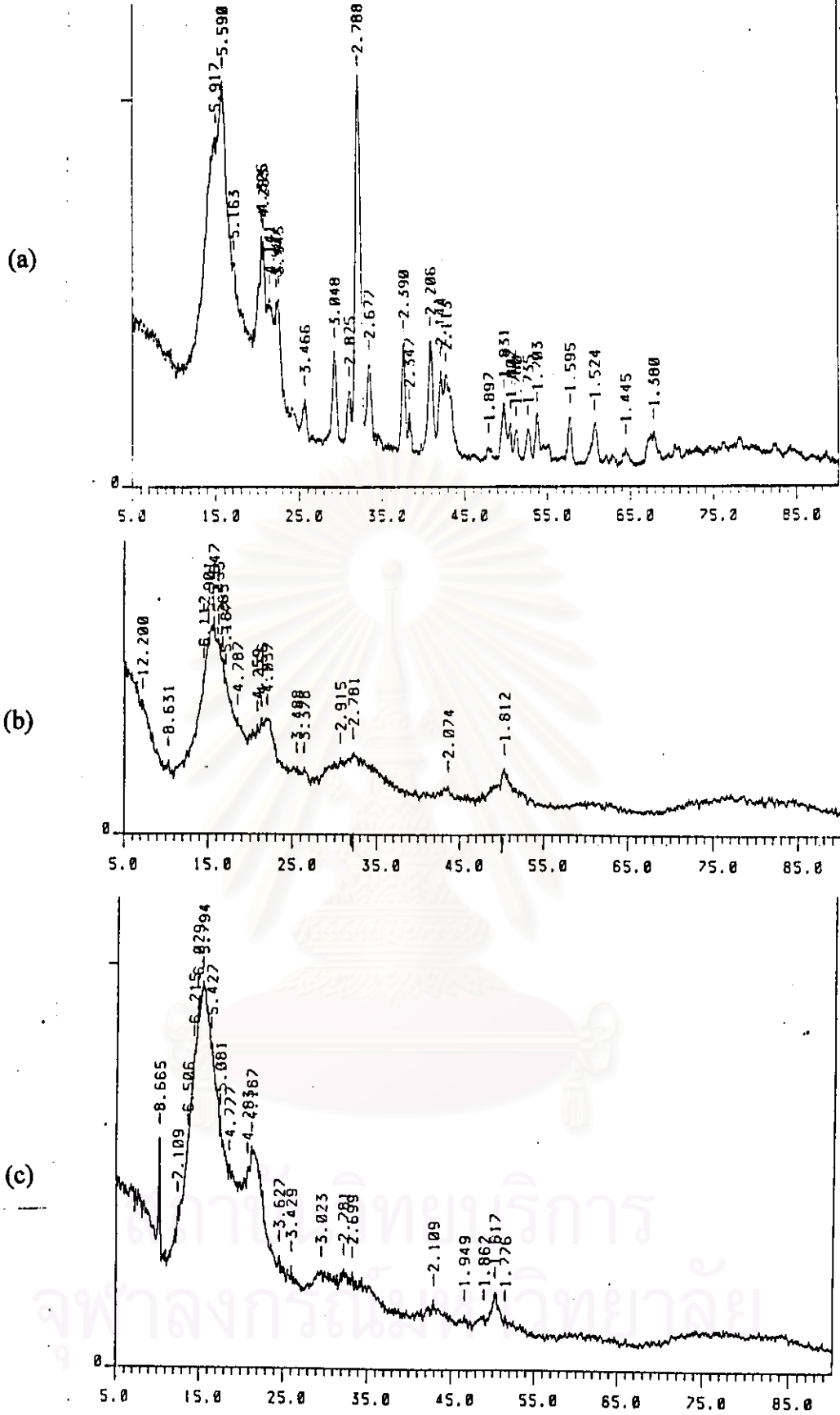


Figure 5.1 X-ray diffraction patterns of (a)  $\text{MgCl}_2$

(b)  $\text{MgCl}_2 / 2\text{-ethyl hexanol} / \text{phthalic anhydride} / \text{TiCl}_4$

(c)  $\text{MgCl}_2 / 2\text{-ethyl hexanol} / \text{phthalic anhydride} / \text{TiCl}_4 / \text{diethyl phthalate}$

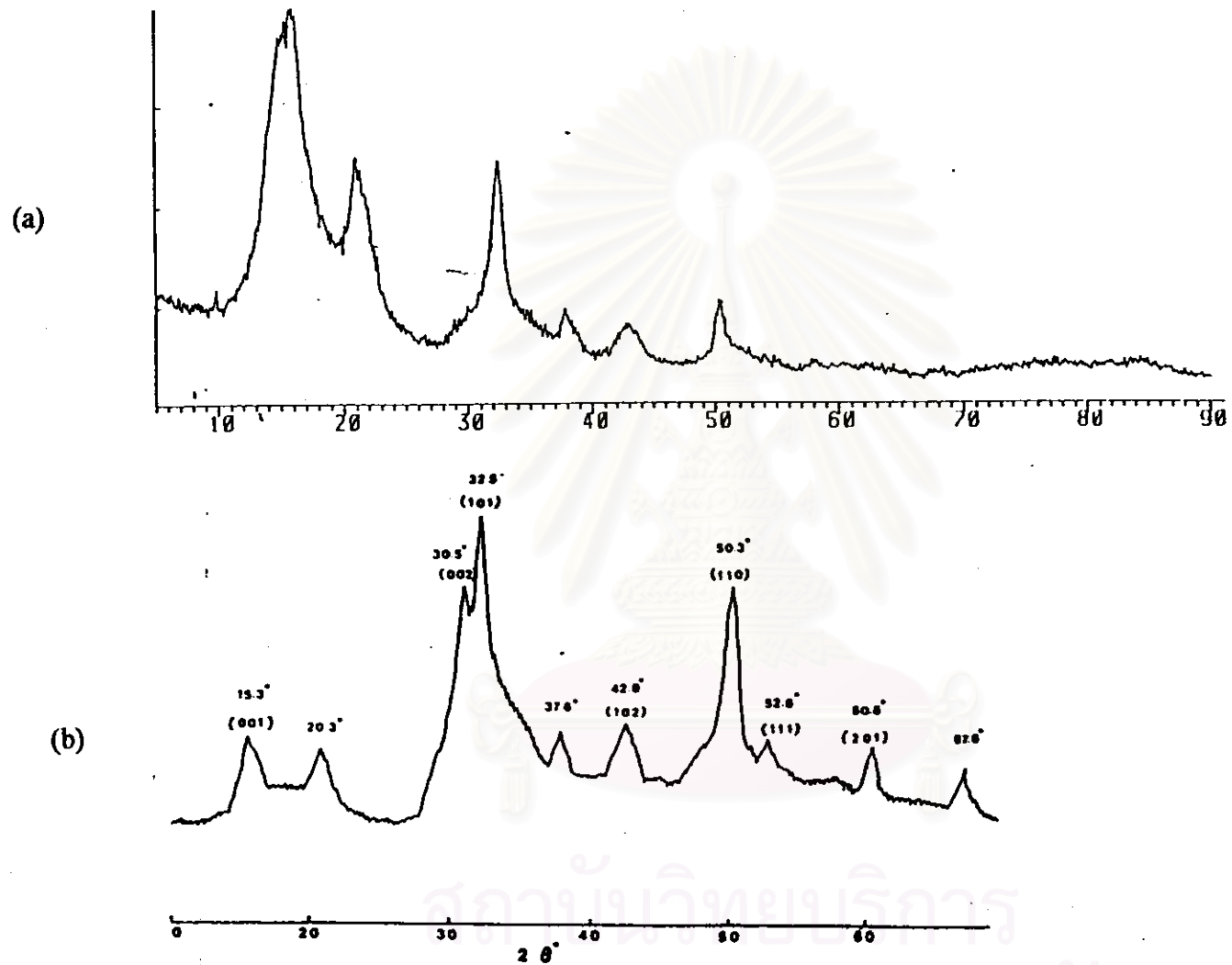


Figure 5.2 X-ray diffraction patterns of Ziegler-Natta catalyst prepared by (a) this work (b) You Liang Hu and Chien [121]

Table 5.3 Effect of external electron donors on the activities and active sites of prepared catalyst.

Catalyst with external donors	Active sites (CO molecules/g cat.)	Activity (g PP/g Ti-hr)
NO EXTERNAL BASE	$1.56 \times 10^{18}$	2064
TMES	$1.10 \times 10^{18}$	1950
DMDES	$0.72 \times 10^{18}$	1562
MTES	$0.68 \times 10^{18}$	1164
TES	$0.60 \times 10^{18}$	897
PTES	$0.84 \times 10^{18}$	1618

This can be suggested that the catalytic activity depends on the number of active sites. It can be noted that more ethoxy groups may have more electrons from oxygen of ethoxy group to donate to the vacant site of the catalyst[123]. The more electrons can block the vacant site tightly and difficult to be removed. Subsequently, the lower the number of active site of the catalyst, less amount of monomers can coordinate to the vacant site. Therefore, the catalytic activity is decreased.

Relationship between activities and active sites of supported Ziegler-Natta catalyst using various external electron donors is shown Figure 5.3. It was found the catalyst in the absence of external electron donor shows the highest active sites. It may indicated that this catalyst has more Ti accessible to CO molecules compared with the others. By adding the different external electron donors in some portions to the of supported Ziegler-Natta catalyst, external electron donors can occupy some of Ti active sites whereas the others still remain. This caused the lower of active sites of the catalyst in the presence of external electron donors. Thus, CO adsorption of the catalysts adding some external electron donors are less than CO adsorption of the catalyst adding no bases.

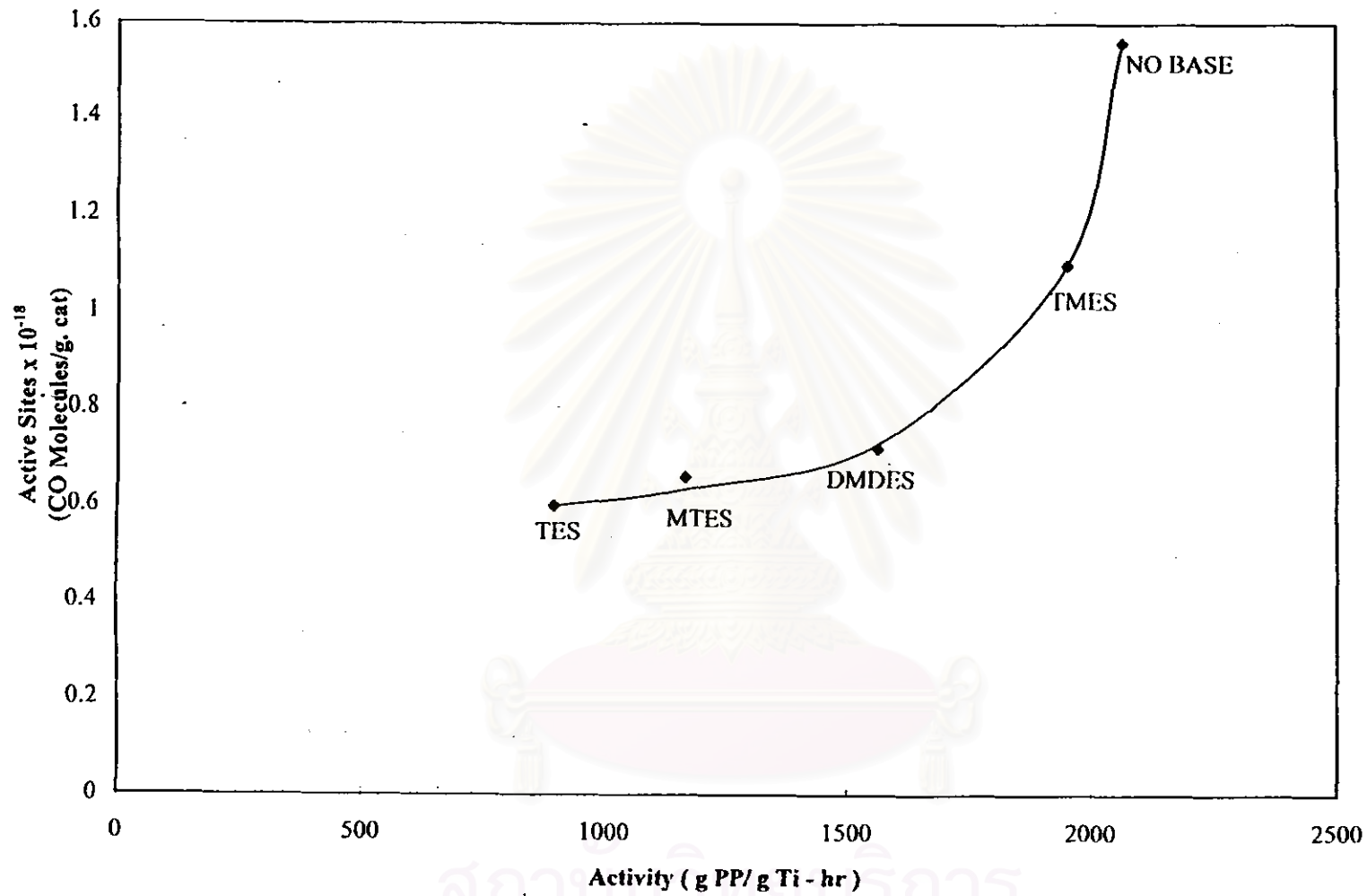


Figure 5.3 Relationship between activities and active sites of supported catalysts.

From this figure, it was also found that the relationship of activities and active sites of TES, MTES and DMDES are similar in trend but TMES shows a difference. Catalysts with the three former bases have almost linear relationship while TMES shows the difference that its active sites loses in a large number whereas its activity slightly decreases. It may be suggested that the prepared catalyst has both active and inactive Ti that external electron donors can block these sites in a random manner. The proposed model for linear relationship of three bases is that each external electron donors occupied all of Ti inactive sites which remained in the small portions and some of Ti active sites. Subsequently, increasing in activity is in proportional to increasing of active sites. In the case of TMES, though it occupied both inactive and active Ti but it cannot block all of inactive Ti. Thus active sites value measured by CO molecules is higher than the expected value. The line passed along TMES seems to be a curve because CO can block inactive which do not participate in the polymerization and thus do not have an activity.

## 5.2 CATALYTIC ACTIVITY AND ISOTACTICITY OF PRODUCTS

The catalytic activity and the isotacticity of propylene polymerization in this work are shown in Figure 5.4 and Figure 5.5, respectively. It was found that the catalytic system with internal electron donor show higher activity but almost the same isotacticity compared with the catalytic system with no internal electron donor. It was also found that the activity was decreased in order : PTES > TES > MTES > DMDES > TMES > no base thus when increased the number of alkoxy group, activity was decreased. On the other hand, isotacticity of the polypropylene was increased by increasing the number of ethoxy groups. Comparisons of the effect of external electron donors in unsupported Ziegler-Natta catalyst system, supported Ziegler-Natta catalyst system in the absence of internal electron donor prepared by ball-milling method and supported Ziegler-Natta catalyst system in the presence of internal electron donor prepared by recrystallizing method on the catalytic activity and isotacticity of propylene products are presented in Figures 5.6 and 5.7. It is found that the supported



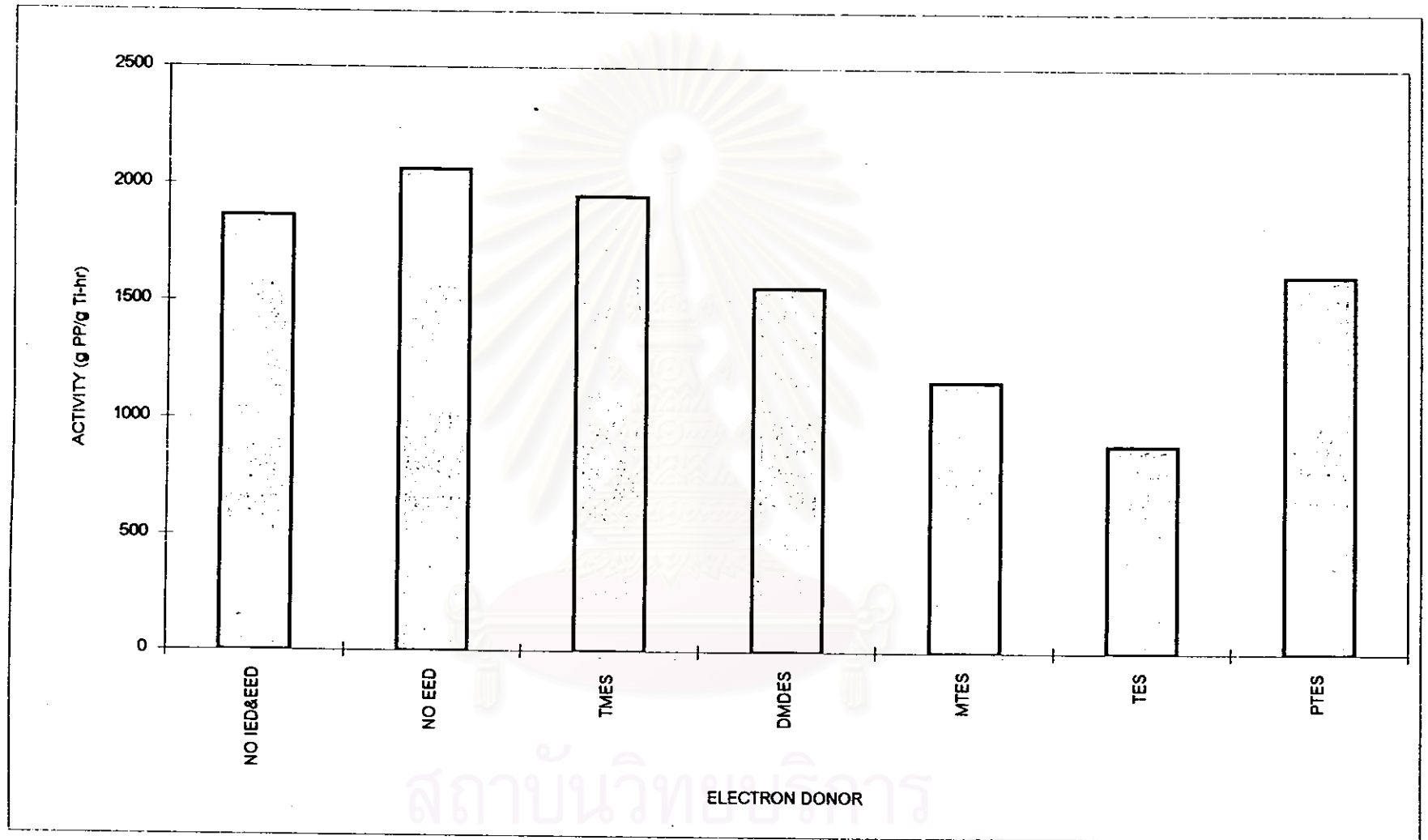


Figure 5.4 Effect of electron donors on the activity of the supported catalyst.

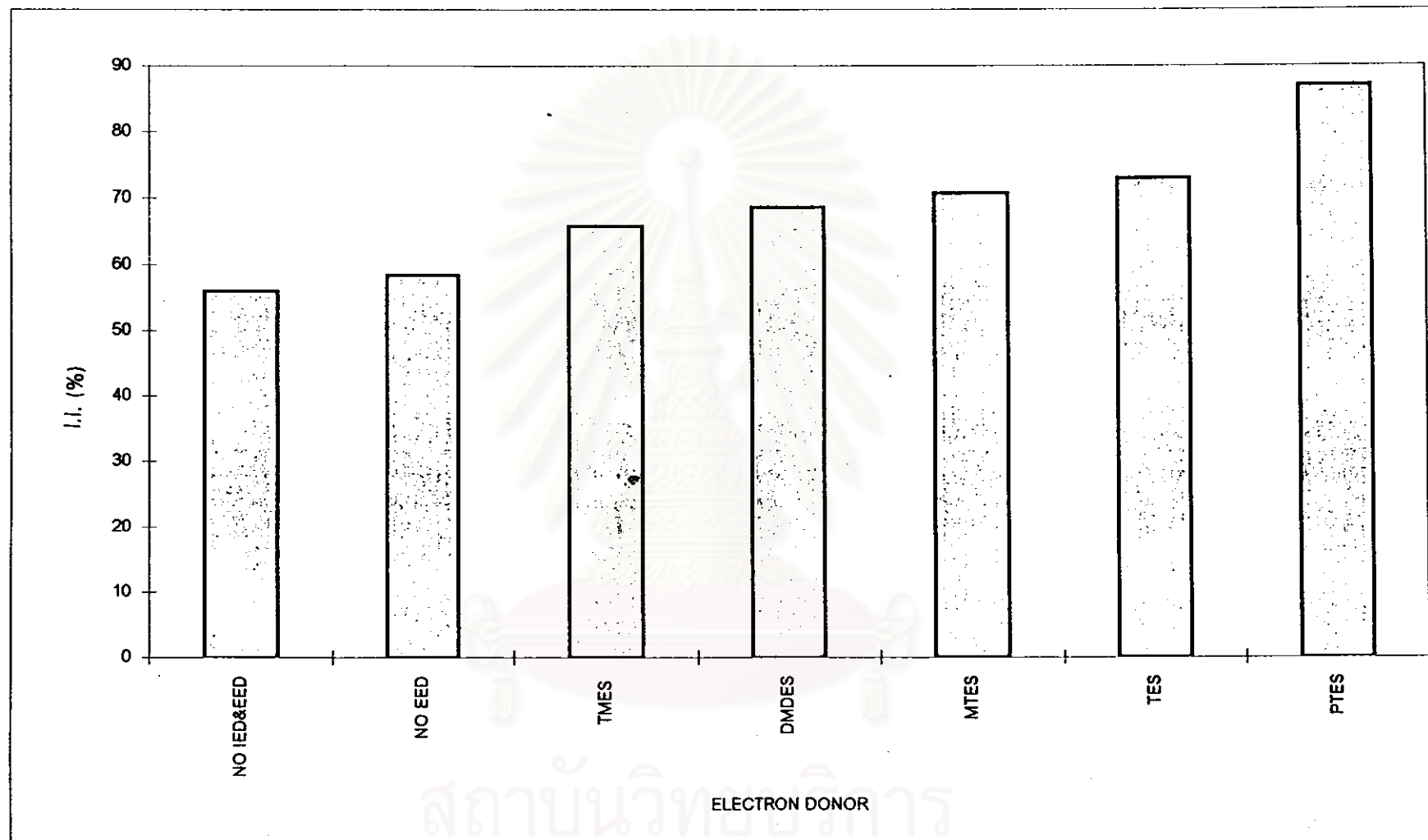


Figure 5.5 Effect of electron donors on the isotacticity of the supported catalyst.

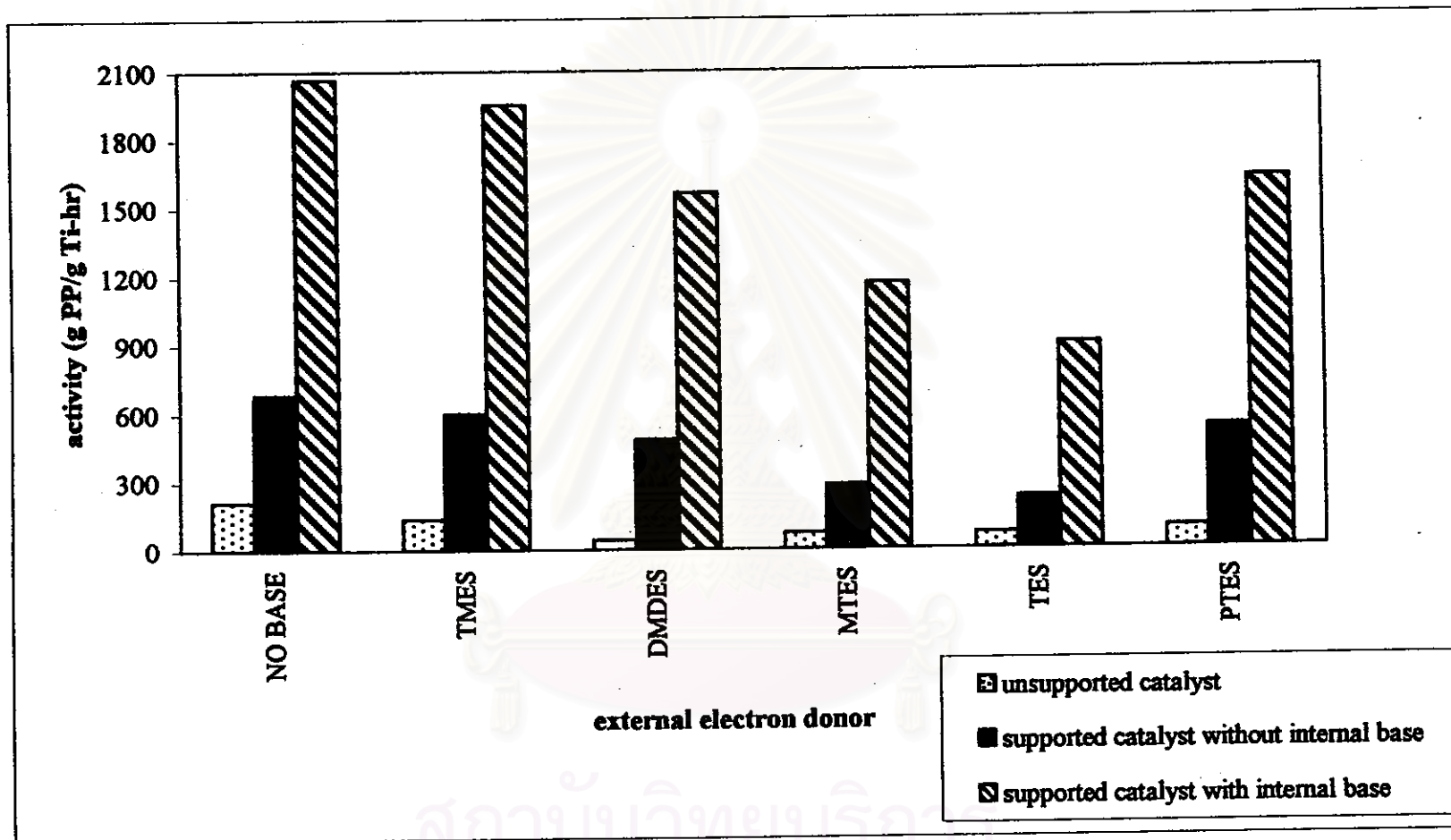


Figure 5.6 Comparison of catalytic activity of unsupported catalyst and supported catalyst with and without internal electron donor

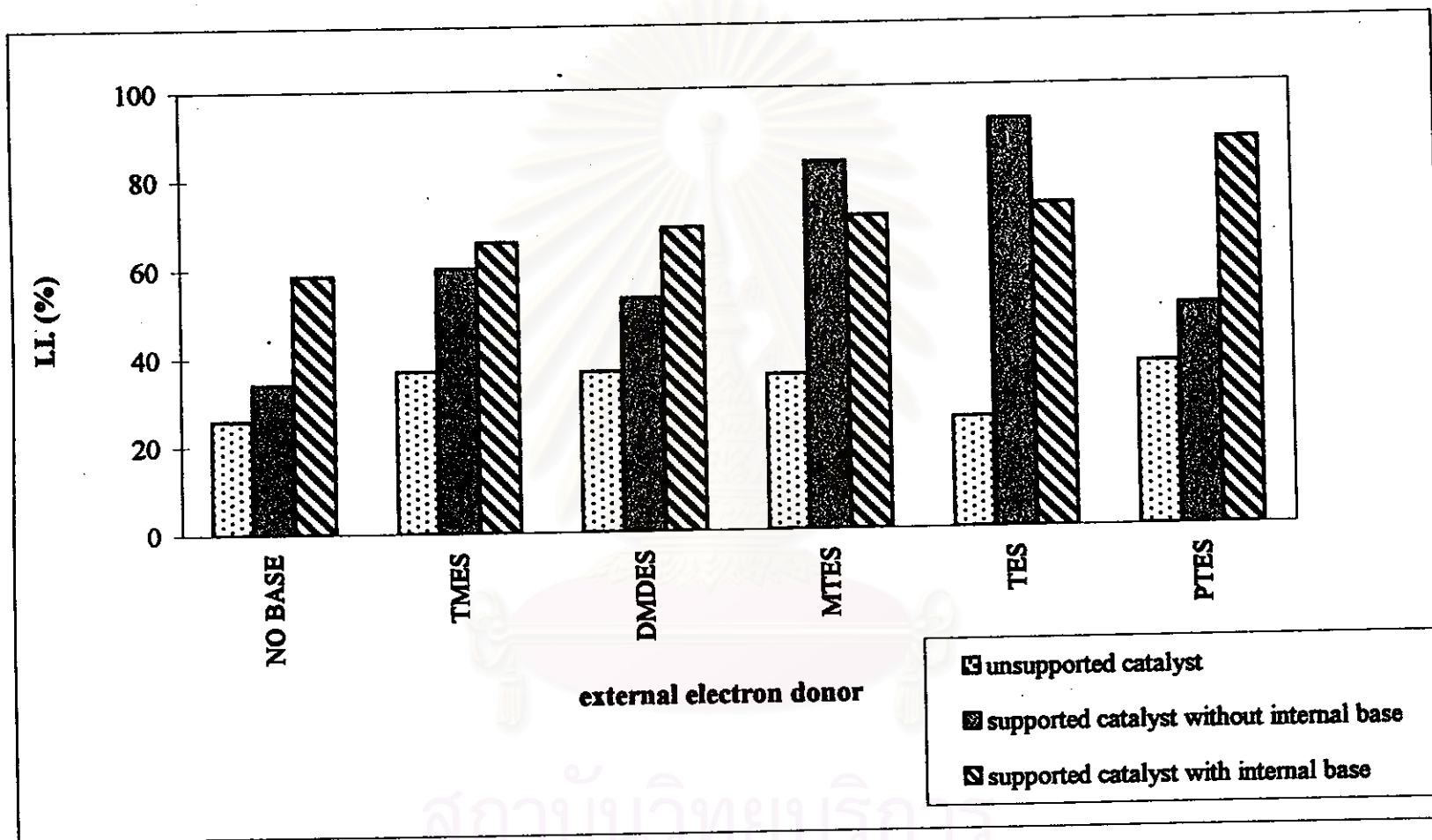


Figure 5.7 Comparison of isotacticity of polypropylene products using unsupported catalyst and supported catalyst with and without internal electron donor

catalyst shows the higher activity and provides higher isotacticity of polypropylene than unsupported catalyst does. Comparing between supported catalyst in the absence and presence of internal electron donor using the various external electron donors prepared by different methods it can be suggested that the most of the catalysts prepared by using the internal electron donor showed higher activities and isotacticities. In addition, it can be noted that the increment of activities showed more remarkable than that of isotacticities.

Decrement of activity when the number of alkoxy groups increases maybe due to the ability of uncoordinated alkoxy groups in alkoxy silane  $\cdot$   $\text{AlEt}_3$  complex deactivates the active centers of the catalyst [11]. Because  $\text{AlEt}_3$  had a strong tendency to form dimer to each other as shown in Figure 5.8 [1] it caused electron deficiency in the aluminium atom of  $\text{AlEt}_3$  which had coordination number 3. This structure was stable and inactive. Electron donors were added in the system to prevent this behavior by forming complex with  $\text{AlEt}_3$  [1,115]. At room temperature,  $\text{AlEt}_3$  and alkoxy silane instantly form 1:1 complex independent of the number of alkoxy groups in the silane [115]. This kind of complex was suggested in the increasing the isotacticity by activating Ti sites to be isotactic centers [48]. If the silane had originally more than one alkoxy group, there remain the other alkoxy groups uncoordinated in  $\text{AlEt}_3$ -donor complex [115]. This uncoordinated alkoxy groups blocked the active sites and resulted in decreasing activity.

Effect of size of alkyl ligand of Si in triethoxysilane was also shown. It was found that PTES showed the higher activity isotacticity than MTES. This may be because it had larger hydrocarbon group thus it had the steric hindrance that PTES could not reach the active site. Subsequently, the activity of PTES is higher than MTES. In addition, the higher isotacticity of PTES may be due to its steric hindrance that control the stereoregularity of the polymer chain to be isotactic structure as reported by Harkonen et al. [116].

Increment of isotacticity is affected by increasing the number of ethoxy groups. This may be because external electron donors that have more ethoxy groups can block more vacant sites. Subsequently, many atactic sites may be blocked more than isotactic sites [48].

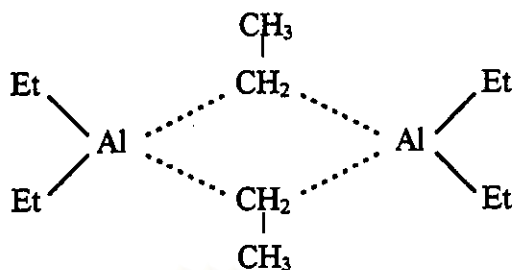


Figure 5. 8 Dimer of  $\text{AlEt}_3$  [116]

Higher activity and higher isotacticity in the supported catalyst system may be due to active sites of supported catalyst had less steric hindrance which give more isolated centers of supported catalyst. This was easier for external electron donor to access [1,36]. From the supported catalyst system prepared by recrystallizing method in the absence and presence of internal electron donor it may be concluded that internal electron donors do not have much effect on isotacticity but have some on activity. The higher activity of the catalytic system with internal electron donor may be because internal electron donor prevents reagglomeration of small  $\text{MgCl}_2$  particles in the preparation of catalyst and thus maintain the high specific surface area of the catalyst as discussed in the previous section. This result is in agreement with Keszler et al. [104].

Comparison between activity and isotacticity of the supported catalyst prepared by ball-milling method and recrystallizing method it was found that the activities of the catalysts prepared by recrystallizing method were higher than the catalyst prepared by ball-milling method in all cases. It was due to the higher surface area of the solid catalyst prepared by recrystallizing method. The transition metal can be fixed to the surface of a higher surface carrier. If done properly, the metal atom remains isolated, and greater number of transition metal have the potential to become more active centers [1]. However, the sequence of activity of the external electron donor was not depend of the method of the preparation of the catalyst. In addition, the order of activity of the external electron donor was the same irrespective of the presence or absence of internal electron donor.

### 5.3 CHARACTERIZATION OF POLYPROPYLENE PRODUCTS

#### 5.3.1 Microstructure Determination

The infrared spectra of polypropylene produced from supported Ziegler-Natta catalyst by using diethyl phthalate as the internal electron donor but different external electron donor are presented in Figure 5.8. The infrared identification of polypropylene for each peak is assigned to the organic groups as summarized in Table 5.4.

Table 5.4 Identification of infrared spectrum of polypropylene [122].

Wave Number (cm <sup>-1</sup> )	Assignment
1378/1460	CH <sub>3</sub> bending
1630	(trans)-R <sub>1</sub> C=CR <sub>2</sub> -
2850/2920	-(CH <sub>2</sub> )-, -(CH <sub>3</sub> )- stretching
3448	Hydroxyl group (-OH)

The wave numbers of 1378 and 1460 cm<sup>-1</sup> are the bending modes of CH<sub>3</sub>. The wave number of 1630 cm<sup>-1</sup> is the (trans)-R, C=R<sub>2</sub>-. In addition, the wave numbers of 2850 and 2920 cm<sup>-1</sup> were the stretching modes of -(CH<sub>2</sub>)- / -(CH<sub>3</sub>)-. From this work, all the figures show the peak at wave number of 1378 cm<sup>-1</sup> which is characteristic branched chain in obtained the polypropylene. It was found that each obtained polypropylene and standard peak of polypropylene in the FT-IR library software are 80-90 % alike. As this result, it can be confirmed that the products obtained from the polymerization are all polypropylene.

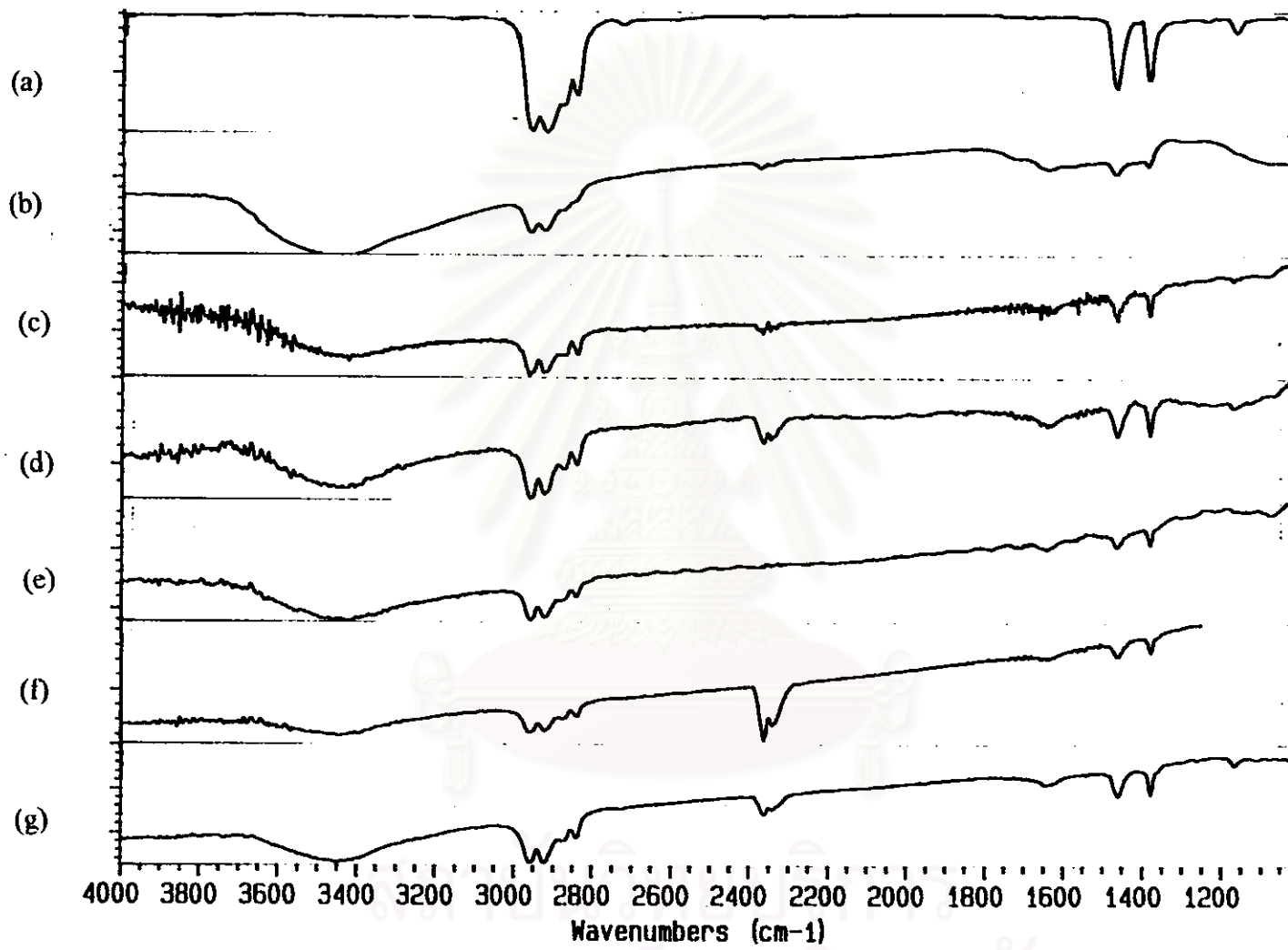


Figure 5.9 Infrared spectra of polypropylene in (a) FT-IR library compared with infrared spectra of polypropylene produced by  $\text{MgCl}_2/\text{diethyl phthalate}/\text{TiCl}_4\text{-AlEt}_3/$  (b) no external base (c) TMES (d) DMDDES (e) MTES (f) TES (g) PTES catalytic system



### 5.3.2 Melting Temperature ( $T_m$ )

Figure 5.9 presents the melting temperature of polypropylene produced from the supported Ziegler-Natta catalyst with different external electron donors used as catalyst modifiers. The results of external electron donors on the melting temperature of produced polypropylene are summarized in Table 5.5. From this result, the melting temperatures show no significant differences. This can indicate that polypropylene produced by different external electron donors are similar in molecular weight[117].

Table 5.5 Effect of external electron donor on melting temperature of polypropylene

Type of external electron donor	Catalytic activity (g PP/g Ti hr.)	Melting temperature ( $T_m$ ) (°C)
no base	2064	153.13
TMES	1950	152.68
DMDDES	1562	153.57
MTES	1164	153.13
TES	897	150
PTES	1618	151.79

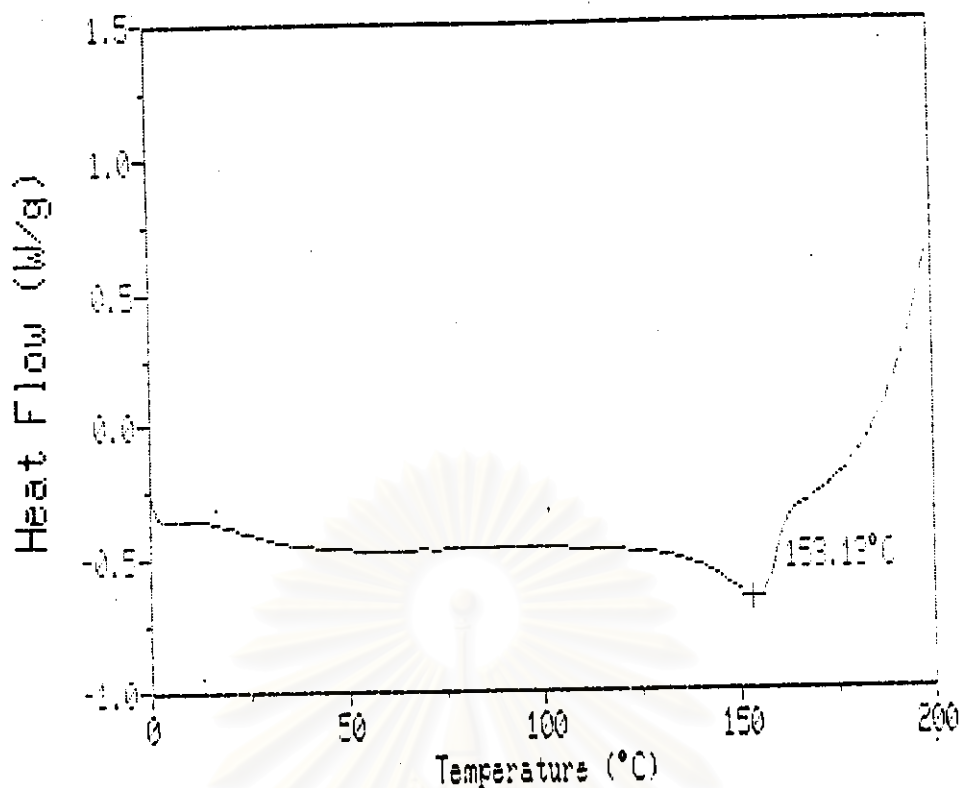


Figure 5.9 (a) DSC curve of polypropylene produced by  $\text{MgCl}_2$ /diethyl phthalate/ $\text{TiCl}_4$ - $\text{AlEt}_3$  catalyst system

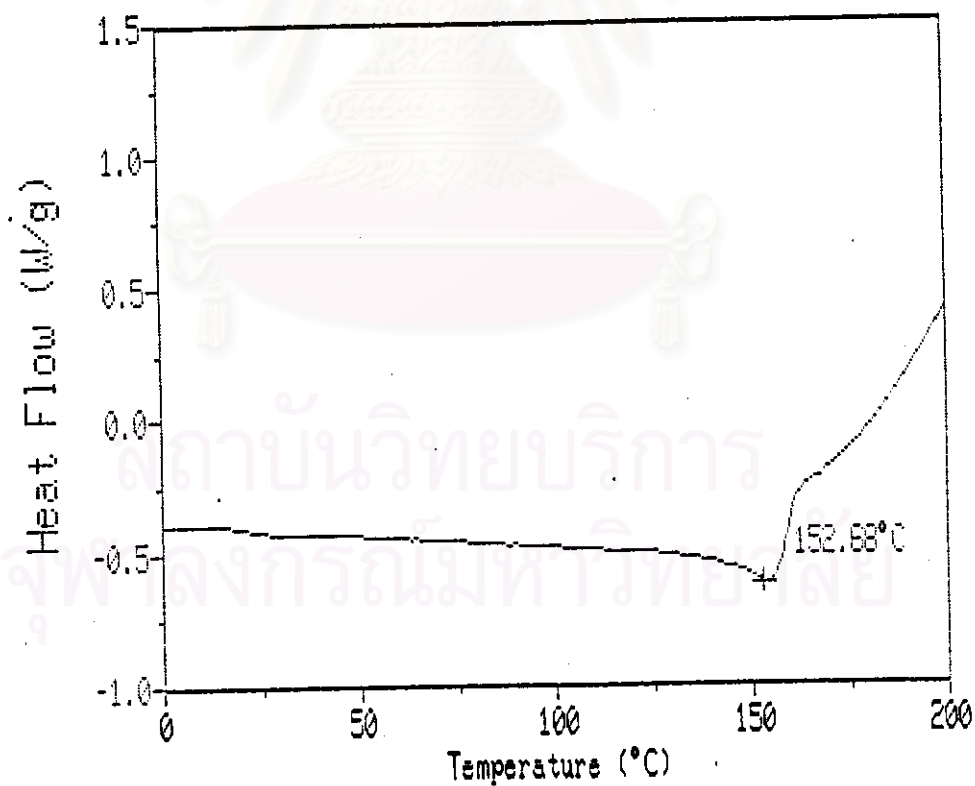


Figure 5.9 (b) DSC curve of polypropylene produced by  $\text{MgCl}_2$ /diethyl phthalate/ $\text{TiCl}_4$ - $\text{AlEt}_3$ -TMES catalyst system

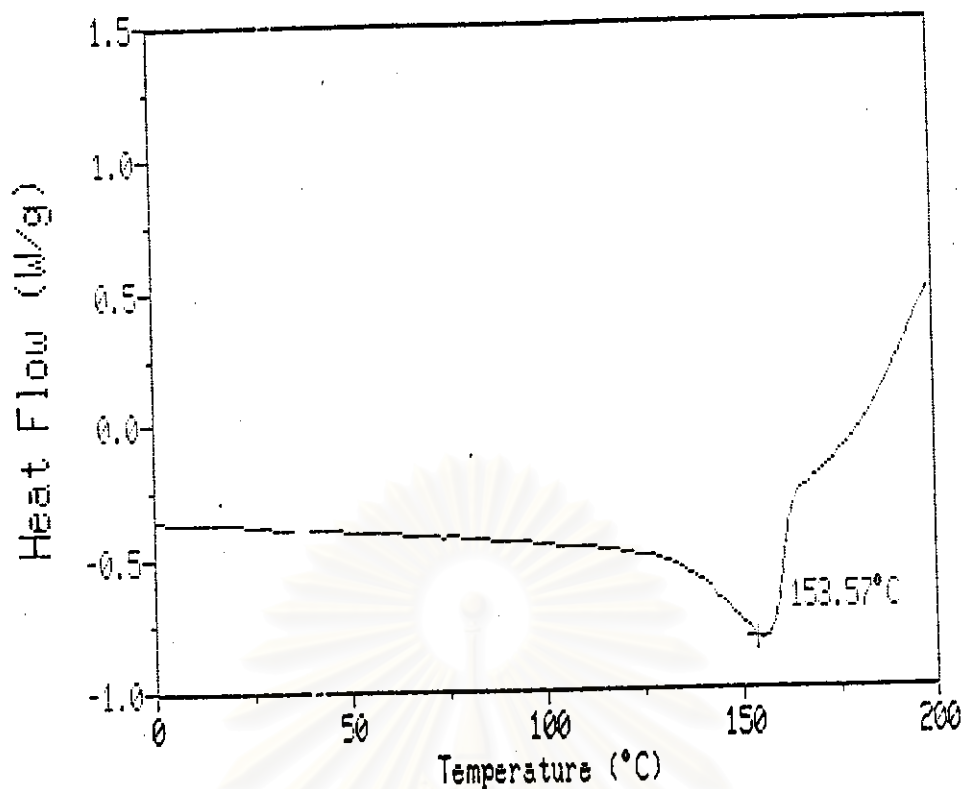


Figure 5.9 (c) DSC curve of polypropylene produced by  $\text{MgCl}_2$ /diethyl phthalate/ $\text{TiCl}_4$ - $\text{AlEt}_3$ /DMDES catalyst system

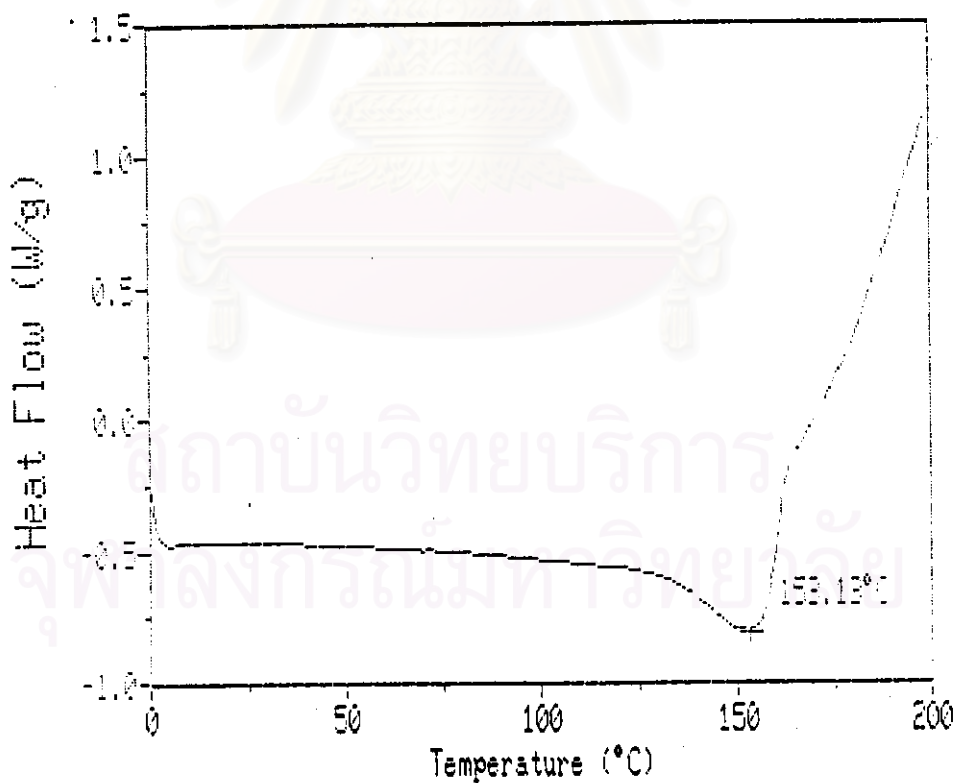


Figure 5.9 (d) DSC curve of polypropylene produced by  $\text{MgCl}_2$ /diethyl phthalate/ $\text{TiCl}_4$ - $\text{AlEt}_3$ /MTES catalyst system

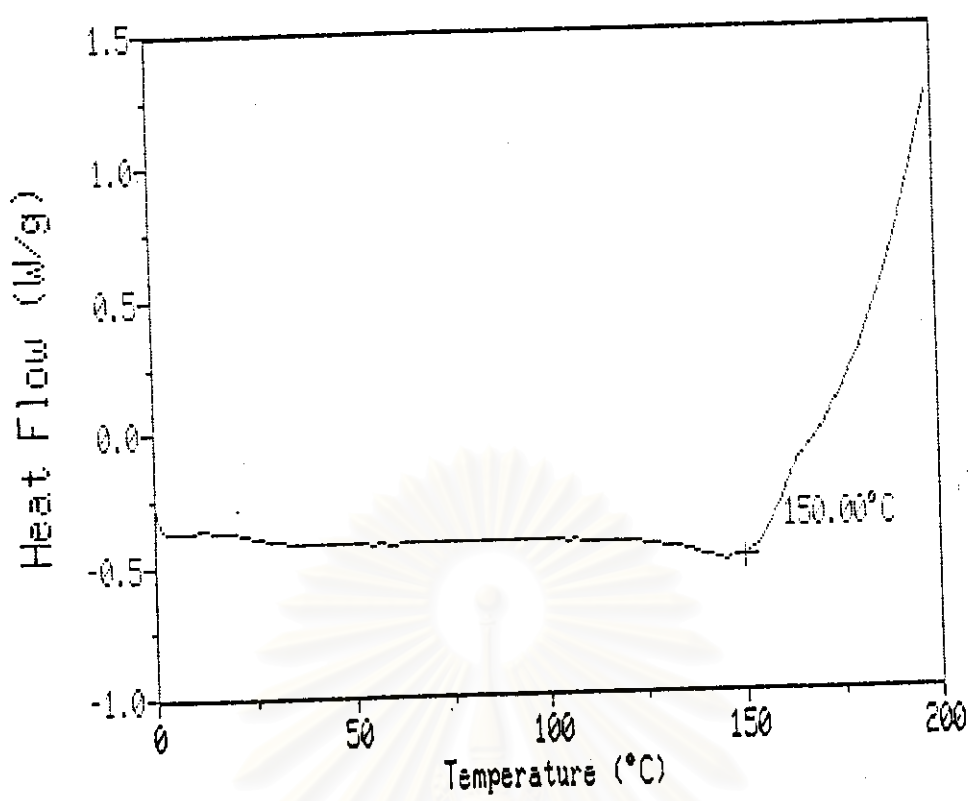


Figure 5.9 (e) DSC curve of polypropylene produced by MgCl<sub>2</sub>/diethyl phthalate/TiCl<sub>4</sub>-AlEt<sub>3</sub>/TES catalyst system

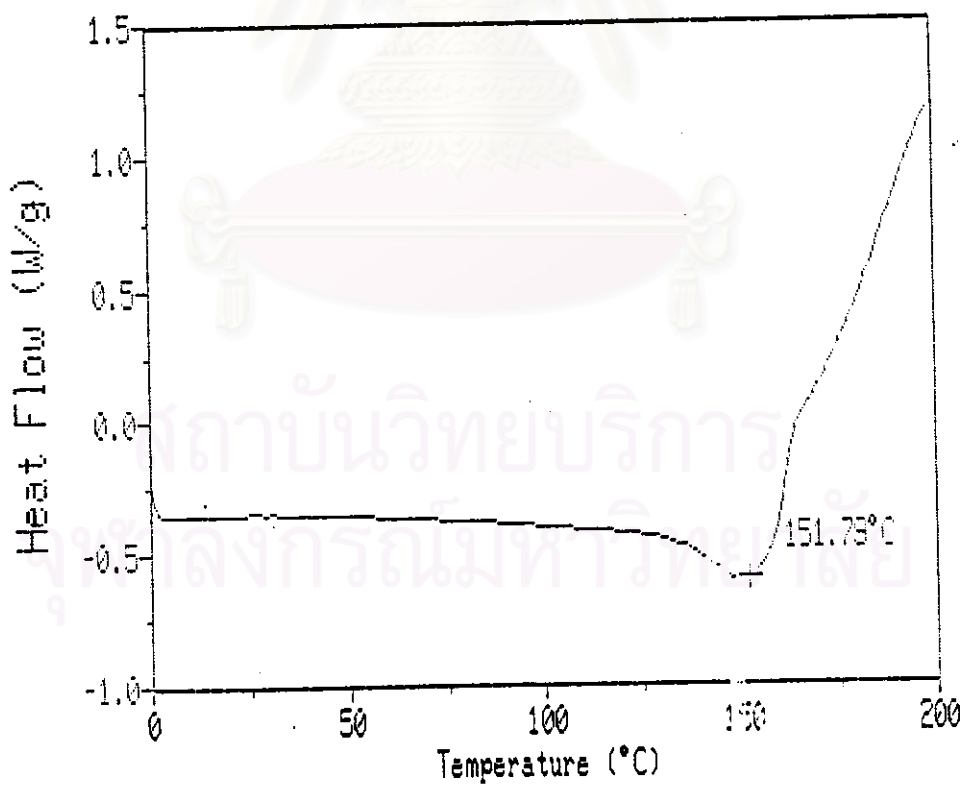


Figure 5.9 (f) DSC curve of polypropylene produced by MgCl<sub>2</sub>/diethyl phthalate/TiCl<sub>4</sub>-AlEt<sub>3</sub>/PTES catalyst system

### 5.3.3 Morphology of polypropylene

Morphology of polypropylene by using Scanning Electron Microscope is presented in Figure 5.10. It was found that those particles comprising of small particles were bounded together. Morphologies of polypropylene in the presence and absence of external electron donors are similar. All have globulelike particles. But the polypropylene obtained without external electron donor seems to have smaller sizes than polypropylene with external electron donors. However, all morphologies of obtained polypropylene show no significant differences.



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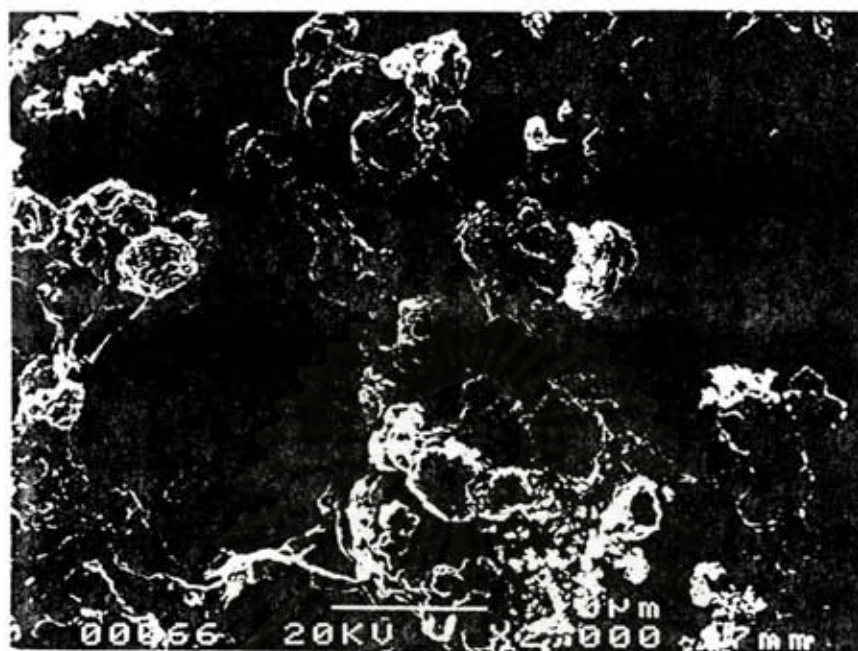


Figure 5.10 (a) Scanning Electron Micrograph of polypropylene produced by  $\text{MgCl}_2/\text{diethyl phthalate}/\text{TiCl}_4\text{-AlEt}_3$  catalyst system



Figure 5.10 (b) Scanning Electron Micrograph of polypropylene produced by  $\text{MgCl}_2/\text{diethyl phthalate}/\text{TiCl}_4\text{-AlEt}_3/\text{TMES}$  catalyst system

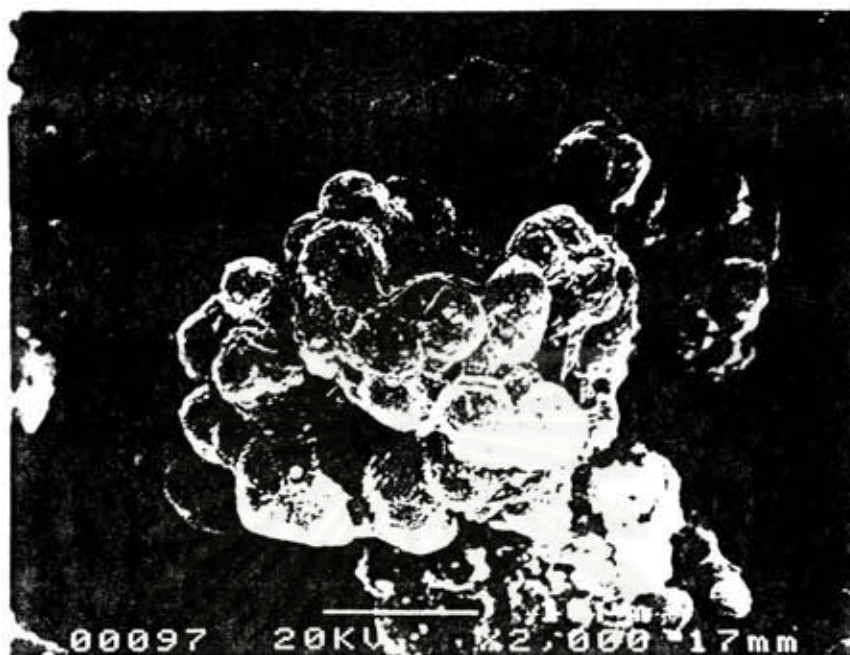


Figure 5.10 (c) Scanning Electron Micrograph of polypropylene produced by  $\text{MgCl}_2$ /diethyl phthalate/ $\text{TiCl}_4$ - $\text{AlEt}_3$ /DMEDES catalyst system

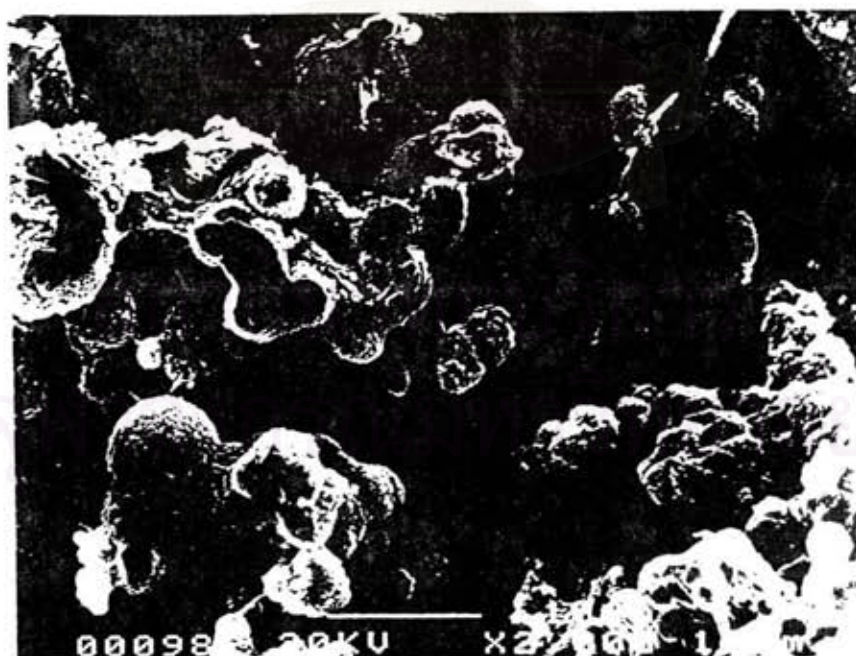


Figure 5.10 (d) Scanning Electron Micrograph of polypropylene produced by  $\text{MgCl}_2$ /diethyl phthalate/ $\text{TiCl}_4$ - $\text{AlEt}_3$ /MTES catalyst system

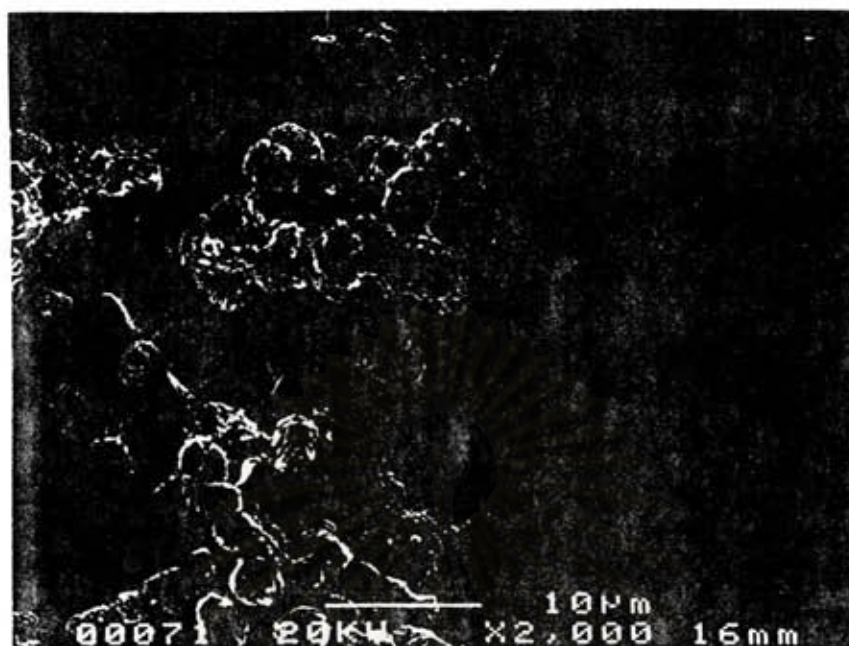


Figure 5.10 (e) Scanning Electron Micrograph of polypropylene produced by MgCl<sub>2</sub>/diethyl phthalate/TiCl<sub>4</sub>-AlEt<sub>3</sub>/TES catalyst system



Figure 5.10 (f) Scanning Electron Micrograph of polypropylene produced by MgCl<sub>2</sub>/diethyl phthalate/TiCl<sub>4</sub>-AlEt<sub>3</sub>/PTES catalyst system