# CHAPTER IV
# RESULTS AND DISCUSSION

## 4.1 Effect of Al/Ti Ratio

### 4.1.1 Effect of Al/Ti Ratio on Activity and Isotactic Index

Figures 4.1 and 4.2 show effect of Al/Ti ratio on activity and isotactic index at De/Al ratio equal 0.05. They showed that activity increased with increasing Al/Ti ratio and slightly increased with more Al/Ti ratio but isotactic index decreased slightly with increasing Al/Ti ratio for five different external donors. Moreover, IBIPDMS was the best for activity and good for isotactic index with a little lower than DIPDMS.

Generally, triethylaluminum needs to stabilize the active sites or to avoid contamination by poisons. In this experiment, it is thought that triethylaluminum helps to create new active sites but retards the isotactic sites. As mentioned in cocatalyst section, some equilibrium reaction model were proposed by Sacchi *et al.* (1991, 1996), when TEA increased, it formed complex with external donor and then this complex formed new complex with free site to give new active site. The isotactic index, however, decreases because internal and external donors coordinating with active sites could be removed by TEA as Sacchi *et al.* (1991, 1996) suggested. Xu *et al.* (1997) used DPDMS (diphenyldimethoxysilane) as an external donor and found the same result of a decreasing isotactic index. Dumas and Hsu (1989) found that the optimum activity behavior occur because sites of widely different activities also have different rates of deactivation.

Similar effect on activity and isotactic index of TEA were also found in same catalyst system at De/Al ratio equal 1.00 and 2.00 as shown on

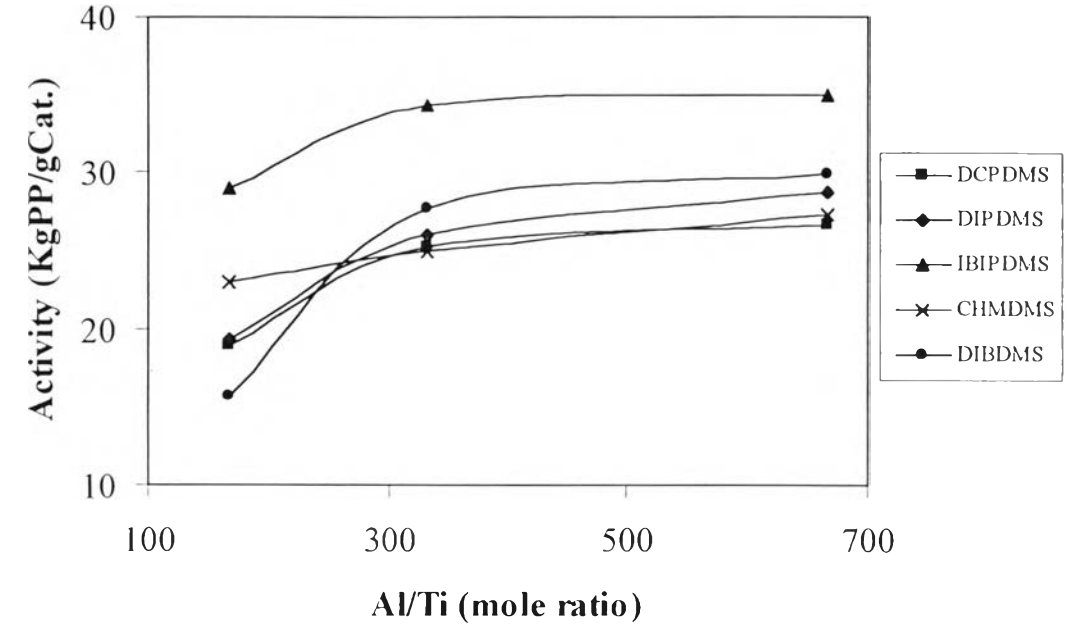


**Figure 4.1** Effect of Al/Ti ratio on activity at De/Al ratio equal 0.05. Polymerization conditions: polymerization temperature = 70°C; hydrogen 0.07 mole; polymerization time = 1 h

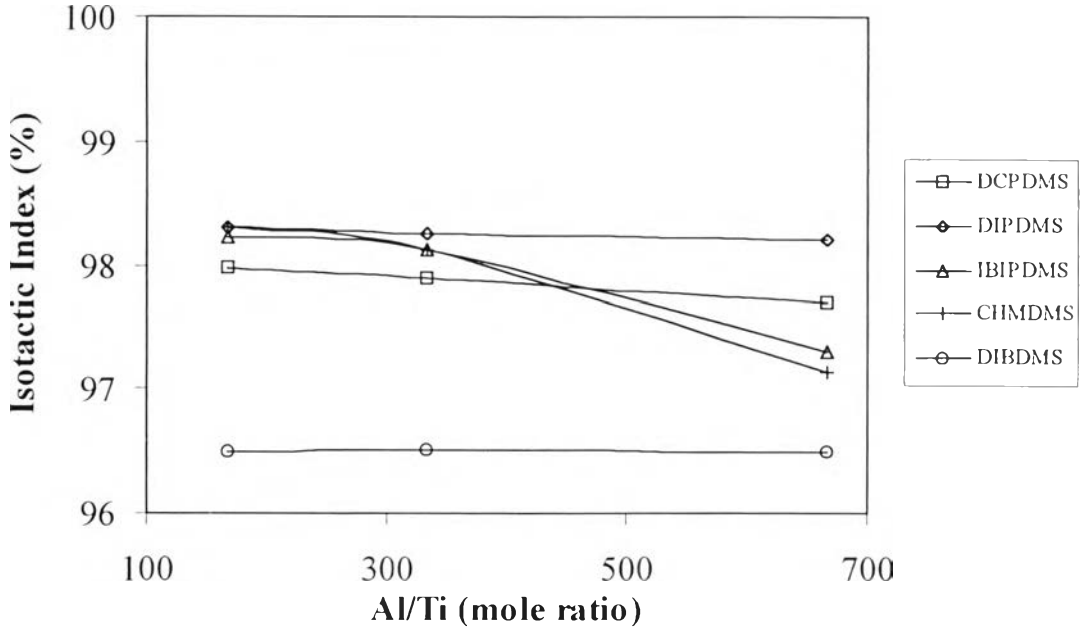


**Figure 4.2** Effect of Al/Ti ratio on isotactic index at De/Al ratio equal 0.05. Polymerization conditions: polymerization temperature = 70°C; hydrogen 0.07 mole; polymerization time = 1 h

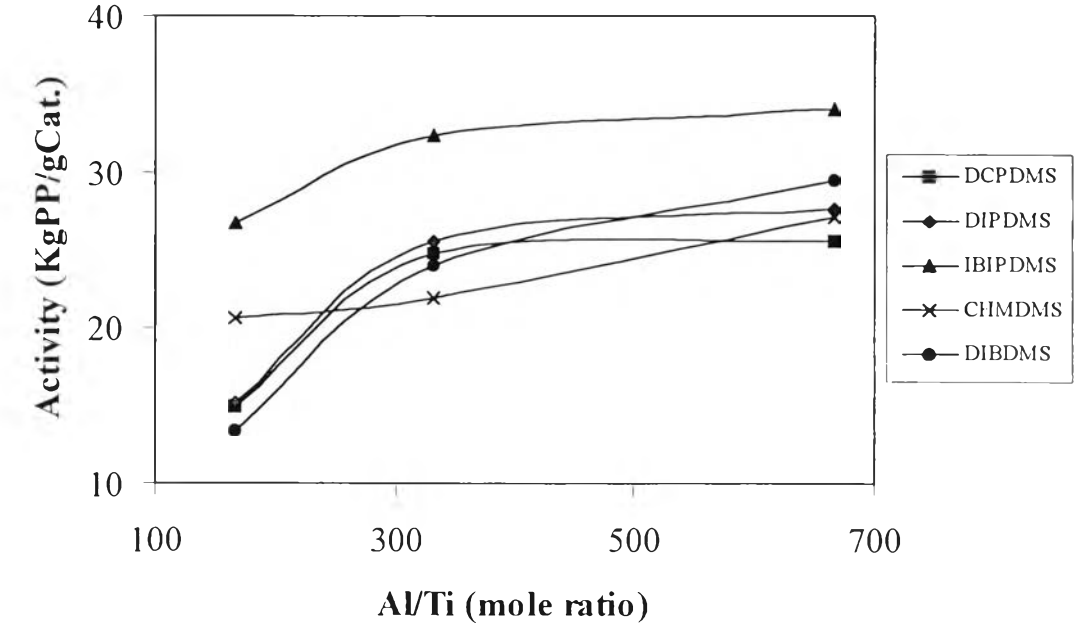


**Figure 4.3** Effect of Al/Ti ratio on activity at De/Al ratio equal 0.10. Polymerization conditions: polymerization temperature = 70°C; hydrogen 0.07 mole; polymerization time = 1 h

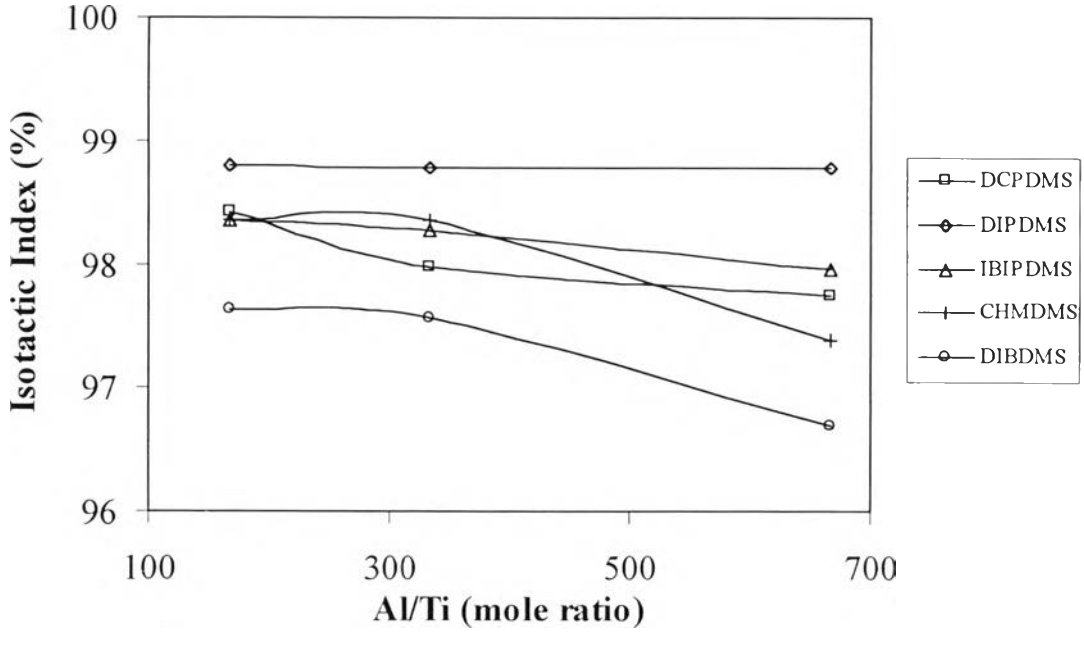


**Figure 4.4** Effect of Al/Ti ratio on isotactic index at De/Al ratio equal 0.10. Polymerization conditions: polymerization temperature = 70°C; hydrogen 0.07 mole; polymerization time = 1 h

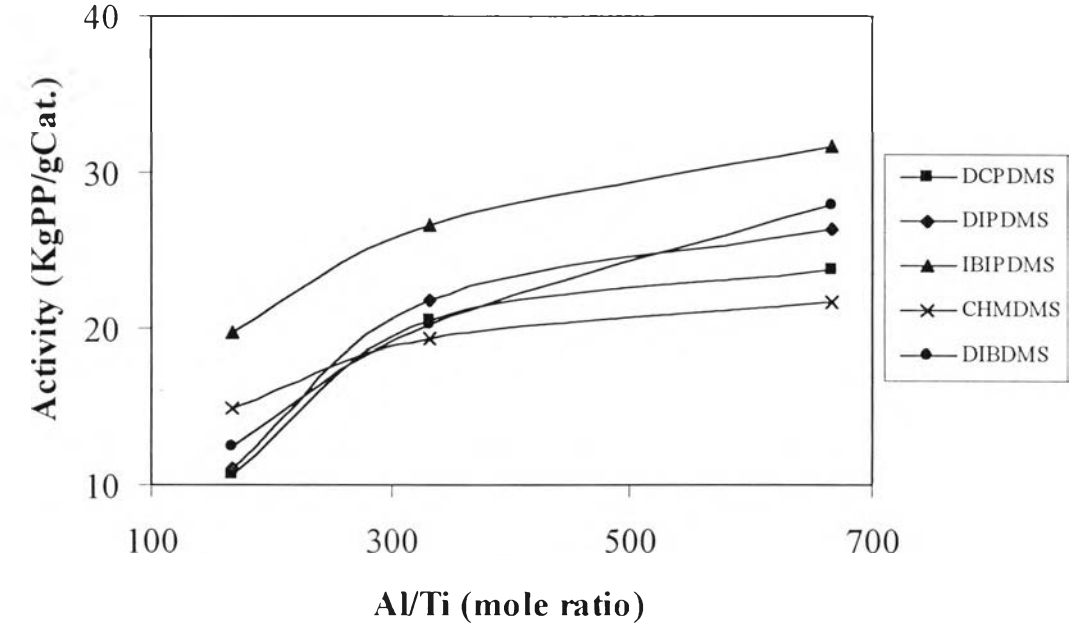


**Figure 4.5** Effect of Al/Ti ratio on activity at De/Al ratio equal 0.20. Polymerization conditions: polymerization temperature = 70°C; hydrogen 0.07 mole; polymerization time = 1 h

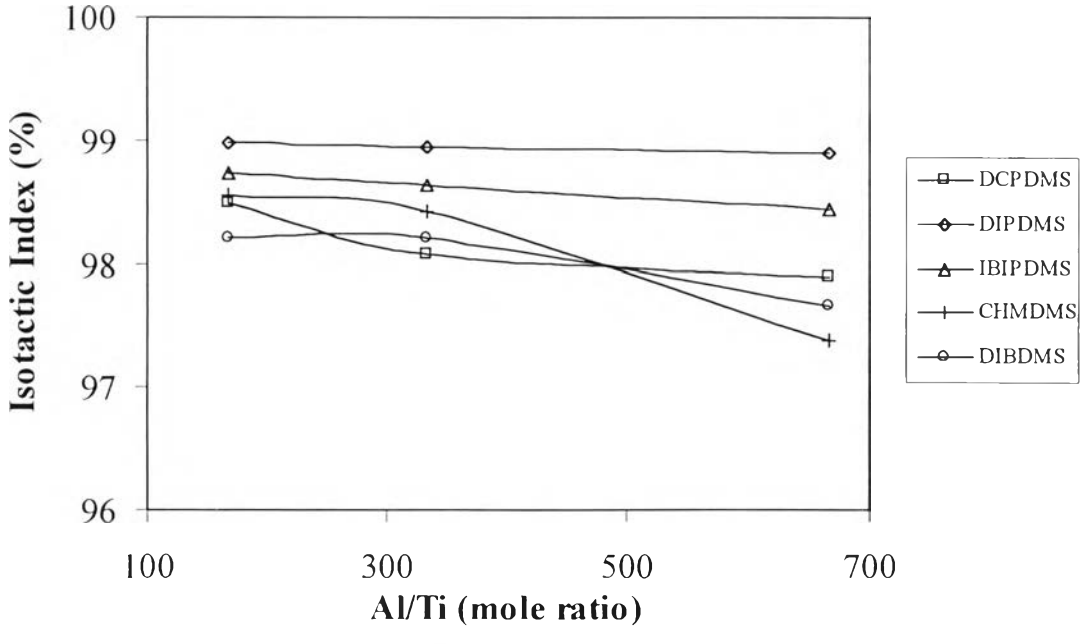


**Figure 4.6** Effect of Al/Ti ratio on isotactic index at De/Al ratio equal 0.20. Polymerization conditions: polymerization temperature = 70°C; hydrogen 0.07 mole; polymerization time = 1 h

Figures 4.3, 4.4, 4.5 and 4.6. Figure 4.7 shows effect of Al/Ti ratio on activity and isotactic index without external donor.

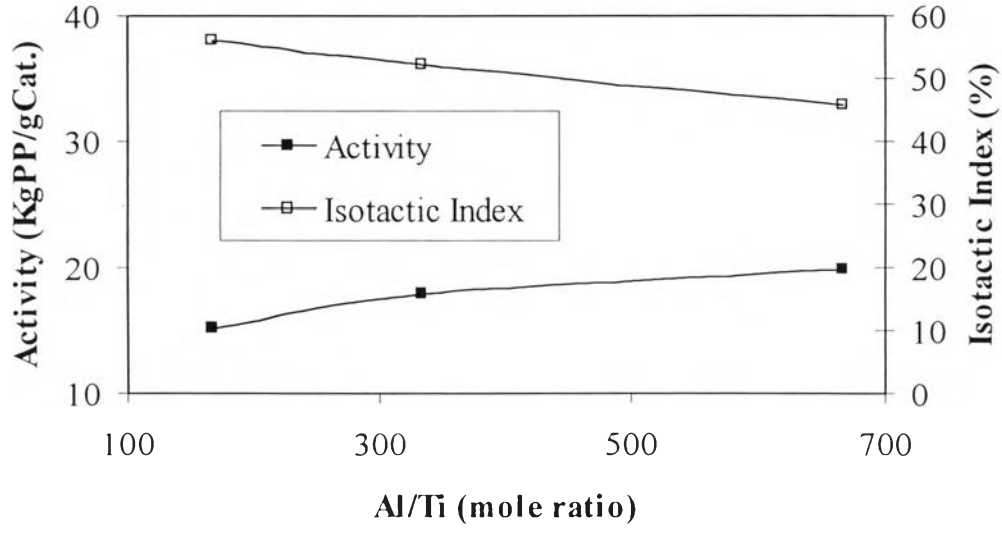


**Figure 4.7** Effect of Al/Ti ratio on activity and isotactic index without external donor. Polymerization conditions: polymerization temperature = 70° C; hydrogen 0.07 mole; polymerization time = 1 h

For external donor itself, Figures 4.8 and 4.9 show the effect of Al/Ti ratio on activity and isotactic index with IBIPDMS and without external donor. Activity increased with increasing Al/Ti ratio and slightly increased with more Al/Ti ratio but isotactic index slightly decreased with increasing Al/Ti ratio at the same De/Al ratio. For different De/Al ratio, activity showed the maximum with small amounts of external donor used (0.05 De/Al) and decreased with increasing De/Al ratio but isotactic index increased with increasing De/Al ratio, which will be discussed in this chapter, effect of De/Al ratio section. In other words, only small amount of external donor effectively increases isotactic index. The other external donors gave the same trend for both activity and isotactic index more or less, depended on types of external donor (see Table 4.1).

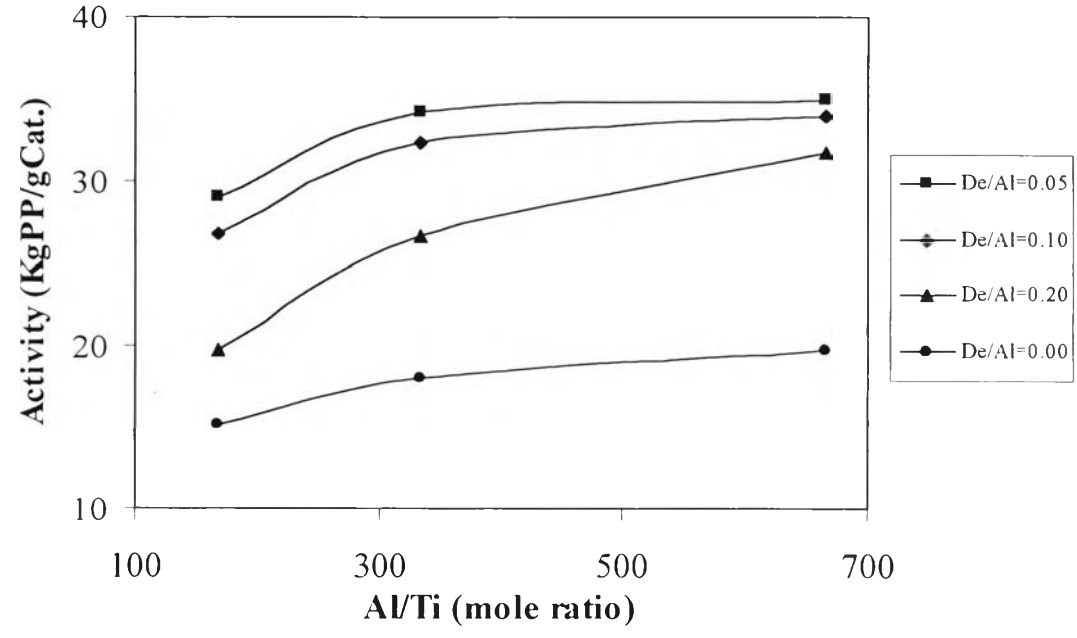


**Figure 4.8** Effect of Al/Ti ratio on activity with IBIPDMS and without external donor. Polymerization conditions: polymerization temperature = 70° C; hydrogen 0.07 mole; polymerization time = 1 h

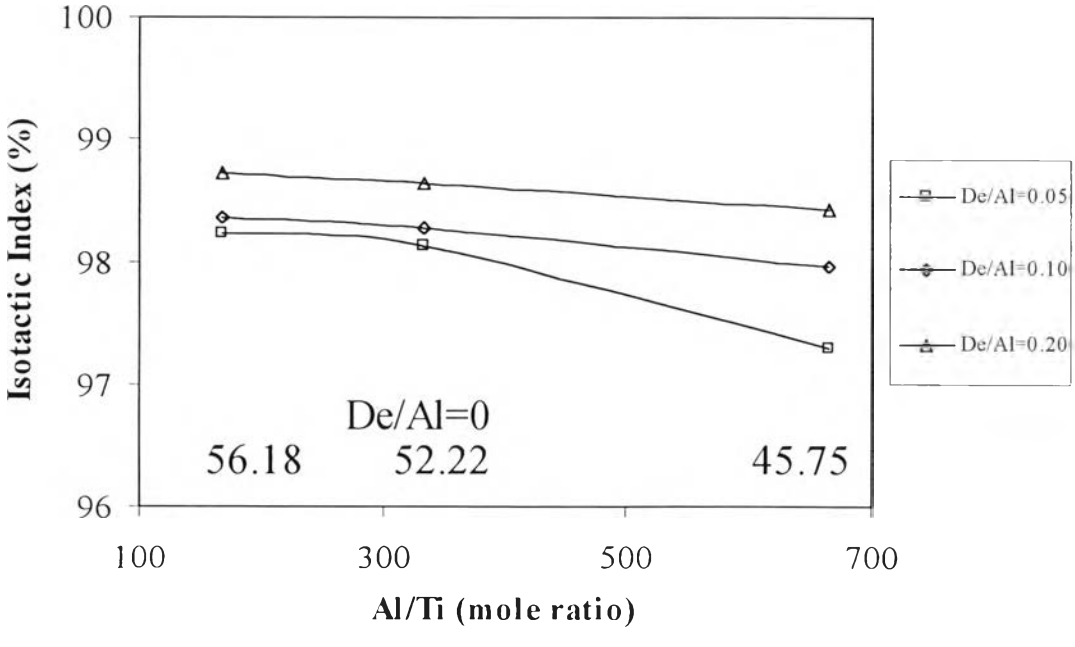


**Figure 4.9** Effect of Al/Ti ratio on isotactic index with IBIPDMS and without external donor. Polymerization conditions: polymerization temperature = 70° C; hydrogen 0.07 mole; polymerization time = 1 h

**Table 4.1** Experimental results on effect of external donors and triethyaluminum

| Donor | Al/Ti | Activity* | I.I† | Activity* | I.I† | Activity* | I.I† |
|---|---|---|---|---|---|---|---|
| | | De/Al = 0.05 | | De/Al = 0.1 | | De/Al = 0.2 | |
| DCPDMS | 666 | 26.6 | 97.7 | 25.5 | 97.8 | 23.7 | 97.9 |
| | 333 | 25.2 | 97.9 | 24.9 | 98.0 | 20.5 | 98.1 |
| | 167 | 19.0 | 98.0 | 14.9 | 98.4 | 10.7 | 98.5 |
| DIPDMS | 666 | 28.7 | 98.2 | 27.7 | 98.8 | 26.4 | 98.9 |
| | 333 | 25.9 | 98.3 | 25.6 | 98.8 | 21.8 | 99.0 |
| | 167 | 19.3 | 98.3 | 15.2 | 98.8 | 11.1 | 99.0 |
| IBIPDMS | 666 | 35.0 | 97.3 | 34.0 | 98.0 | 31.7 | 98.4 |
| | 333 | 34.2 | 98.1 | 32.3 | 98.3 | 26.6 | 98.6 |
| | 167 | 29.0 | 98.2 | 26.8 | 98.4 | 19.7 | 98.7 |
| CHMDMS | 666 | 27.3 | 97.1 | 27.1 | 97.4 | 21.7 | 97.4 |
| | 333 | 24.9 | 98.1 | 22.0 | 98.4 | 19.3 | 98.4 |
| | 167 | 23.0 | 98.3 | 20.7 | 98.4 | 14.9 | 98.6 |
| DIBDMS | 666 | 29.9 | 96.5 | 29.5 | 96.7 | 27.9 | 97.7 |
| | 333 | 27.6 | 96.5 | 24.1 | 97.6 | 20.2 | 98.2 |
| | 167 | 15.7 | 96.5 | 13.4 | 97.6 | 12.5 | 98.2 |

| Donor | Al/Ti | Activity* | I.I† |
|---|---|---|---|
| | | De/Al = 0 | |
| NO DONOR | 666 | 19.8 | 45.8 |
| | 333 | 18.0 | 52.2 |
| | 167 | 15.2 | 56.2 |

*Catalyst activity in KgPP/gCat.

†Isotactic index in wt%.

4.1.2 Effect of Al/Ti Ratio on Molecular Weight

Table 4.2 shows the effect of Al/Ti ratio on number average molecular weight ($\overline{M}_n$), weight average molecular weight ($\overline{M}_w$), and polydispersity index ($\overline{M}_w/\overline{M}_n$). It had no significant changes in $\overline{M}_n$, $\overline{M}_w$, and $\overline{M}_w/\overline{M}_n$ with Al/Ti ratio and also with De/Al ratio. However, DCPDMS, DIPDMS, and IBIPDMS show rather increase in MW with De/Al ratio. CHMDMS and DIBDMS have relatively decreasing $\overline{M}_w/\overline{M}_n$ with De/Al ratio indicating that size of these chains becomes closer. Chien and Kuo (1986a) found that for their CW catalyst ($MgCl_2$/EB/p-cresol/$AlEt_3$/$TiCl_4$ supproted catalyst), between Al/Ti = 42 to 334, the TEA concentration essentially has no effect on $\overline{M}_n$, and $\overline{M}_w$ of either whole or isotactic polymer. Yang and Hsu (1995b), however, showed that for their catalyst ($MgCl_2$/DOP/$TiCl_4$-alkyl aluminum/external donor catalyst) by the addition of a small amount of 2,2,6,6-tetramethyl piperidine (TMPIP) or dimethoxydiphenyl silane (DMDPS), molecular weights of the whole and isotactic polymers are increased by almost a factor of two. Further addition of the base seems to have no clear effect on the molecular weight. On the other hand, $\overline{M}_n$, and $\overline{M}_w$ of the atatic polymer decrease slightly with increasing base/TEA ratios. Unlike TMPIP or DMDPS, t-butylmethyl ether (TBME) have no obvious effects on either the molecular weights or MWD of whole polymer or the isotactic and atactic polymers. $\overline{M}_n$ and $\overline{M}_w$ of all the catalyst system with external donors, however, were more than the catalyst system without external donor. It may be thought that the isospecific sites of the catalyst system with external donors gives high number average and weight average molecular weight.

4.1.3 Effect of Al/Ti Ratio on Melting Temperature

Melting temperature of several external donors at any constant Al/Ti used (i.e., 167, 333, and 666 mole ratio) or any De/Al ratio (i.e., 0.05, 0.10, and 0.20) and without external donor is shown in Table 4.3. It can be

**Table 4.2** Effect of Al/Ti ratio on molecular weight

| Donor | Al/Ti mole ratio | $\overline{M}_n$ *10$^{-4}$ | $\overline{M}_w$ *10$^{-5}$ | $\overline{M}_w/\overline{M}_n$ | $\overline{M}_n$ *10$^{-4}$ | $\overline{M}_w$ *10$^{-5}$ | $\overline{M}_w/\overline{M}_n$ | $\overline{M}_n$ *10$^{-4}$ | $\overline{M}_w$ *10$^{-5}$ | $\overline{M}_w/\overline{M}_n$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | De/Al mole ratio = 0.05 | | | De/Al mole ratio = 0.1 | | | De/Al mole ratio = 0.2 | | |
| DCPDMS | 666 | 12.99 | 19.60 | 15.09 | 14.88 | 20.59 | 13.83 | 20.02 | 24.66 | 12.32 |
| | 333 | 13.17 | 18.01 | 13.68 | 13.94 | 20.04 | 14.37 | 13.78 | 20.53 | 14.91 |
| | 167 | 12.09 | 17.77 | 14.70 | 19.13 | 23.24 | 12.14 | 16.32 | 23.72 | 14.53 |
| DIPDMS | 666 | 14.82 | 20.28 | 13.69 | 17.08 | 19.58 | 11.46 | 19.76 | 21.59 | 10.92 |
| | 333 | 15.93 | 18.64 | 11.70 | 16.36 | 21.30 | 13.02 | 19.01 | 21.64 | 11.38 |
| | 167 | 15.30 | 18.50 | 12.10 | 14.90 | 19.38 | 13.01 | 15.56 | 20.73 | 13.32 |
| IBIPDMS | 666 | 16.05 | 20.80 | 12.96 | 16.83 | 21.68 | 12.88 | 16.65 | 22.25 | 13.36 |
| | 333 | 14.10 | 19.62 | 13.91 | 15.31 | 19.68 | 12.85 | 16.72 | 21.29 | 12.74 |
| | 167 | 15.22 | 18.36 | 12.06 | 18.03 | 22.42 | 12.44 | 14.14 | 19.67 | 13.91 |
| CHMDMS | 666 | 14.16 | 17.48 | 12.34 | 14.48 | 18.08 | 12.48 | 17.72 | 17.56 | 9.91 |
| | 333 | 14.68 | 19.60 | 13.35 | 15.60 | 18.45 | 11.82 | 17.06 | 19.63 | 11.51 |
| | 167 | 15.74 | 18.86 | 11.98 | 15.55 | 17.58 | 11.31 | 16.41 | 19.98 | 12.18 |
| DIBDMS | 666 | 14.15 | 17.69 | 12.50 | 14.02 | 16.64 | 11.87 | 16.90 | 16.59 | 9.82 |
| | 333 | 12.60 | 18.39 | 14.60 | 13.58 | 15.77 | 11.61 | 14.48 | 17.54 | 12.11 |
| | 167 | 15.34 | 16.68 | 10.87 | 13.72 | 16.08 | 11.72 | 14.63 | 17.46 | 11.93 |
| Donor | Al/Ti mole ratio | $\overline{M}_n$ *10$^{-4}$ | $\overline{M}_w$ *10$^{-5}$ | $\overline{M}_w/\overline{M}_n$ | | | | | | |
| | | De/Al mole ratio = 0 | | | | | | | | |
| NO DONOR | 666 | 8.76 | 8.89 | 10.14 | | | | | | |
| | 333 | 11.07 | 10.92 | 9.86 | | | | | | |
| | 167 | 9.88 | 8.32 | 8.42 | | | | | | |

seen that melting temperatures of polypropylene prepared with external donor itself give nearly the same value at any Al/Ti ratio and De/Al ratio. The same effect is also found in other external donors more or less. Melting temperature depends on the type of external donors. However, all of external donors gave melting temperatures higher than without external donor.

It can be thought that catalyst system having external donor gives more isotactic index than that without external donor as shown on the previous section. So more isotactic index gives more crystallinity and affects on higher melting temperature. DCPDMS, DIPDMS, and IBIPDMS have high molecular weight such that they exhibit high $T_m$ compared to CHMDMS and DIBDMS which are low molecular weight showing low $T_m$.

### 4.1.4 Effect of Al/Ti Ratio on Crystallization Temperature

Table 4.4 shows crystallization temperature of several external donors at any constant Al/Ti used (i.e., 167, 333, and 666 mole ratio) with any

**Table 4.3** Effect of Al/Ti ratio on melting temperature

| Melting temperature (°C) | | | | |
|---|---|---|---|---|
| Donor | Al/Ti mole ratio | De/Al mole ratio 0.05 | De/Al mole ratio 0.1 | De/Al mole ratio 0.2 |
| DCPDMS | 666 | 165 | 164 | 165 |
| | 333 | 162 | 164 | 165 |
| | 167 | 164 | 165 | 165 |
| DIPDMS | 666 | 164 | 164 | 164 |
| | 333 | 164 | 164 | 164 |
| | 167 | 164 | 164 | 164 |
| IBIPDMS | 666 | 164 | 164 | 164 |
| | 333 | 164 | 164 | 164 |
| | 167 | 164 | 164 | 164 |
| CHMDMS | 666 | 162 | 162 | 163 |
| | 333 | 163 | 162 | 163 |
| | 167 | 162 | 162 | 163 |
| DIBDMS | 666 | 163 | 163 | 163 |
| | 333 | 162 | 162 | 163 |
| | 167 | 162 | 162 | 163 |

| Donor | Al/Ti mole ratio | De/Al mole ratio 0 |
|---|---|---|
| NO DONOR | 666 | 160 |
| | 333 | 159 |
| | 167 | 161 |

**Table 4.4** Effect of Al/Ti ratio on crystallization temperature

| Crystallization temperature (°C) | | | | |
|---|---|---|---|---|
| Donor | Al/Ti mole ratio | De/Al mole ratio 0.05 | De/Al mole ratio 0.1 | De/Al mole ratio 0.2 |
| DCPDMS | 666 | 121 | 118 | 119 |
| | 333 | 112 | 116 | 116 |
| | 167 | 117 | 117 | 117 |
| DIPDMS | 666 | 119 | 119 | 119 |
| | 333 | 117 | 117 | 119 |
| | 167 | 118 | 118 | 118 |
| IBIPDMS | 666 | 120 | 119 | 121 |
| | 333 | 121 | 119 | 121 |
| | 167 | 121 | 121 | 121 |
| CHMDMS | 666 | 116 | 115 | 117 |
| | 333 | 117 | 116 | 116 |
| | 167 | 115 | 115 | 116 |
| DIBDMS | 666 | 117 | 117 | 117 |
| | 333 | 115 | 118 | 118 |
| | 167 | 117 | 116 | 116 |

| Donor | Al/Ti mole ratio | De/Al mole ratio 0 |
|---|---|---|
| NO DONOR | 666 | 111 |
| | 333 | 109 |
| | 167 | 107 |

De/Al ratio (i.e., 0.05, 0.10, and 0.20) and without external donor. The results show that crystallization temperature of polypropylene prepared with external donor itself had nearly the same value at any Al/Ti ratio and De/Al ratio. The same effect is also found in other external donors more or less; crystallization temperature depends on the type of external donors. However, all of external donors exhibit crystallization temperatures higher than without external donor.

It can be considered that catalyst system having external donor gives more isotactic index than without external donor as shown on the previous section. More isotactic index increases the stereoregularity of polymeric chains to facilitate crystallization process, results in higher crystallization temperature and gives more crystallinity. Moreover, high molecular weight material crystallizes faster than the small one. IBIPDMS and DIPDMS show high isotactic index and molecular weight such that their $T_c$ are higher than the others.

### 4.1.5 Effect of Al/Ti Ratio on Melt Flow Rate

Melt flow rate (MFR) of the catalyst system without external donor was very high comparing to the catalyst system with external donor. When Al/Ti increased, MFR showed very slight increase in accordance with slight increase in molecular weight; however, when De/Al increased, MFR significantly decreased at constant Al/Ti ratio for all external donors as shown on Table 4.5. It can be thought that when De/Al increases, isotactic index and molecular weight increase (from result) significantly so that high viscosity material is obtained resulting to decrease MFR. Moreover, it can be seen that an order of the MFR was as following at any constant Al/Ti ratio and De/Al ratio.

NO DONOR > DIBDMS > CHMDMS > IBIPDMS > DIPDMS > DCPDMS

**Table 4.5** Effect of Al/Ti ratio on melt flow rate

| Melt flow rate (g/10min) | | | | |
|---|---|---|---|---|
| Donor | Al/Ti mole ratio | De/Al mole ratio 0.05 | De/Al mole ratio 0.1 | De/Al mole ratio 0.2 |
| DCPDMS | 666 | 3.2 | 3.1 | 2.7 |
| | 333 | 3.7 | 3.0 | 3.0 |
| | 167 | 3.0 | 2.7 | 2.6 |
| DIPDMS | 666 | 7.9 | 7.3 | 6.9 |
| | 333 | 7.6 | 7.3 | 6.7 |
| | 167 | 7.2 | 7.0 | 6.4 |
| IBIPDMS | 666 | 9.1 | 8.8 | 8.5 |
| | 333 | 9.0 | 8.8 | 8.3 |
| | 167 | 8.9 | 8.1 | 8.3 |
| CHMDMS | 666 | 13.7 | 13.4 | 11.0 |
| | 333 | 12.6 | 12.0 | 10.3 |
| | 167 | 11.5 | 11.3 | 10.1 |
| DIBDMS | 666 | 20.7 | 18.9 | 16.9 |
| | 333 | 20.5 | 18.6 | 16.8 |
| | 167 | 19.8 | 18.9 | 16.8 |

| Donor | Al/Ti mole ratio | De/Al mole ratio 0 |
|---|---|---|
| NO DONOR | 666 | 234 |
| | 333 | 201 |
| | 167 | 191 |

## 4.2 Effect of De/Al Ratio

### 4.2.1 Effect of De/Al Ratio on Activity and Isotactic Index

Figures 4.10 and 4.11 show effect of De/Al ratio on activity and isotactic index at Al/Ti ratio equal 167. They illustrated that activity decreased with increasing De/Al ratio but isotactic index increased slightly with increasing De/Al ratio for five different external donors. Similar effect on activity and isotactic index of TEA were also found in the same catalyst system at Al/Ti ratio equal 333 and 666 as shown on Figures 4.12, 4.13, 4.14 and 4.15. When comparing with any Al/Ti change, activity line of each external donor increased with the same slope or a little higher slope by an increase of Al/Ti, but isotactic index line of each external donor slightly decreased with the same slope by an increase of Al/Ti. Moreover, they can be seen that IBIPDMS was the best for activity and good for isotactic index with a little lower than DIPDMS.

Usually, Lewis base must be added to both the catalyst and the cocatalyst for this fourth generation catalyst. It is known that a suitable matching of their chemical characters is necessary. Both the activity and the stereospecificity, based on the couple phthalate/silane, are remarkably higher in the fourth generation. In this experiment, it is considered that Lewis base helps to create new active sites with small amounts of external donor and retard activity of active sites as more external donor is added, and to create the isotactic sites with increasing De/Al ratio. Yang and Hsu (1995a) used dimethoxydiphenyl silane (DMDPS) and 2,2,6,6-tetramethyl piperidine (TMPIP) and found similar effects on activity and isotactic index in the catalyst system containing a high level of phthaloyl dichloride (POC) complex which was formed by the reaction between $TiCl_4$ and DOP. From molecular structure of external donors (Figure 3.1), It can be thought from steric hindered effect that distance from Si atom to a branching molecule and

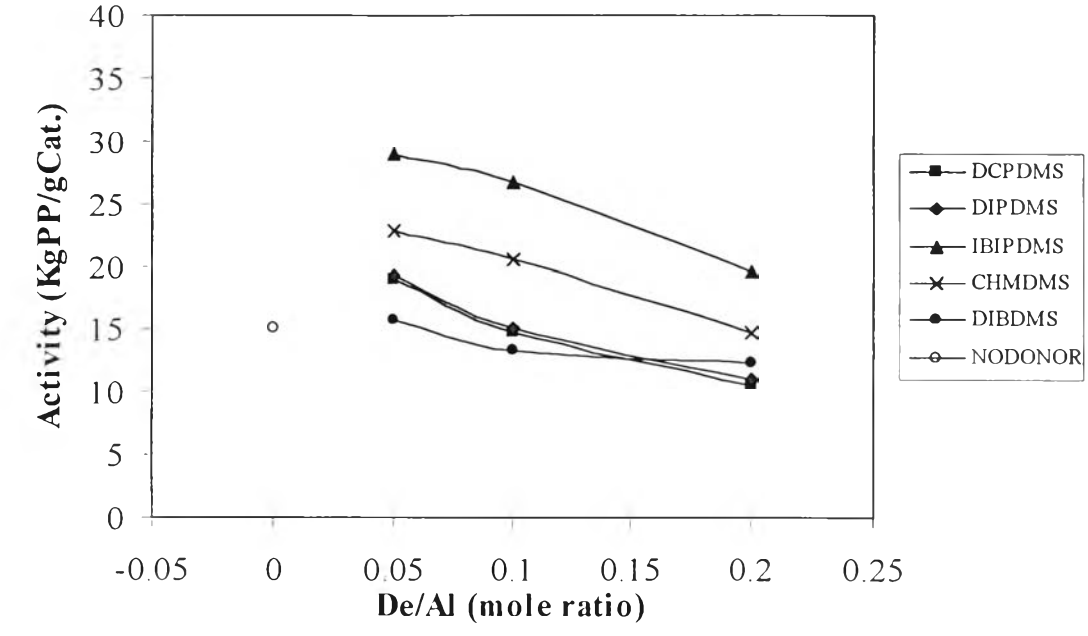


**Figure 4.10** Effect of De/Al ratio on activity at Al/Ti ratio equal 167. Polymerization conditions: polymerization temperature = 70°C; hydrogen 0.07 mole; polymerization time = 1 h

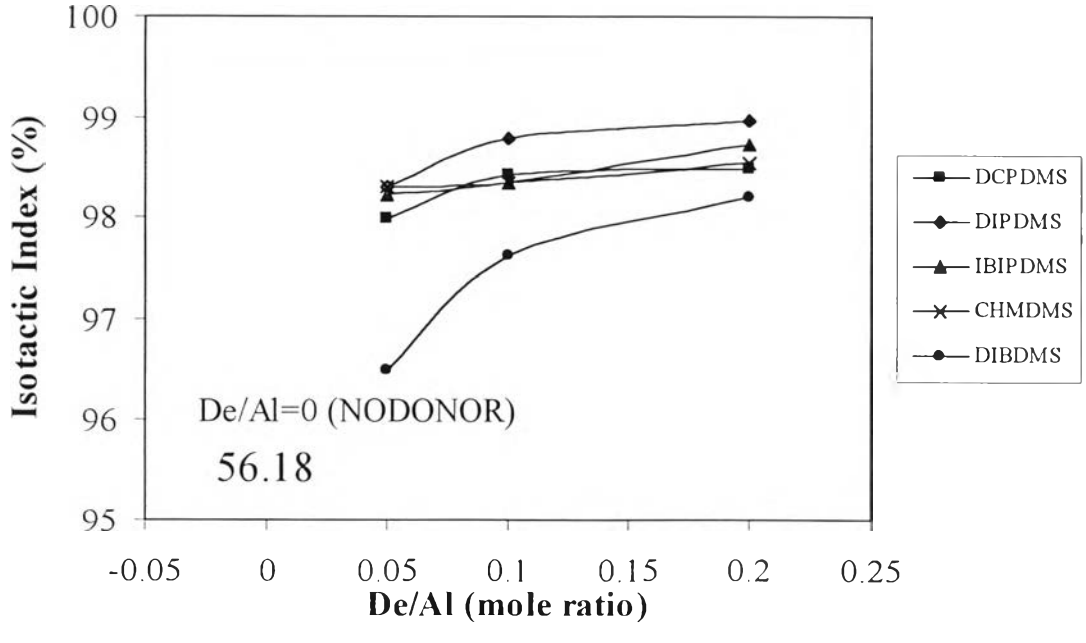


**Figure 4.11** Effect of De/Al ratio on isotactic index at Al/Ti ratio equal 167. Polymerization conditions: polymerization temperature = 70°C; hydrogen 0.07 mole; polymerization time = 1 h

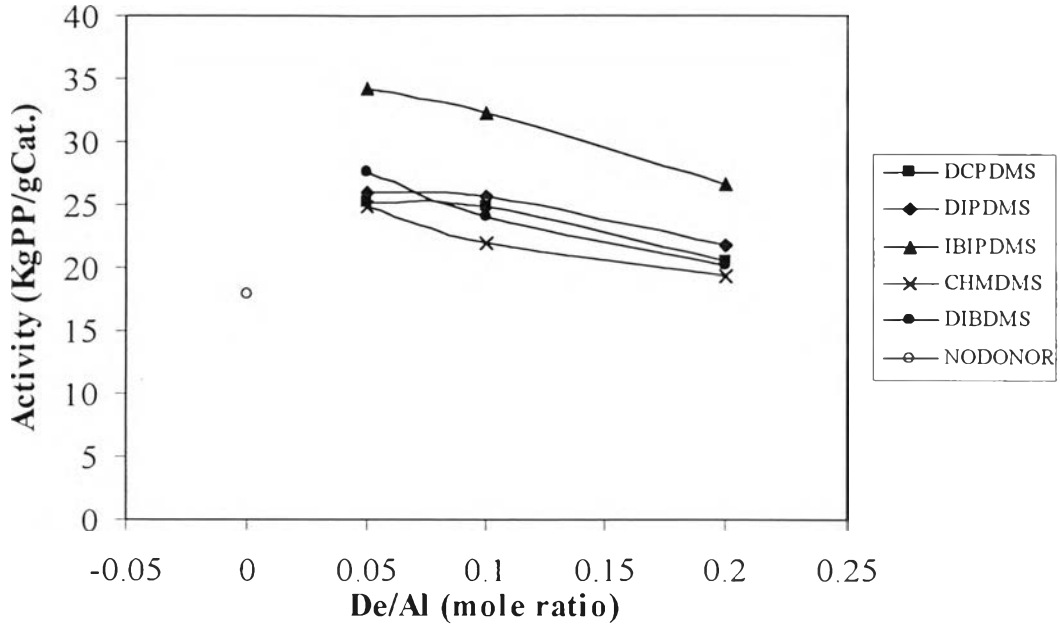


**Figure 4.12** Effect of De/Al ratio on activity at Al/Ti ratio equal 333. Polymerization conditions: polymerization temperature = 70°C; hydrogen 0.07 mole; polymerization time = 1 h

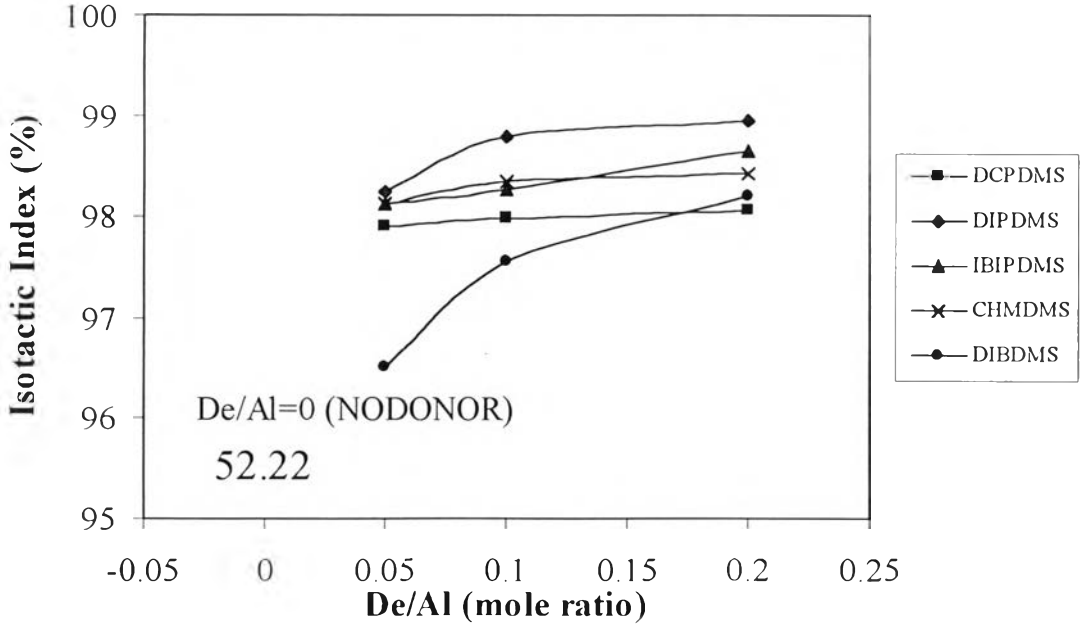


**Figure 4.13** Effect of De/Al ratio on isotactic index at Al/Ti ratio equal 333. Polymerization conditions: polymerization temperature = 70°C; hydrogen 0.07 mole; polymerization time = 1 h

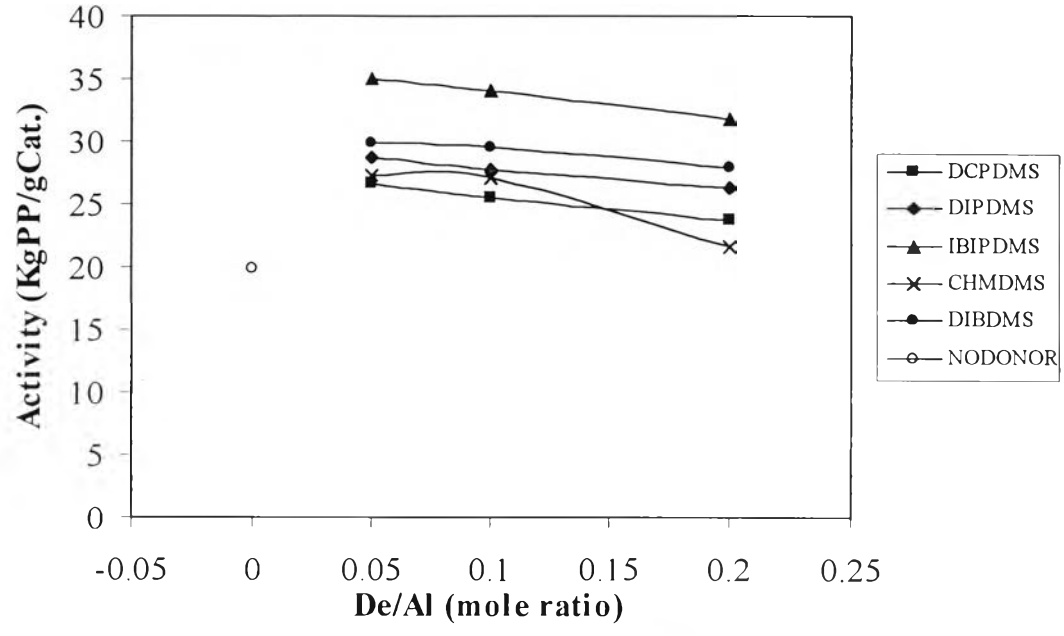


**Figure 4.14** Effect of De/Al ratio on activity at Al/Ti ratio equal 666. Polymerization conditions: polymerization temperature = 70°C; hydrogen 0.07 mole; polymerization time = 1 h

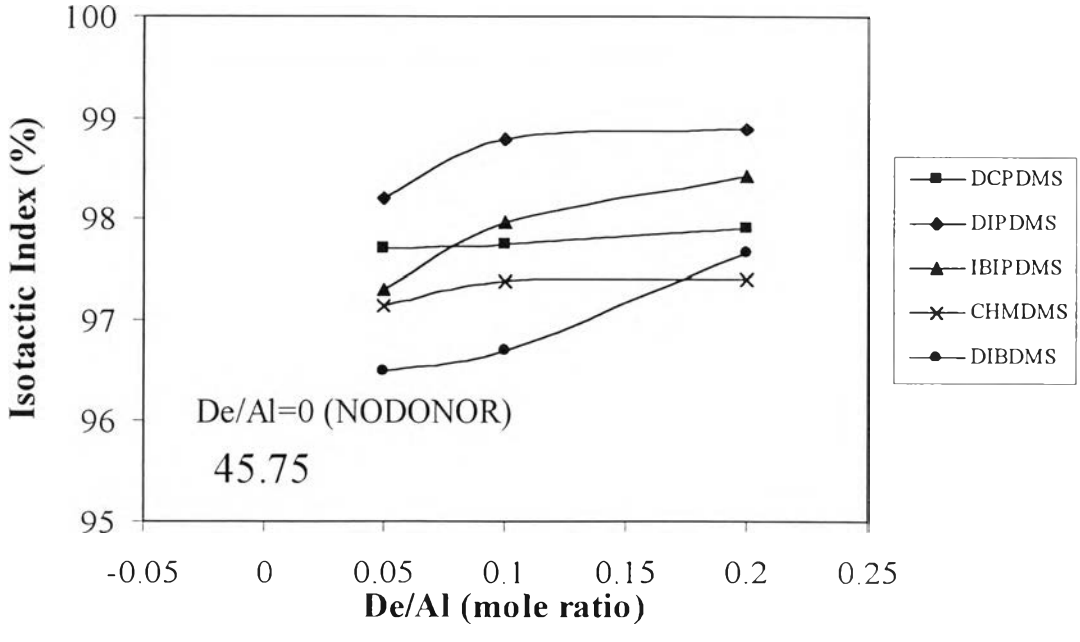


**Figure 4.15** Effect of De/Al ratio on isotactic index at Al/Ti ratio equal 666. Polymerization conditions: polymerization temperature = 70°C; hydrogen 0.07 mole; polymerization time = 1 h

hydrogen atom at a branching molecule of DIPDMS is the nearest length and the most hindrance, which should give the most isotacitc index as results show. The distance from Si atom to a branching molecule and hydrogen atom at a branching molecule of DIBDMS is the longest length, which should give the most activity. But the results did not show the most activity which had no clear effect. The combination of Isobutyl and Isopropyl of silica compound that is Isobutylisopropyldimethoxysilane (IBIPDMS), however, gave the most activity, which suggested the synergism occurring with combining two of molecules.

For external donor itself, as mentioned before in this chapter (effect of Al/Ti ratio), Figures 4.16 and 4.17 show the effect of De/Al ratio on activity and isotactic index with IBIPDMS and without external donor. Activity increased with small amounts of external donor used and decreased with increasing De/Al ratio but isotactic index increased with increasing De/Al ratio. Yang and Hsu (1995c) proposed the model for the possible tranformations of active sites on the $MgCl_2$/dioctylphthalate (DOP)/$TiCl_4$ catalyst under the influence of an external base in Figure 4.18. When the concentration of external donor is low, the external donor can convert the aspecific sites into high isospecific sites by complexing with one of two vacancies in the aspecific sites. As the concentration of the external donor increases, poisoning, not only of the low isospecific sites but also the high isospecific sites takes place. Kakugo *et al.* (1988) also proposed the structural model that the addition of electron donor converts the non-stereospecific centers to ones of high isospecificity, whereas the low isospecific centers are performed inactive.

The other external donors gave the same trend for both activity and isotactic index more or less, depended on types of external donor (see Table 4.1).

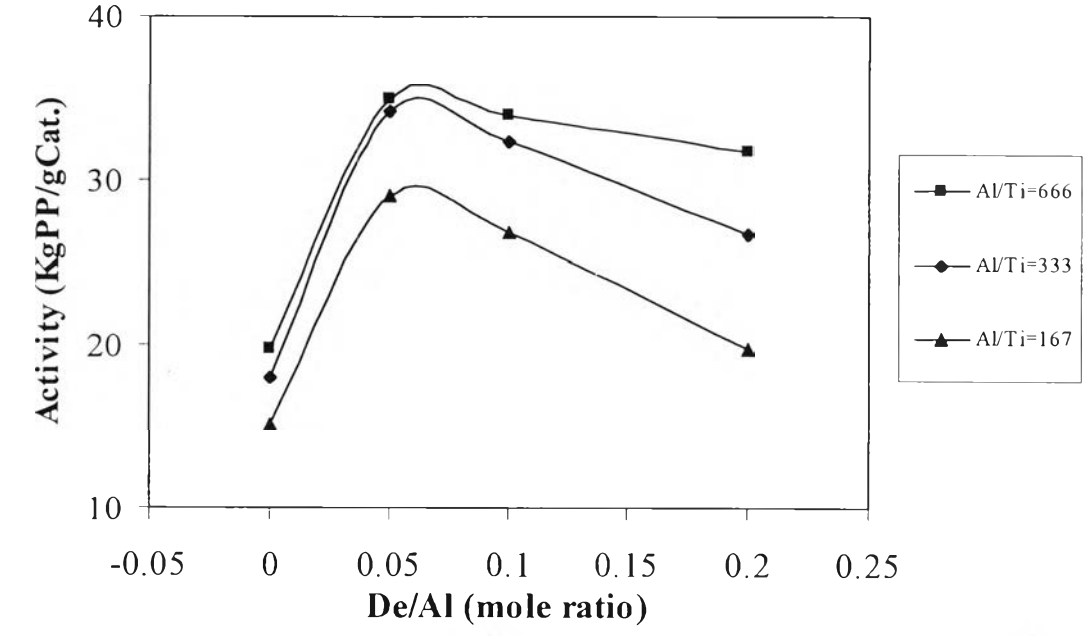


**Figure 4.16** Effect of De/Al ratio on activity with IBIPDMS and without external donor. Polymerization conditions: polymerization temperature = 70° C; hydrogen 0.07 mole; polymerization time = 1 h

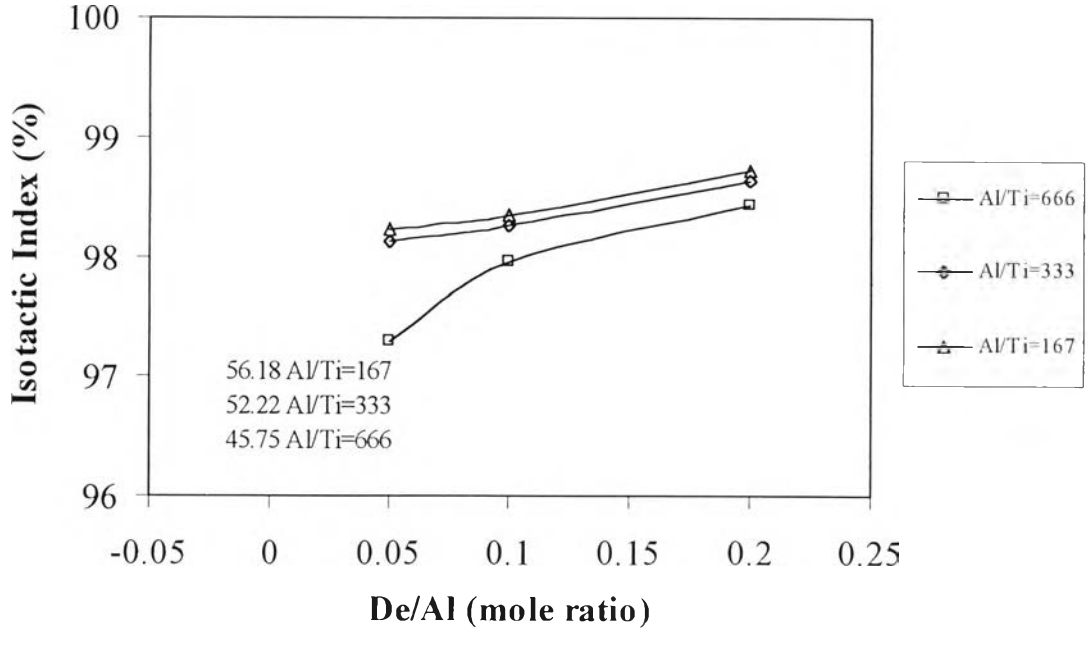


**Figure 4.17** Effect of De/Al ratio on isotactic index with IBIPDMS and without external donor. Polymerization conditions: polymerization temperature = 70°C; hydrogen 0.07 mole; polymerization time = 1 h

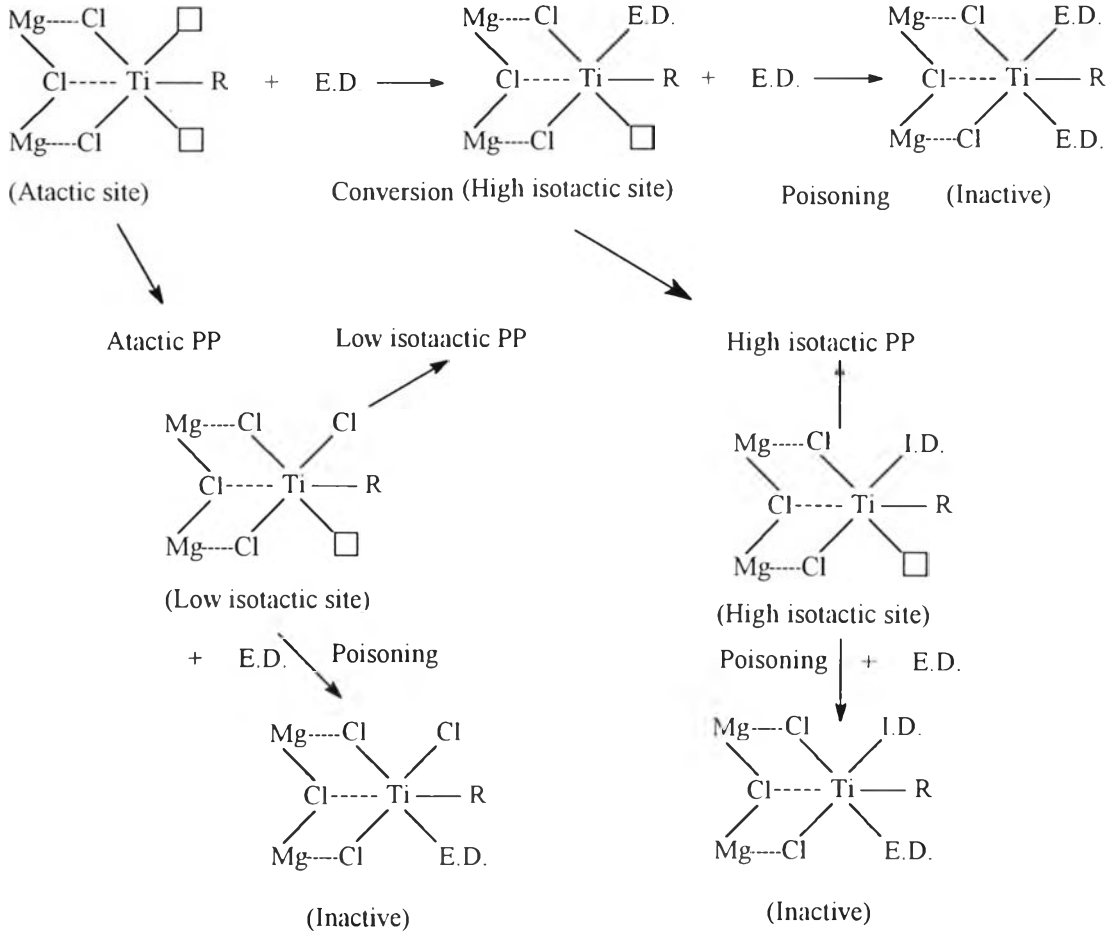


**Figure 4.18** A proposed model for the possible transformations of active sites on the $MgCl_2$/dioctylphthalate(DOP)/$TiCl_4$ catalyst under the influence of an external base (Yang and Hsu, 1995c)

4.2.2 Effect of De/Al Ratio on Molecular Weight

Effect of De/Al ratio on molecular weight was shown and discussed previously in section 4.1.5 effect of Al/Ti ratio on molecular weight.

4.2.3 Effect of De/Al Ratio on Melting Temperature

Effect of De/Al ratio on melting temperature was shown and discussed previously in section 4.1.2 effect of Al/Ti ratio on melting temperature.

4.2.4 Effect of De/Al Ratio on Crystallization Temperature

Effect of De/Al ratio on crystallization temperature was shown and discussed previously in section 4.1.3 effect of Al/Ti ratio on crystallization temperature.

4.2.5 Effect of De/Al Ratio on Melt Flow Rate

Effect of De/Al ratio on melt flow rate was shown and discussed previously in section 4.1.4 effect of Al/Ti ratio on melt flow rate.

## 4.3 Effect of $H_2$ Concentration

### 4.3.1 Effect of $H_2$ Concentration on Activity and Isotactic Index

Generally, hydrogen is used as a molecular weight controlling agent for ethylene and α-olefins polymerization by Ziegler-Natta catalysts. Figures 4.19 and 4.20 show effect of hydrogen on activity and isotactic index. The results showed that when $H_2$ increased, activity increased and isotactic index decreased with all external donors and also without external donor. Furthermore, IBIPDMS was the best for activity and DIPDMS was the best for isotactic index. Lee and Jeong (1993) used the $Mg(OEt)_2$/benzoyl chloride (BC)/$TiCl_4$-TEA/ED catalyst system and found that when MPT was used as ED, the same effects for both activity and isotactic index with increasing hydrogen pressure from zero to 0.016 MPa were found. When PTES was used as ED, it showed the same effects for activity with increasing hydrogen pressure from zero to 0.016 MPa and the same effect for isotactic index at higher hydrogen pressure between 0.016 to 0.064 MPa. They suggested that the effects of hydrogen on activity and isospecificity for the catalyst system depended on the kind and amount of ED although the detailed mechanism is not yet known. However, based on the results obtained in this study, the reactivation of the dormant sites by hydrogen is a feasible reason for the activity enhancement but many of these dormant sites are aspecific sites.

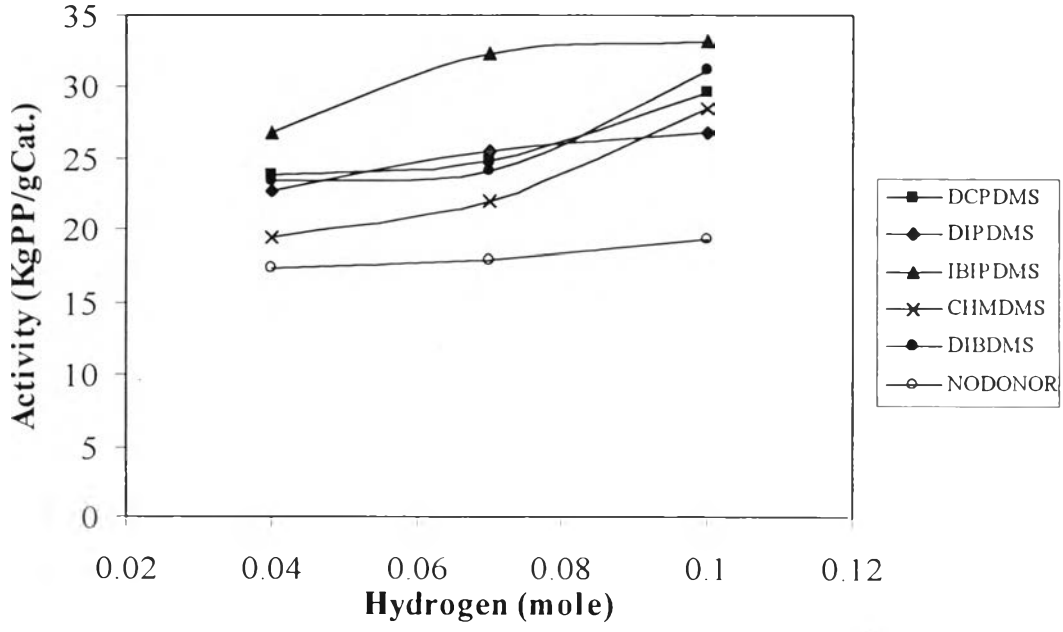


**Figure 4.19** Effect of hydrogen on activity. Polymerization conditions: polymerization temperature = 70°C; Al/Ti ratio = 333; De/Al ratio = 0.10; polymerization time = 1 h

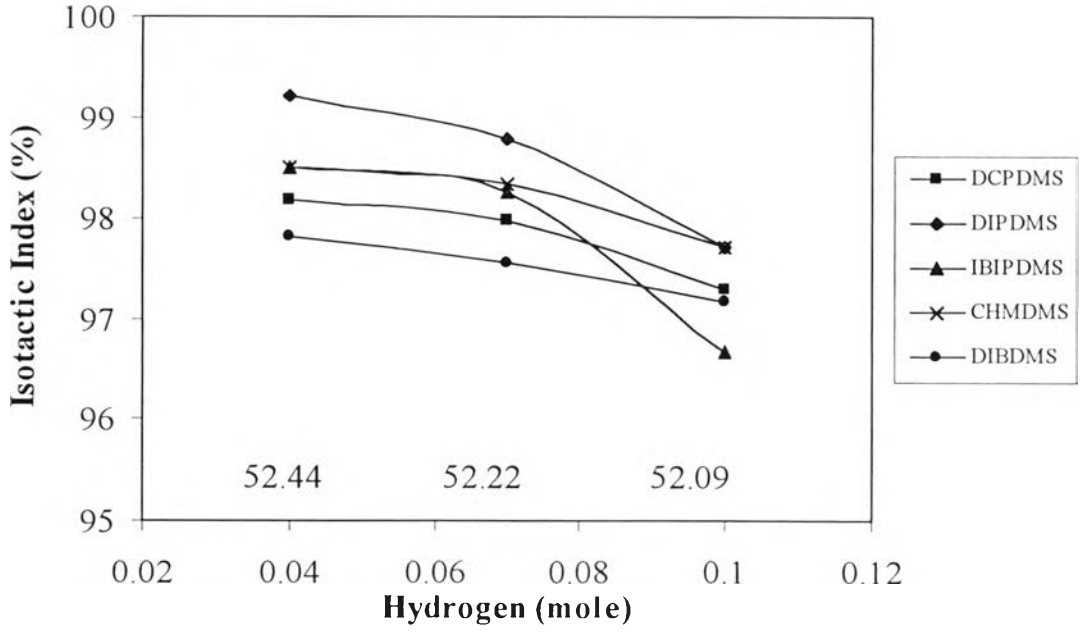


**Figure 4.20** Effect of hydrogen on isotactic index. Polymerization conditions: polymerization temperature = 70°C; Al/Ti ratio = 333; De/Al ratio = 0.10; polymerization time = 1 h

4.3.2 Effect of $H_2$ Concentration on Molecular Weight

Table 4.6 shows effect of $H_2$ concentration on number average molecular weight ($\overline{M}_n$), weight average molecular weight ($\overline{M}_w$), and polydispersity index ($\overline{M}_w/\overline{M}_n$). The result showed that $\overline{M}_n$ and $\overline{M}_w$ decreased with increasing amount of hydrogen for all kind of external donors and without external donor. Concerning the influence of hydrogen on the molecular weight, many authors (Chien and Kuo, 1986b; Kim *et al.*, 1990; Lee and Jeong, 1993; and Mori *et al.*, 1999) have found the same effect depends on the square root of the partial pressure of hydrogen in heterogeneous catalyst systems (Boor, 1979). Effect of hydrogen on polydispersity index ($\overline{M}_w/\overline{M}_n$) is unclear.

It may be concluded that the number average molecular weight ($\overline{M}_n$) decreases by the chain transfer reaction of the amount of hydrogen in heterogeneous catalyst systems.

4.3.3 Effect of $H_2$ Concentration on Melting Temperature

Melting temperature of DCPDMS, DIPDMS, and IBIPDMS was constant at 164°C, CHMDMS was 162-163°C, DIBDMS was 159-163°C and NODONOR was 159-161°C, which are shown on Table 4.7. It can be seen, however, that melting temperature of catalyst system without external donor was slightly lower than catalyst system with other external donors.

It can be thought that $H_2$ had no significant effect on melting temperature with any external donor or without external donor.

4.3.4 Effect of $H_2$ Concentration on Crystallization Temperature

Table 4.8 shows effect of $H_2$ concentration on crystallization temperature of the catalyst system with and without external donor. It was shown that melting temperature of DCPDMS was 112-116°C, DIPDMS was 117-119°C, IBIPDMS was 119-121°C, CHMDMS was 115-117°C, DIBDMS

**Table 4.6** Effect of hydrogen concentration on molecular weight

| Moleculare weight | | | | |
|---|---|---|---|---|
| Donor | $H_2$ mole | De/Al mole ratio=0.1 | | |
| | | $\overline{M}_n$ $*10^{-4}$ | $\overline{M}_w$ $*10^{-5}$ | $\overline{M}_w/\overline{M}_n$ |
| DCPDMS | 0.04 | 21.78 | 28.63 | 13.15 |
| | 0.07 | 13.94 | 20.04 | 14.37 |
| | 0.1 | 13.80 | 18.92 | 13.71 |
| DIPDMS | 0.04 | 16.56 | 27.02 | 16.32 |
| | 0.07 | 16.36 | 21.30 | 13.02 |
| | 0.1 | 13.02 | 16.84 | 12.93 |
| IBIPDMS | 0.04 | 18.88 | 25.43 | 13.47 |
| | 0.07 | 15.31 | 19.68 | 12.85 |
| | 0.1 | 15.20 | 20.18 | 13.28 |
| CHMDMS | 0.04 | 15.87 | 20.01 | 12.61 |
| | 0.07 | 15.60 | 18.45 | 11.82 |
| | 0.1 | 13.73 | 16.52 | 12.03 |
| DIBDMS | 0.04 | 22.29 | 18.91 | 8.48 |
| | 0.07 | 13.58 | 15.77 | 11.61 |
| | 0.1 | 12.19 | 16.78 | 13.77 |
| Donor | $H_2$ mole | De/Al mole ratio = 0 | | |
| | | $\overline{M}_n$ $*10^{-4}$ | $\overline{M}_w$ $*10^{-5}$ | $\overline{M}_w/\overline{M}_n$ |
| NO DONOR | 0.04 | 11.18 | 11.30 | 10.11 |
| | 0.07 | 11.07 | 10.92 | 9.86 |
| | 0.1 | 8.52 | 8.65 | 10.14 |

**Table 4.7** Effect of hydrogen concentration on melting temperature

| Melting temperature (°C) | | |
|---|---|---|
| Donor | $H_2$ mole | De/Al mole ratio 0.1 |
| DCPDMS | 0.04 | 164 |
| | 0.07 | 164 |
| | 0.1 | 164 |
| DIPDMS | 0.04 | 164 |
| | 0.07 | 164 |
| | 0.1 | 164 |
| IBIPDMS | 0.04 | 164 |
| | 0.07 | 164 |
| | 0.1 | 164 |
| CHMDMS | 0.04 | 162 |
| | 0.07 | 162 |
| | 0.1 | 163 |
| DIBDMS | 0.04 | 159 |
| | 0.07 | 162 |
| | 0.1 | 163 |
| Donor | $H_2$ mole | De/Al mole ratio 0 |
| NO DONOR | 0.04 | 160 |
| | 0.07 | 159 |
| | 0.1 | 161 |

**Table 4.8** Effect of hydrogen concentration on crystallization temperature

| Crystallization temperature (°C) | | |
|---|---|---|
| Donor | $H_2$ mole | De/Al mole ratio 0.1 |
| DCPDMS | 0.04 | 112 |
| | 0.07 | 116 |
| | 0.1 | 114 |
| DIPDMS | 0.04 | 118 |
| | 0.07 | 117 |
| | 0.1 | 119 |
| IBIPDMS | 0.04 | 121 |
| | 0.07 | 119 |
| | 0.1 | 120 |
| CHMDMS | 0.04 | 115 |
| | 0.07 | 116 |
| | 0.1 | 117 |
| DIBDMS | 0.04 | 113 |
| | 0.07 | 118 |
| | 0.1 | 117 |
| Donor | $H_2$ mole | De/Al mole ratio 0 |
| NO DONOR | 0.04 | 108 |
| | 0.07 | 109 |
| | 0.1 | 112 |

was 113-118°C, and NODONOR was 108-112°C that had insignificant effect with increasing amount of hydrogen.

4.3.5 Effect of $H_2$ Concentration on Melt Flow Rate

The result of $H_2$ concentration on melt flow rate on Table 4.9 shows that melt flow rate increased with 1.71-2.88 fold when increasing $H_2$ from 0.04 to 0.07 mole then less increased with 1.41-1.91 fold when increasing $H_2$ from 0.07 to 0.1 mole. Lee and Jeong (1993) also found the same effect, based on the $Mg(OEt)_2$/benzoyl chloride (BC)/$TiCl_4$-TEA/ED catalyst system, that MFR increases with increasing amount of hydrogen. Hydrogen acts as chain transferring agent and facilitates termination step such that lower molecular weight molecules can be resulted. This leads to lower isotactic index, crystallinity and MFR.

It can be observed that when amount of hydrogen increases, isotactic index decreases (from result) that is less crystallinity, which can enlarge a discontinuity effect on increasing MFR. Moreover, it can be seen that an order of the MFR was as following at any hydrogen concentration.

NO DONOR > DIBDMS > CHMDMS > IBIPDMS > DIPDMS > DCPDMS

**Table 4.9** Effect of hydrogen concentration on melt flow rate

| Melt flow rate (g/10min) | | |
|---|---|---|
| Donor | $H_2$ mole | De/Al mole ratio 0.1 |
| DCPDMS | 0.04 | 1.1 |
| | 0.07 | 3.0 |
| | 0.1 | 5.0 |
| DIPDMS | 0.04 | 2.5 |
| | 0.07 | 7.3 |
| | 0.1 | 12.3 |
| IBIPDMS | 0.04 | 3.5 |
| | 0.07 | 8.8 |
| | 0.1 | 16.8 |
| CHMDMS | 0.04 | 7.0 |
| | 0.07 | 12.0 |
| | 0.1 | 17.0 |
| DIBDMS | 0.04 | 10.1 |
| | 0.07 | 18.6 |
| | 0.1 | 29.7 |
| Donor | $H_2$ mole | De/Al mole ratio 0 |
| NO DONOR | 0.04 | 82.0 |
| | 0.07 | 201 |
| | 0.1 | 329 |