

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Effect of Agitator Stirring Speed

The polymerization rate, the amount of HDPE produced and low molecular weight polyethylene (LMWPE) produced were measured when changing the agitator stirring speed from 300 to 900 rpm. From Figures 4.1 and 4.2, it can be seen that above 800 rpm the polymerization rate and the amount of HDPE produced did not change with the stirring speed. The results were similar to the findings of Chareonsuk (1995) and indicated that there was no external mass transfer resistance (Kim et al., 1990). Therefore, the agitator speed at 800 rpm. was chosen for studying in the other parts of this work.

Figure 4.2 also shows that the amount of low molecular weight polyethylene produced is almost constant (in the range of 0.15-0.18 % by weight of HDPE produced) when changing the stirring speed from 600-900 rpm. But there is a significant increase in the amount of low molecular weight polyethylene at 300 rpm. These results are believed to be due to bad mixing and higher temperature in the core of the reactor (also see in part 4.3 Effect of polymerization temperature).

4.2 Effect of Partial Pressure of Hydrogen

The effect of partial pressure of hydrogen was studied by changing partial pressure of hydrogen to partial pressure of ethylene ratio (H_2/C_2H_4

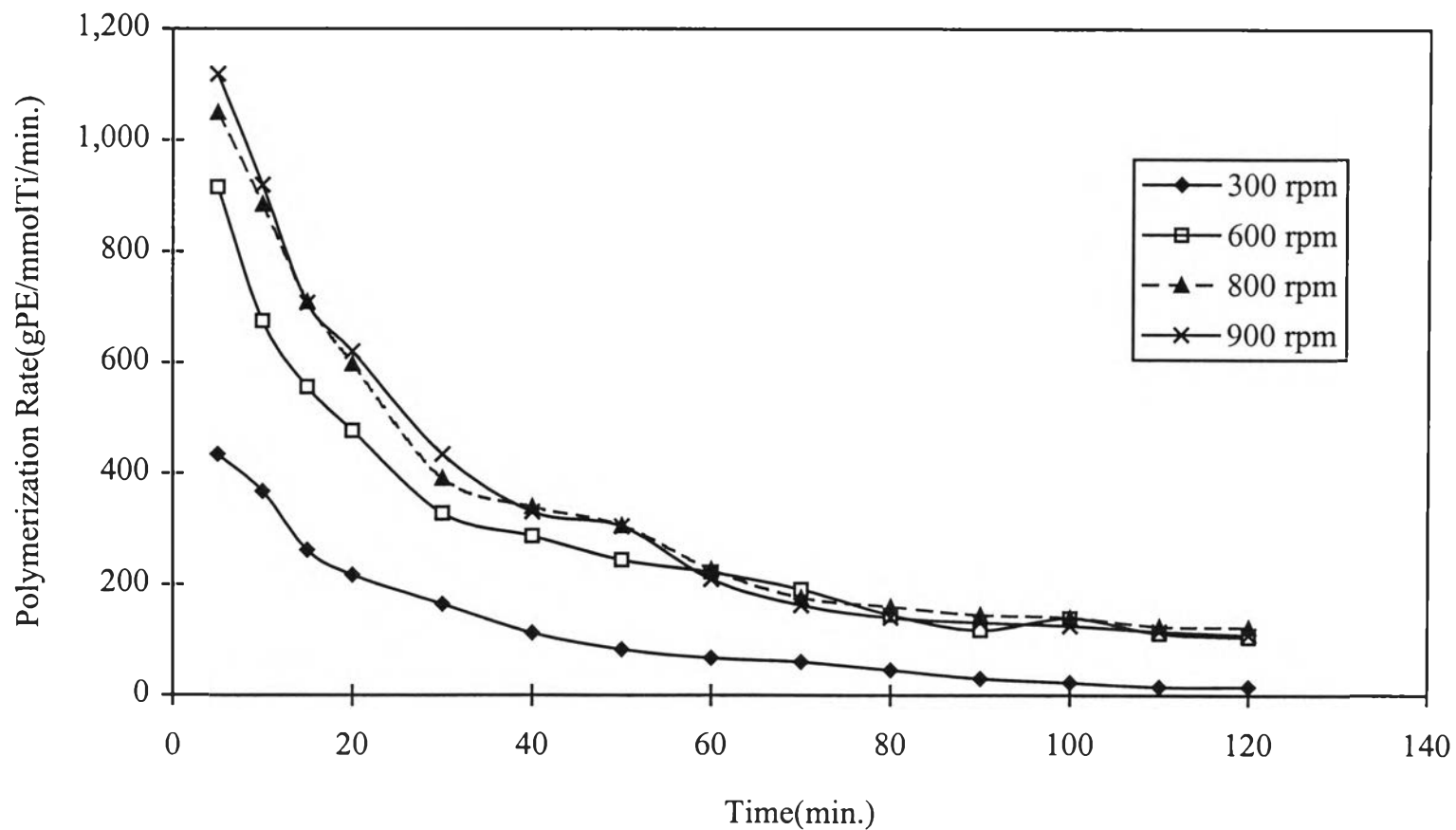


Figure 4.1 Effect of the stirring speed on the polymerization rate.

Condition : $T = 80\text{ }^{\circ}\text{C}$; $[\text{Ti}] = 0.006\text{ mmol/l}$; $\text{Al/Ti} = 100$; $P_{\text{H}_2} = 2.5\text{ kg/cm}^2$; $P_{\text{C}_2\text{H}_4} = 4.5\text{ kg/cm}^2$; $P_t = 8.0\text{ kg/cm}^2$.

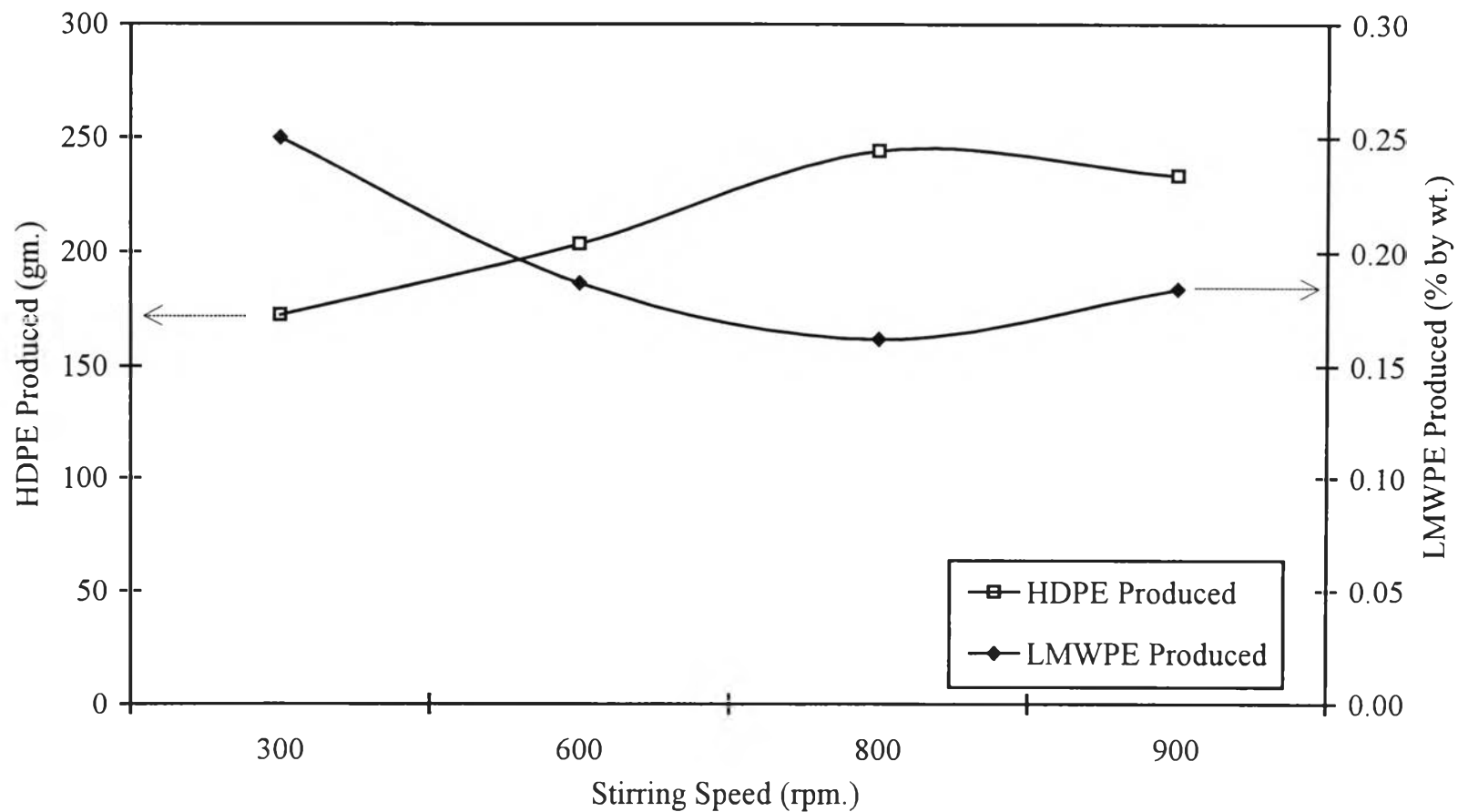


Figure 4.2 Effect of the stirring speed on the amount of HDPE and LMWPE produced.
 Condition : $T = 80\text{ }^{\circ}\text{C}$; $[\text{Ti}] = 0.006\text{ mmol/l}$; $\text{Al/Ti} = 100$; $P_{\text{H}_2} = 2.5\text{ kg/cm}^2$; $P_{\text{C}_2\text{H}_4} = 4.5\text{ kg/cm}^2$;
 $P_t = 8.0\text{ kg/cm}^2$.

ratio) while keeping partial pressure of ethylene constant at 4.5 kg/cm². Figure 4.3 shows that the amount of HDPE produced was slightly increased for the H₂/C₂H₄ ratio is less than 0.33, but at H₂/C₂H₄ ratio greater than 0.33 the amount of HDPE produced is decreased. Kim et al. (1990) proposed that the catalyst has a site that can be activated by hydrogen, so the HDPE produced increase at low H₂/C₂H₄ ratio. The same results were also observed by Marques et al. (1993). Further increasing the H₂/C₂H₄ ratio, the excess amount of hydrogen can not be used to form active sites but competitively adsorbed with ethylene monomer on the vacant active sites, so the HDPE produced decreased or it can reduce the catalyst center further.

As can be seen in Figure 4.3, the amount of low molecular weight polyethylene produced increase from 0.06 to 0.34 % by weight of HDPE produced (about 550 % increase) throughout the H₂/C₂H₄ range of 0.22 to 0.78. These results can be explained that higher H₂/C₂H₄ ratio will give higher hydrogen termination reaction. So the molecular weight of HDPE decreased as shown in Figure 4.4. Therefore, the lower in molecular weight of HDPE by hydrogen termination, the higher in the amount of low molecular weight polyethylene (LMWPE) which is the by-product that soluble in hexane.

4.3 Effect of Polymerization Temperature

Polymerization reaction was carried out in the range of 70 to 90 °C. As shown in Figure 4.5, the increase in the amount of HDPE produced with the increase in temperature upto 80 °C is due to the higher rate of polymerization. But over 80 °C the amount of HDPE produced decreases. These results agree with other workers (Keii et al., 1967; Kim et al., 1990). Keii et al. (1967)

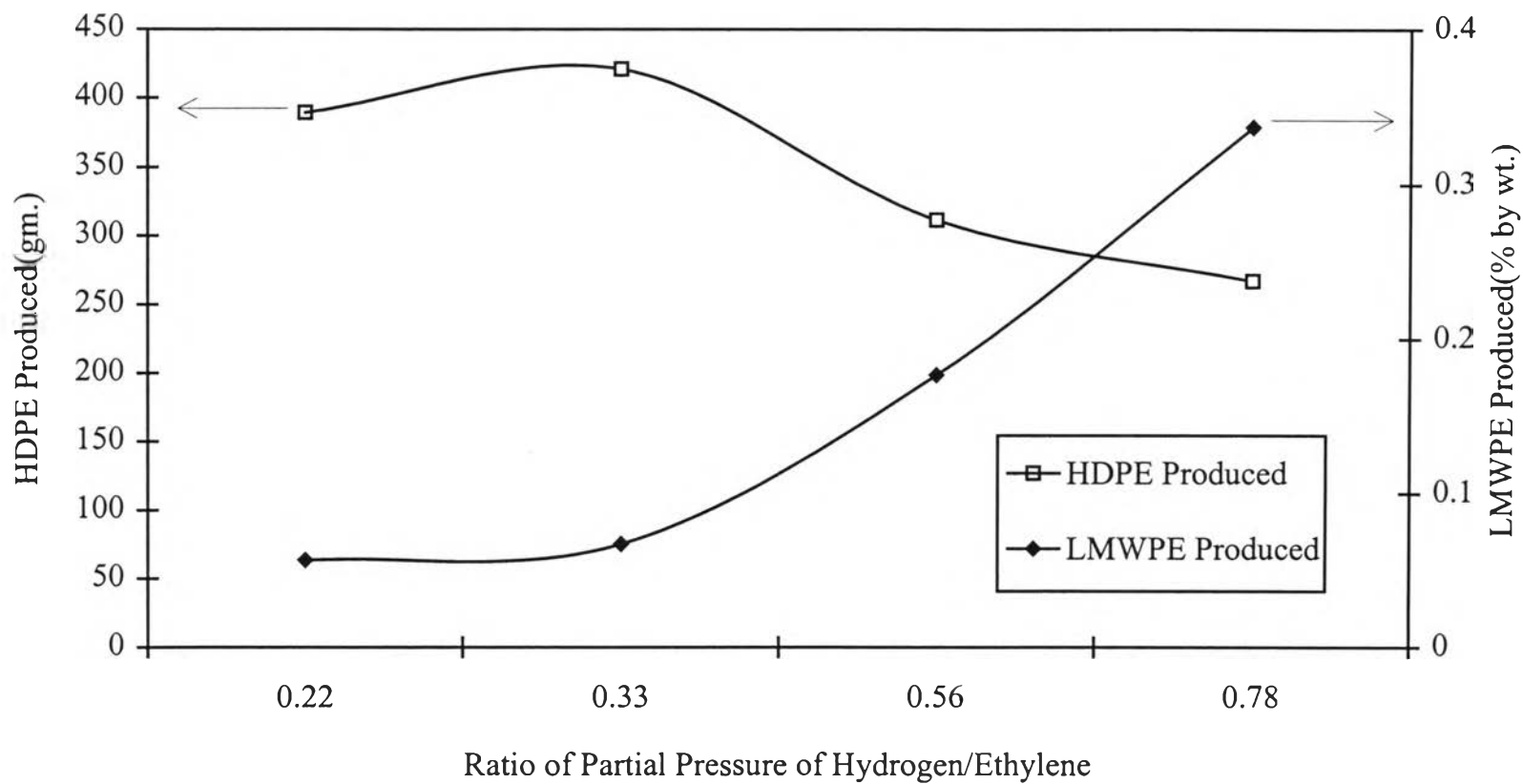


Figure 4.3 Effect of the ratio of partial pressure of hydrogen/ethylene on HDPE and LMWPE produced.
 Condition : $T = 80\text{ }^{\circ}\text{C}$; $[\text{Ti}] = 0.006\text{ mmol/l}$; 800 rpm; $\text{Al/Ti} = 100$; $P_{\text{C}_2\text{H}_4} = 4.5\text{ kg/cm}^2$.

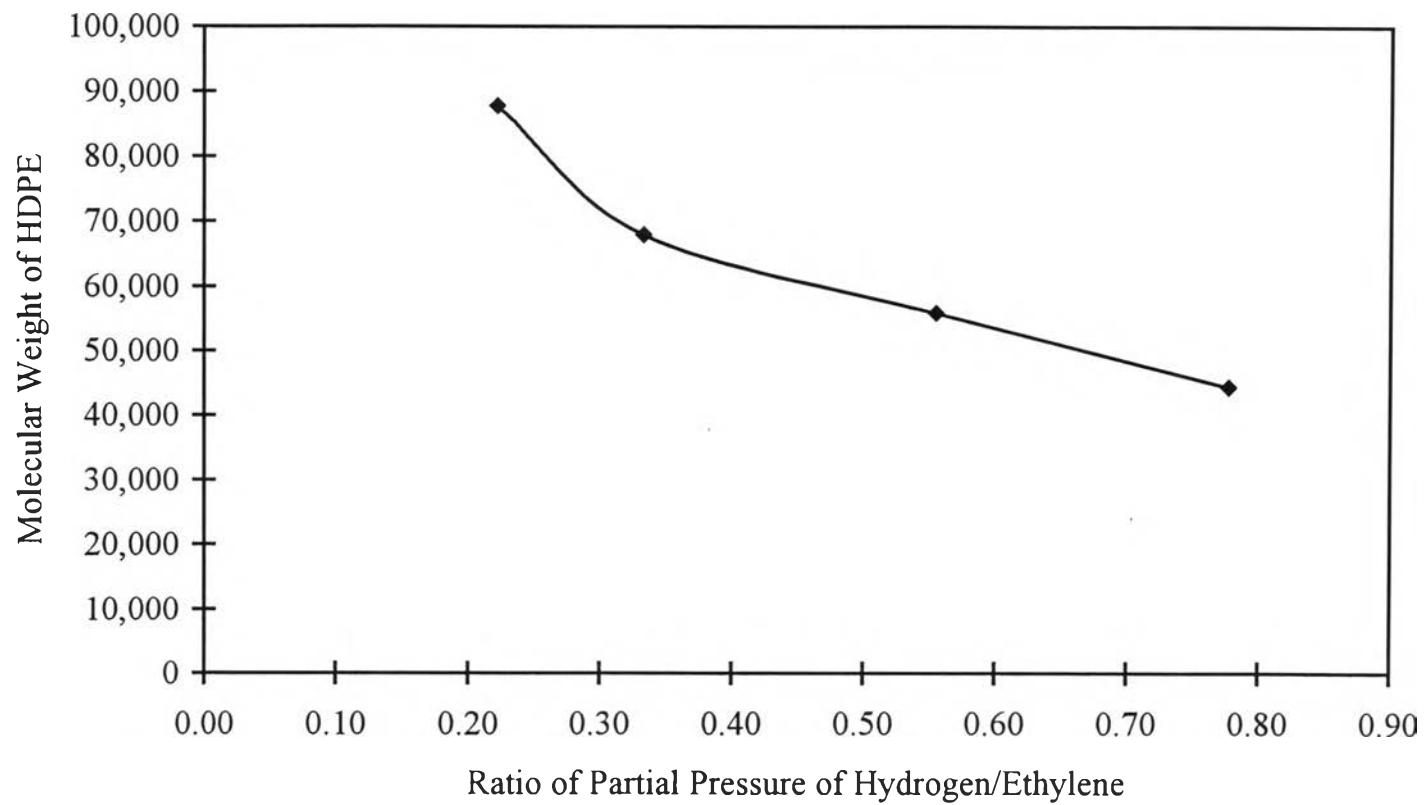


Figure 4.4 Effect of H_2/C_2H_4 ratio on the molecular weight of HDPE.

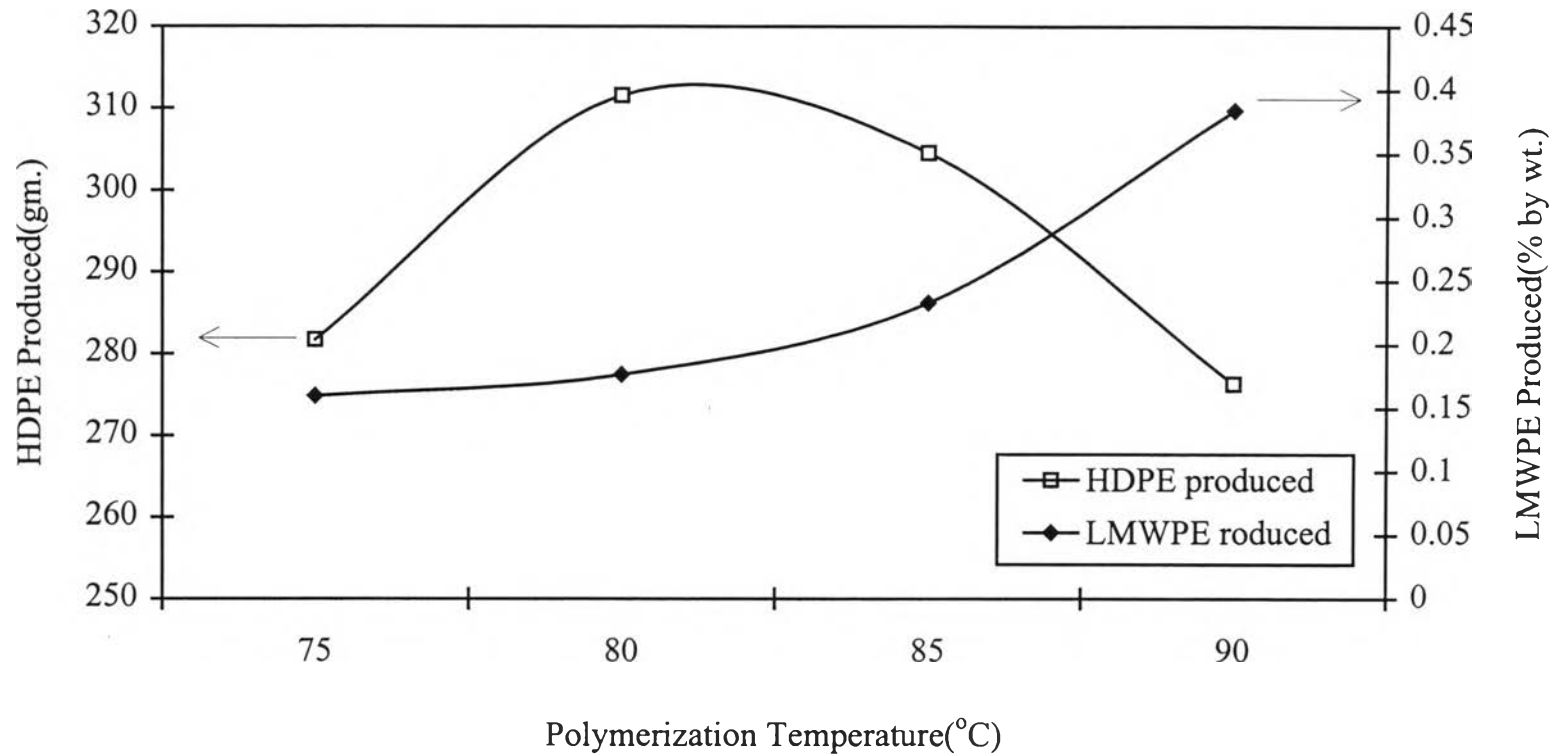
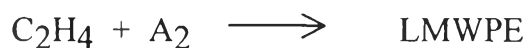
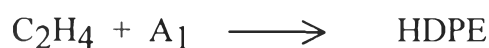


Figure 4.5 Effect of polymerization temperature on HDPE and LMWPE produced.

Condition : [Ti] = 0.006 mmol/l; 800 rpm; Al/Ti = 100; $P_{H_2} = 2.5 \text{ kg/cm}^2$; $P_{C_2H_4} = 4.5 \text{ kg/cm}^2$; $P_t = 8 \text{ kg/cm}^2$.

proposed that the decrease of polymerization rate or the amount of HDPE produced as temperature increased is due to the irreversible destruction of active sites.

When the temperature is increased, the amount of low molecular weight polyethylene increased from 0.06 to 0.34 % by weight of HDPE produced (about 550 % increase as shown in Figure 4.5). Figure 4.6 shows the dependence of the molecular weight of HDPE on the polymerization temperature. It shows that below 80 °C the decrease in molecular weight of HDPE is the reason for the increase in the amount of low molecular weight polyethylene produced. However, at above 80 °C the molecular weight of HDPE is almost constant, the amount of low molecular weight polyethylene still increases. We propose that two reactions have occurred as follows:



Where A is the active site. These two reactions occur on different active sites. Unlike the active sites for HDPE formation (A₁), the active sites for low molecular weight polyethylene formation (A₂) might not be destroyed above 80 °C. Moreover, the observed activation energies of these two reactions were found to be different. Figure 4.7 shows that the Arrhenius plot of the average polymerization rate of HDPE and the activation energy was found to be 3.5 kcal/mole corresponding to the data below 80 °C. And the activation energy of low molecular weight polyethylene was 20 kcal/mole as calculated from Figure 4.8. These values shows that the amount of low molecular weight polyethylene formed is more dependent on temperature than that of HDPE.

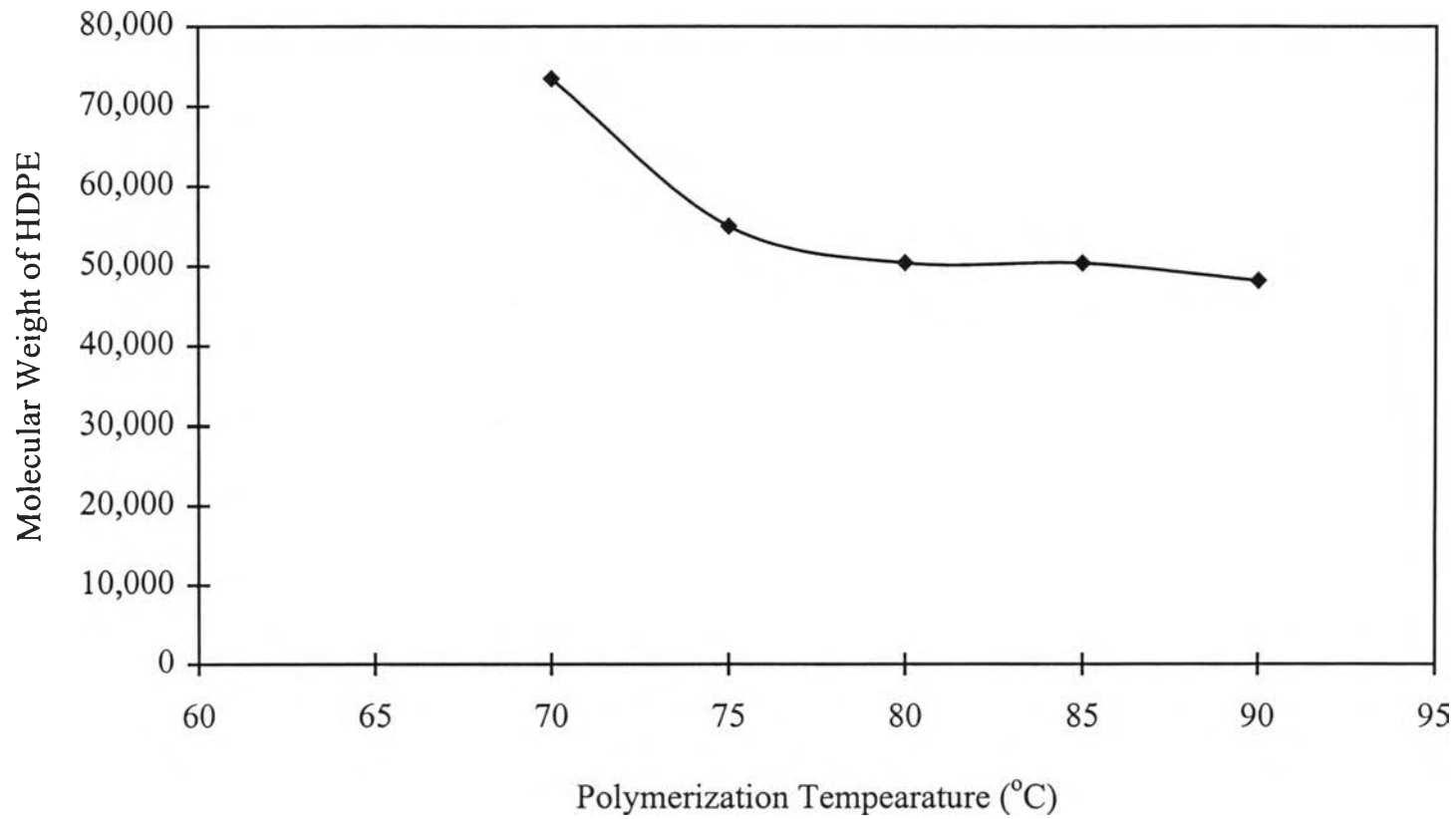


Figure 4.6 Effect of polymerization temperature on molecular weight of HDPE.

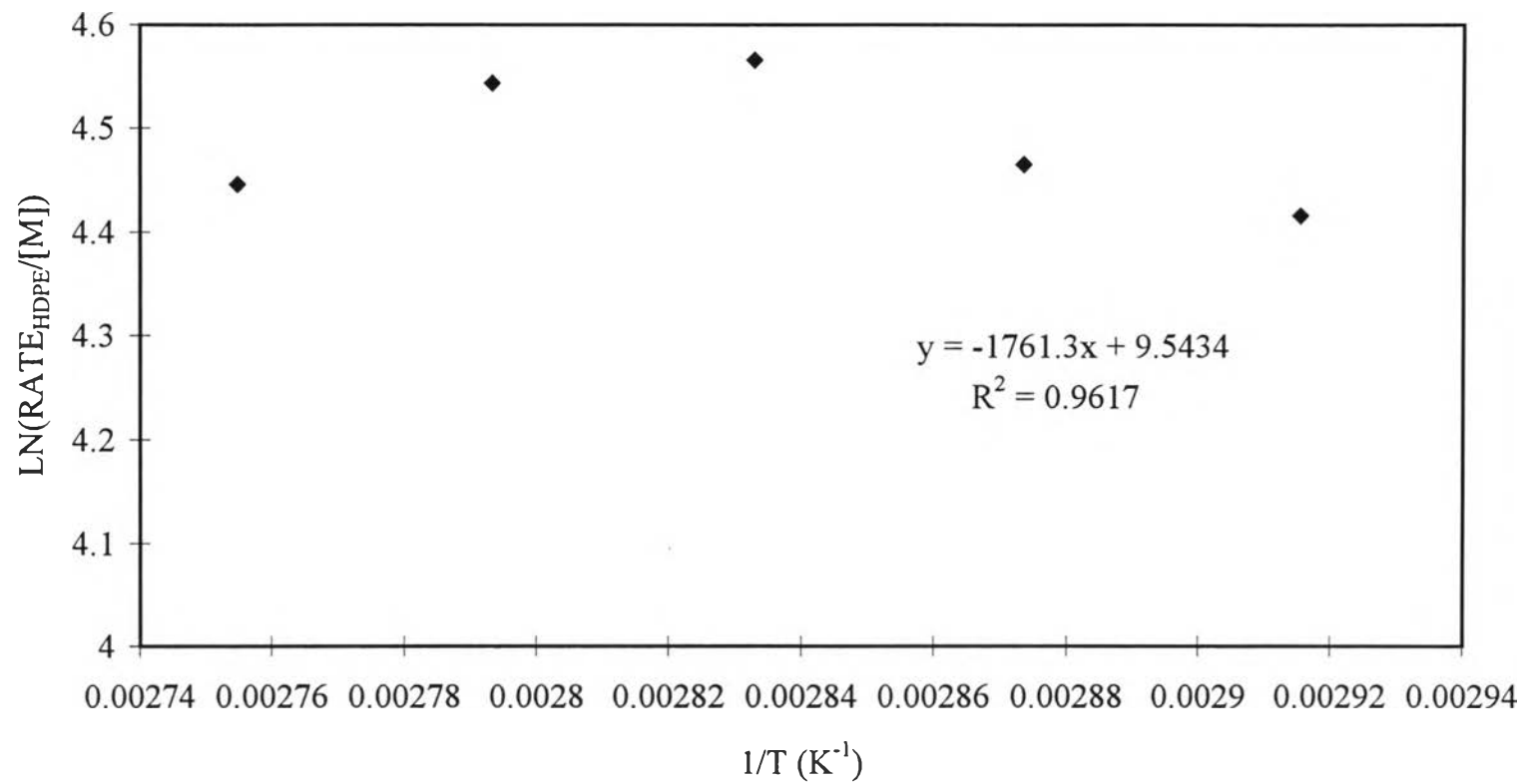


Figure 4.7 Arrhenius plot of the average polymerization rate of HDPE.
 Condition : [Ti] = 0.006 mmol/l; 800 rpm; Al/Ti = 100; P_{H₂} = 2.5 kg/cm²; P_{C₂H₄} = 4.5 kg/cm²;
 P_t = 8 kg/cm².

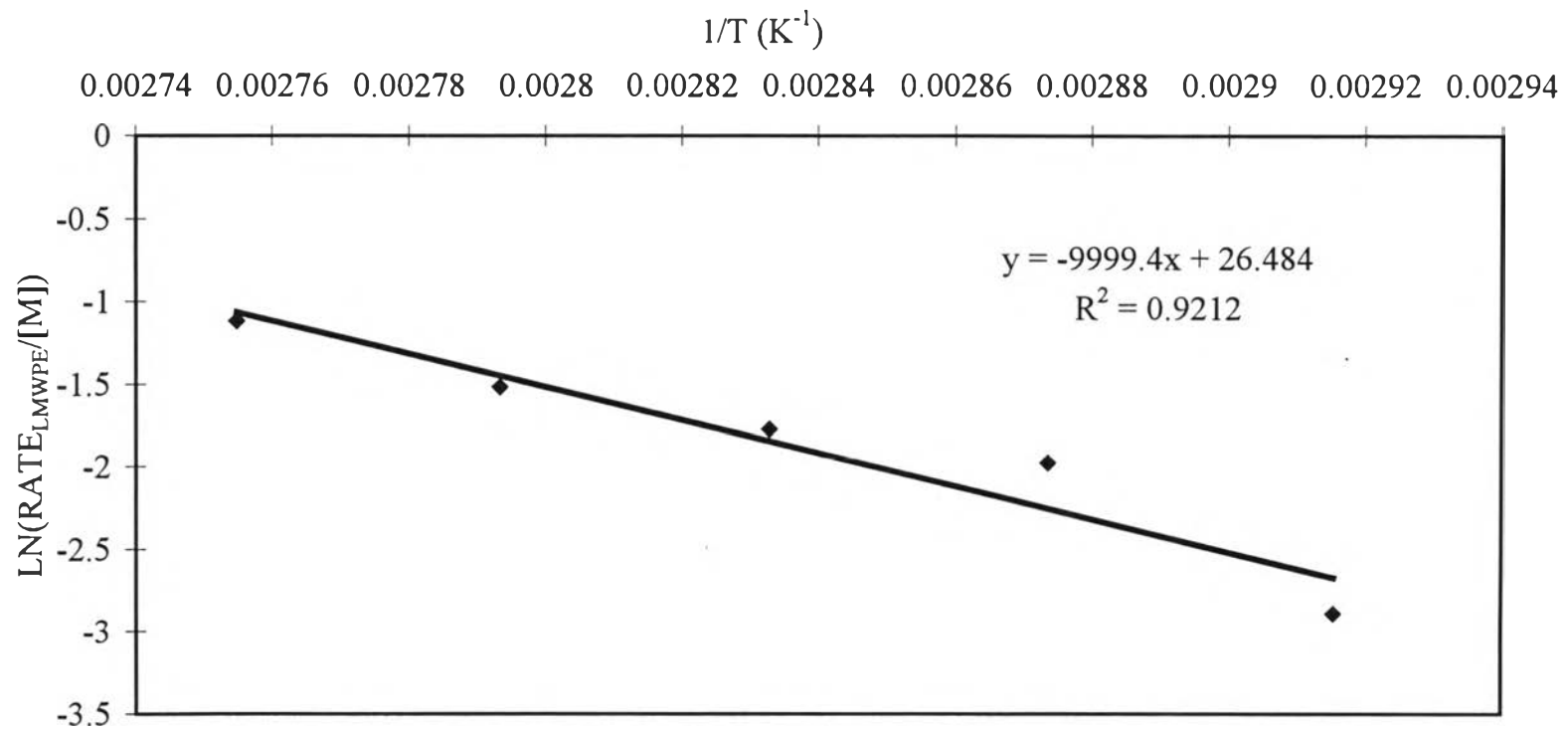


Figure 4.8 Arrhenius plot of the average polymerization rate of LMWPE.
 Condition : [Ti] = 0.006 mmol/l; 800 rpm; Al/Ti = 100; P_{H₂} = 2.5 kg/cm²; P_{C₂H₄} = 4.5 kg/cm²;
 P_t = 8 kg/cm².

And higher temperatures will accelerate the low molecular weight formation. It should be noted that at above 80 °C the decrease in the amount of HDPE produced was not consistent with the calculated activation of HDPE.

4.4 Effect of Alkylaluminum Concentration

The effect of alkylaluminum concentration was investigated by changing aluminum / titanium molar ratio (Al/Ti) from 50 to 300. Figure 4.9 shows that there is an optimum value of Al/Ti about 50-100 when the amount of HDPE produced is maximum. These results are similar to other researchers (Marques et al., 1993; Chareonsuk, 1995). Marques et al. (1993) concluded that at this maximum the active centers are formed completely, or that the maximum equilibrium value of active center has been reached. Further increase in Al/Ti ratio would decrease the amount of HDPE produced. This is believed to be due to over reduction of titanium (Boor, 1979). Another possible explanation is competitive adsorption between triethylaluminum and ethylene monomer for the same active site (Kim et al., 1990; Chareonsuk, 1995).

As also shown in Figure 4.9, the amount of low molecular weight polyethylene produced is not significantly changed (only about 10 % change). Figure 4.10 shows that Al/Ti ratio does not affect the molecular weight of HDPE produced. Similar results were reported by Sripruitkiat (1995).

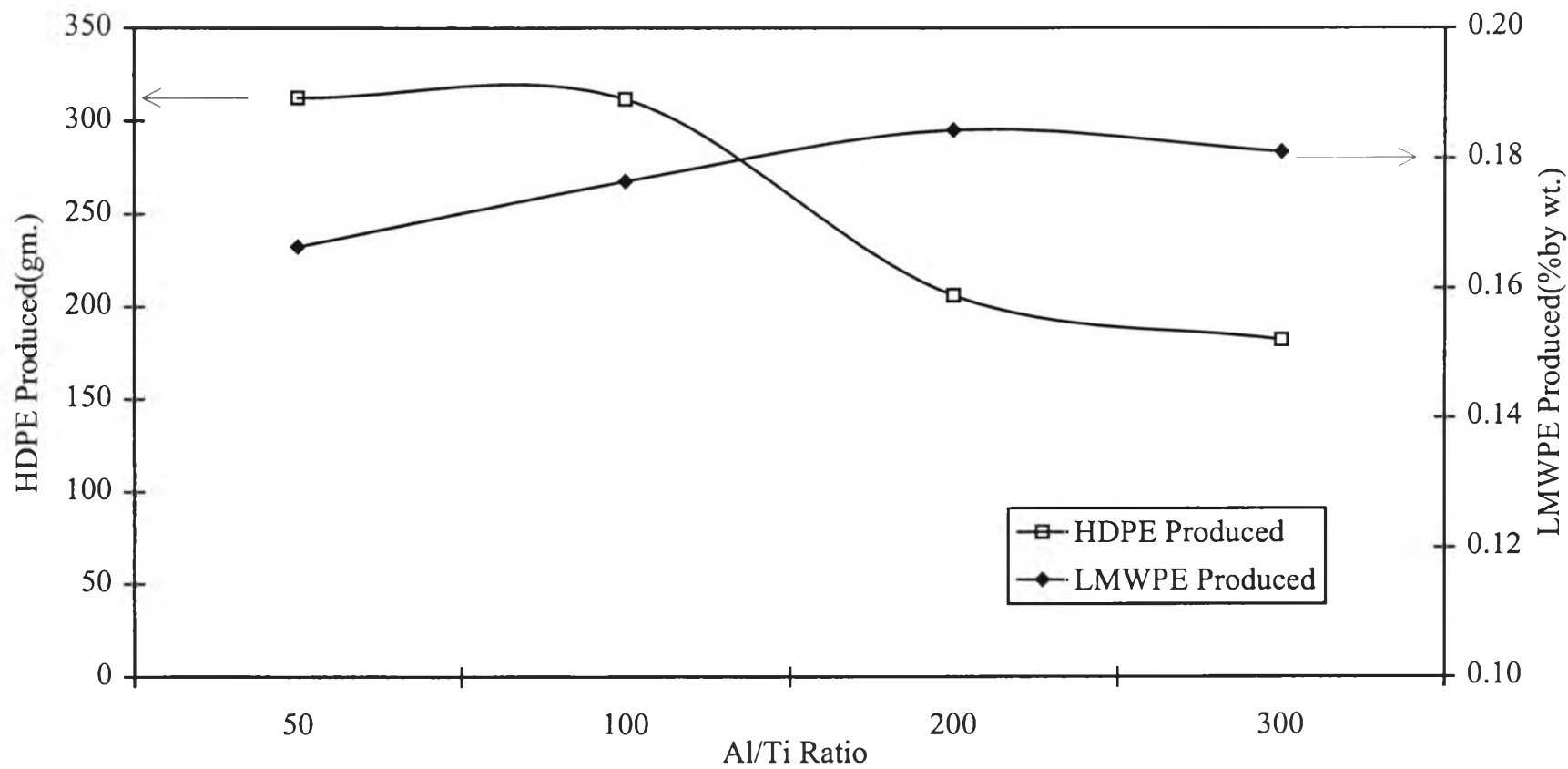


Figure 4.9 Effect of Al/Ti ratio on HDPE and LMWPE produced.

Condition : $T = 80\text{ }^{\circ}\text{C}$; $[\text{Ti}] = 0.006\text{ mmol/l}$; 800 rpm ; $P_{\text{H}_2} = 2.5\text{ kg/cm}^2$; $P_{\text{C}_2\text{H}_4} = 4.5\text{ kg/cm}^2$;
 $P_t = 8.0\text{ kg/cm}^2$.

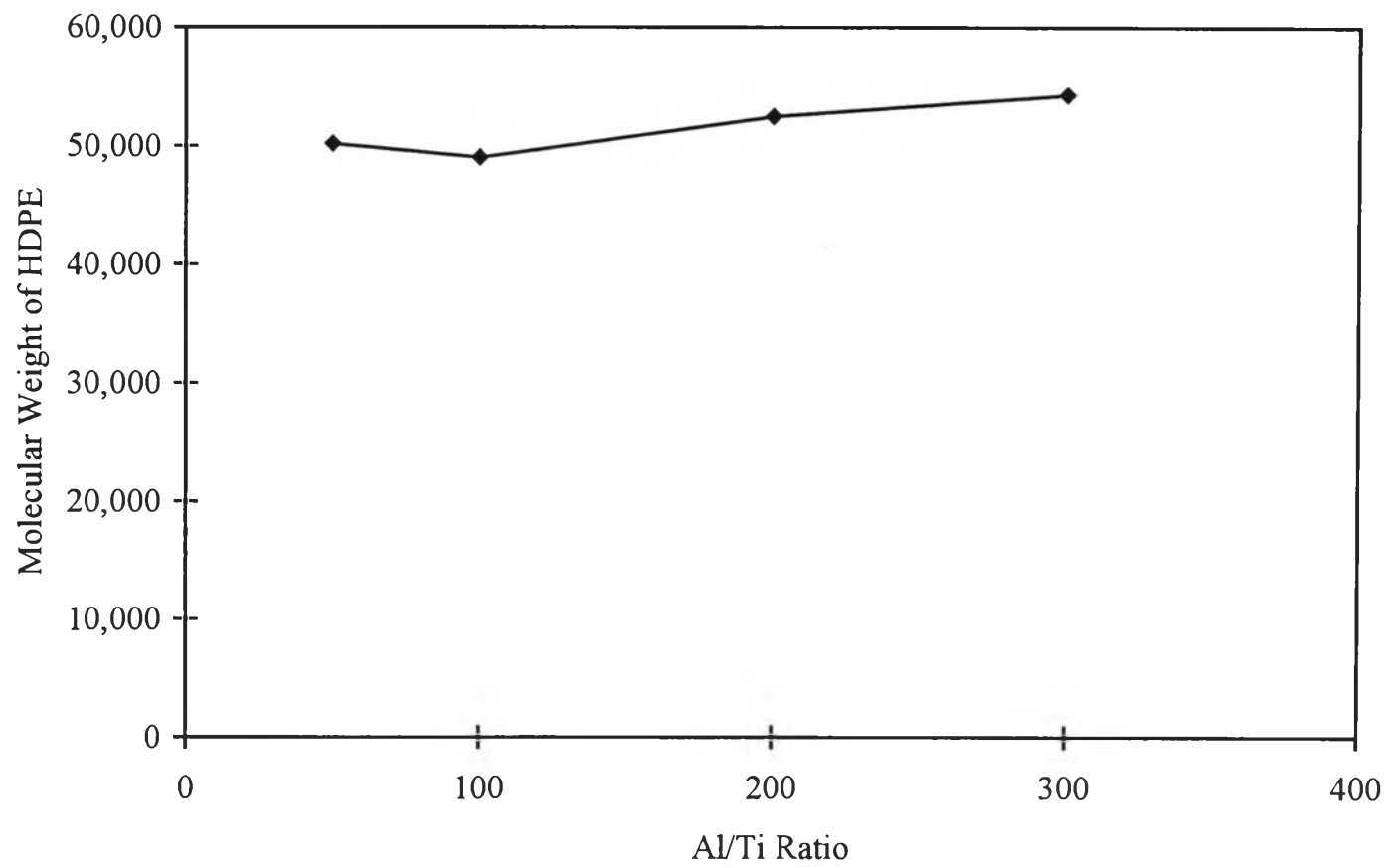


Figure 4.10 Effect of Al/Ti ratio on molecular weight of HDPE.

4.5 Effect of Polymerization Time

Figure 4.11 shows that the amount of HDPE produced increases with polymerization time. While the amount of low molecular weight polyethylene produced is not significantly changed (about 20 %) with polymerization time. So it can be concluded that LMWPE was formed as soon as HDPE formed but on different active sites. And Figure 4.12 shows that the polymerization time does not affect the molecular weight of HDPE. Sripruitkiat (1995) also observed these same results.

4.6 Effect of Molecular Weight of HDPE on the Amount of LMWPE

At below 80 °C, the increase in the amount of low molecular weight polyethylene produced with an increase in H₂/C₂H₄ ratio or increase in polymerization temperature is due to the decreasing of molecular weight of HDPE produced as shown in Fig. 4.13. The relationship can be expressed by the following equation:

$$\log (Y) = 11.8451 - 2.6739 \log (X)$$

where Y = the amount of LMWPE produced (% by wt. of HDPE produced);

X = molecular weight of HDPE.

However, at above 80 °C the molecular weight of HDPE does not decrease but the amount of low molecular weight polyethylene increases. This

phenomenon can be explained by the different types of active sites used for HDPE formed and LMWPE formed as discussed in part 4.3.

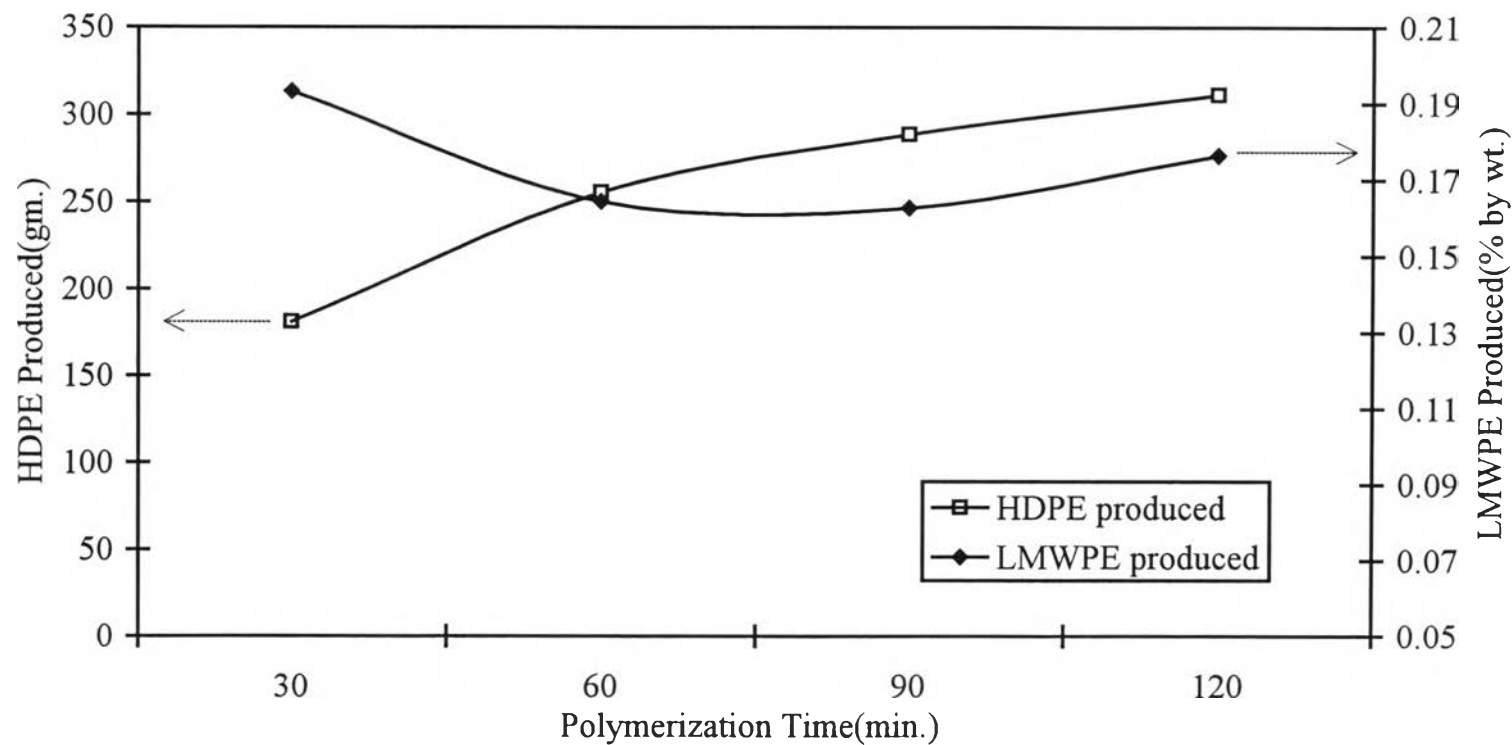


Figure 4.11 Effect of polymerization time on HDPE and LMWPE produced.
 Condition : $T = 80\text{ }^{\circ}\text{C}$; $[\text{Ti}] = 0.006\text{ mmol/l}$; 800 rpm; $\text{Al/Ti} = 100$; $P_{\text{H}_2} = 2.5\text{ kg/cm}^2$; $P_{\text{C}_2\text{H}_4} = 4.5\text{ kg/cm}^2$;
 $P_t = 8.0\text{ kg/cm}^2$.

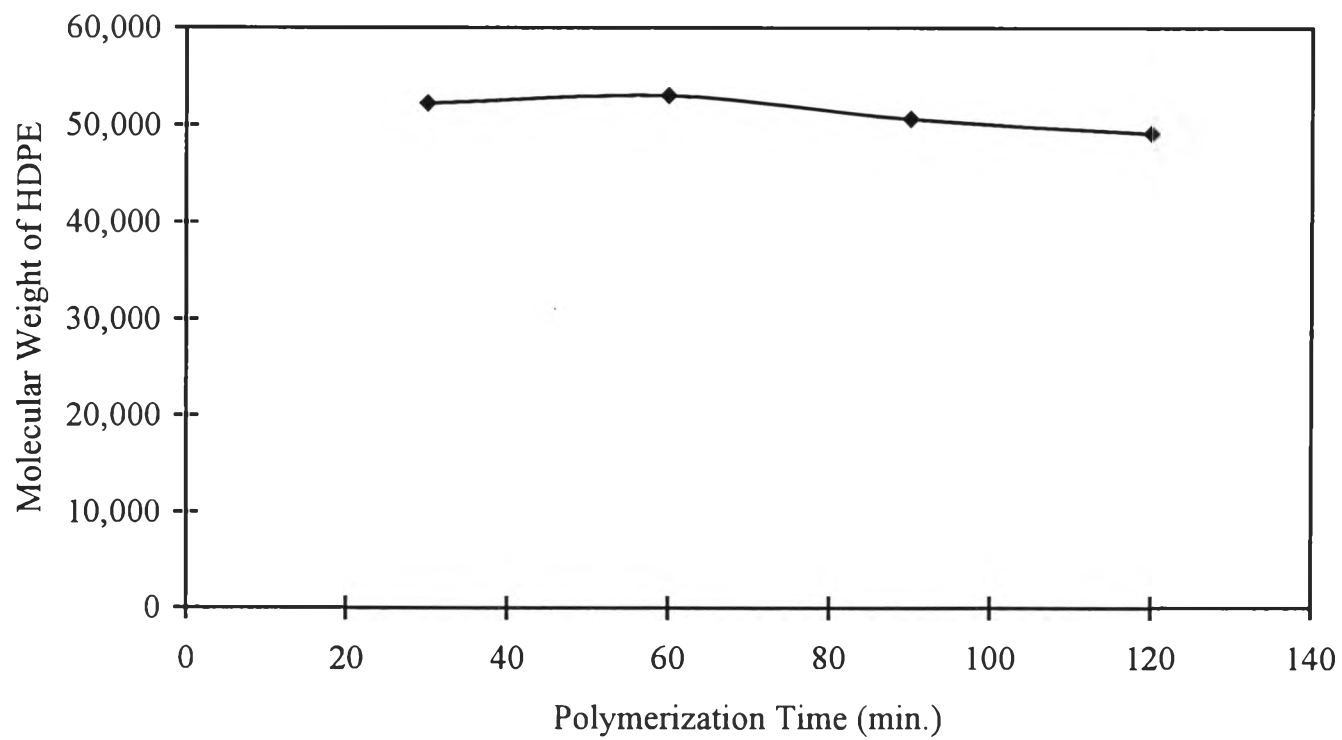


Figure 4.12 Effect of polymerization time on molecular weight of HDPE.

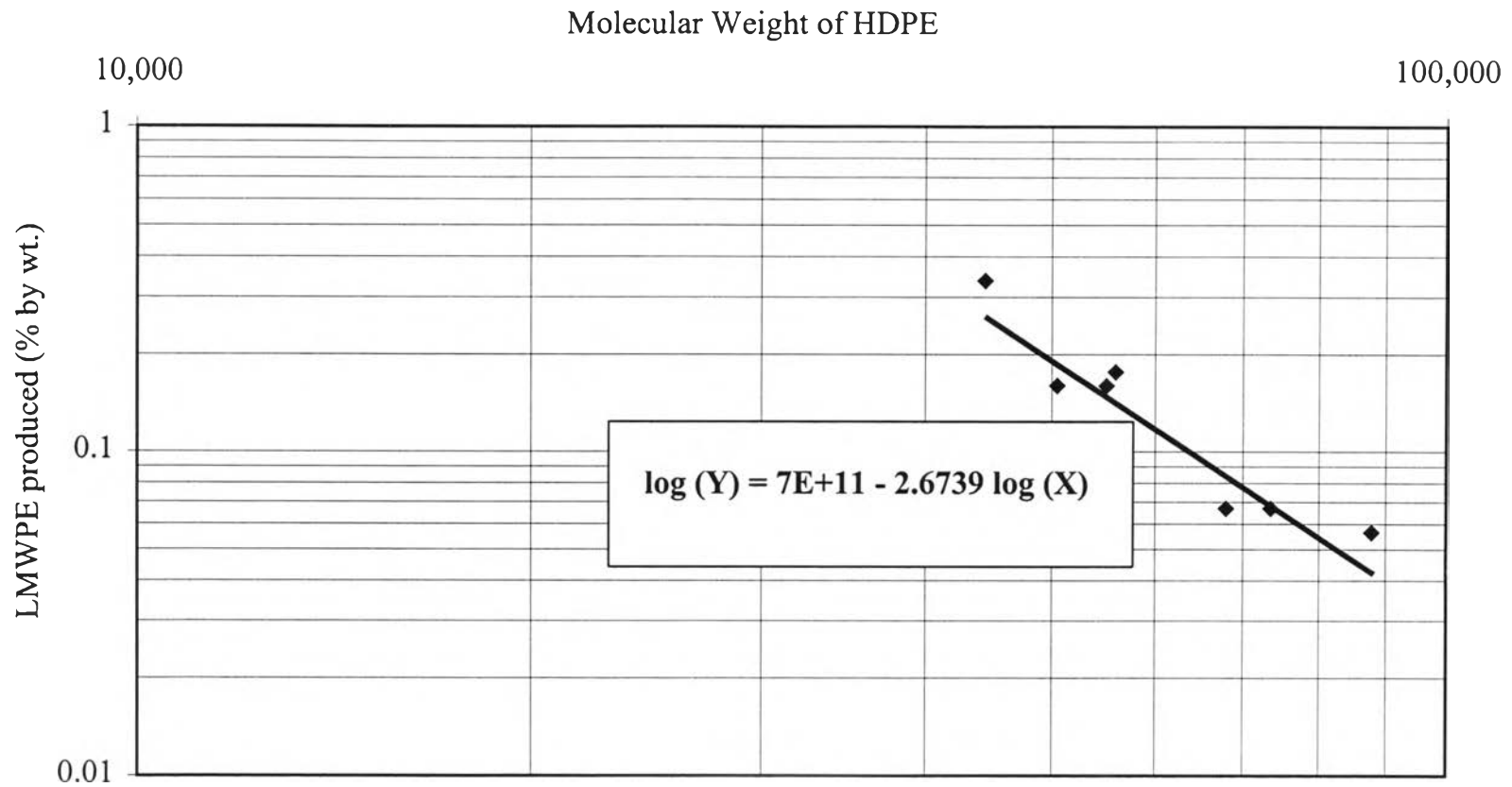


Figure 4.13 The relationship between molecular weight of HDPE and the amount of LMWPE produced.