CHAPTER V

RESULT & DISCUSSIONS

5.1 THE EFFECT OF ETHYLENE PARTIAL PRESSURE

The ethylene polymerization took place on the high activity Ziegler-Natta supported catalyst. The polymerization occurred at the supported Ti active centers after activation by TEA. Both alkyl aluminum compounds with their derivatives and monomers adsorbed on the surface of supported catalyst. The maximum increase of the polymerization rate occurred at the maximum rate of ethylene insertion.

The characteristic curve of ethylene consumption rate versus time showed in Figure 5.1. At low pressure of ethylene, the polymerization rate increased conversely to the partial pressure of ethylene. Whereas, the decline in the reaction rate was observed at the high pressure of ethylene at which the polymerization rate became independent of monomer concentration. The ethylene diffused into the media (n-hexane) then to react at the active sites. The propagation took place at the active centers and the next ethylene molecules approached successively to the active sites for insertion. The polyethylene produced from the titanium active centers and afterward the polyethylene chains started to cover the surface of catalyst. The diffusion limit or mass transfer effect limited the rate after the maximum rate had reached at a certain ethylene partial pressure. The heat transfer effect usually became the serious problem to overcome, but this catalytic polymerization had n-hexane function as heat transfer agent and media.

In the polymerization of olefin, ethylene on a titanium-based catalyst, it generally showed a rapid increase of molecular weight in the first few minutes of polymerization[70]. The shapes of the curves influenced by the chain initiation and catalyst deactivation processes and any changes that may occur during the reaction [71,72].

It seemed reasonable to attribute the increase of molecule weight in the initial observation to the ethylene insertion or polymer growth. The catalyst surface was initially fresh and very suitable to propagate the polymer chains. It took about 20 minutes for the polymer growth process.

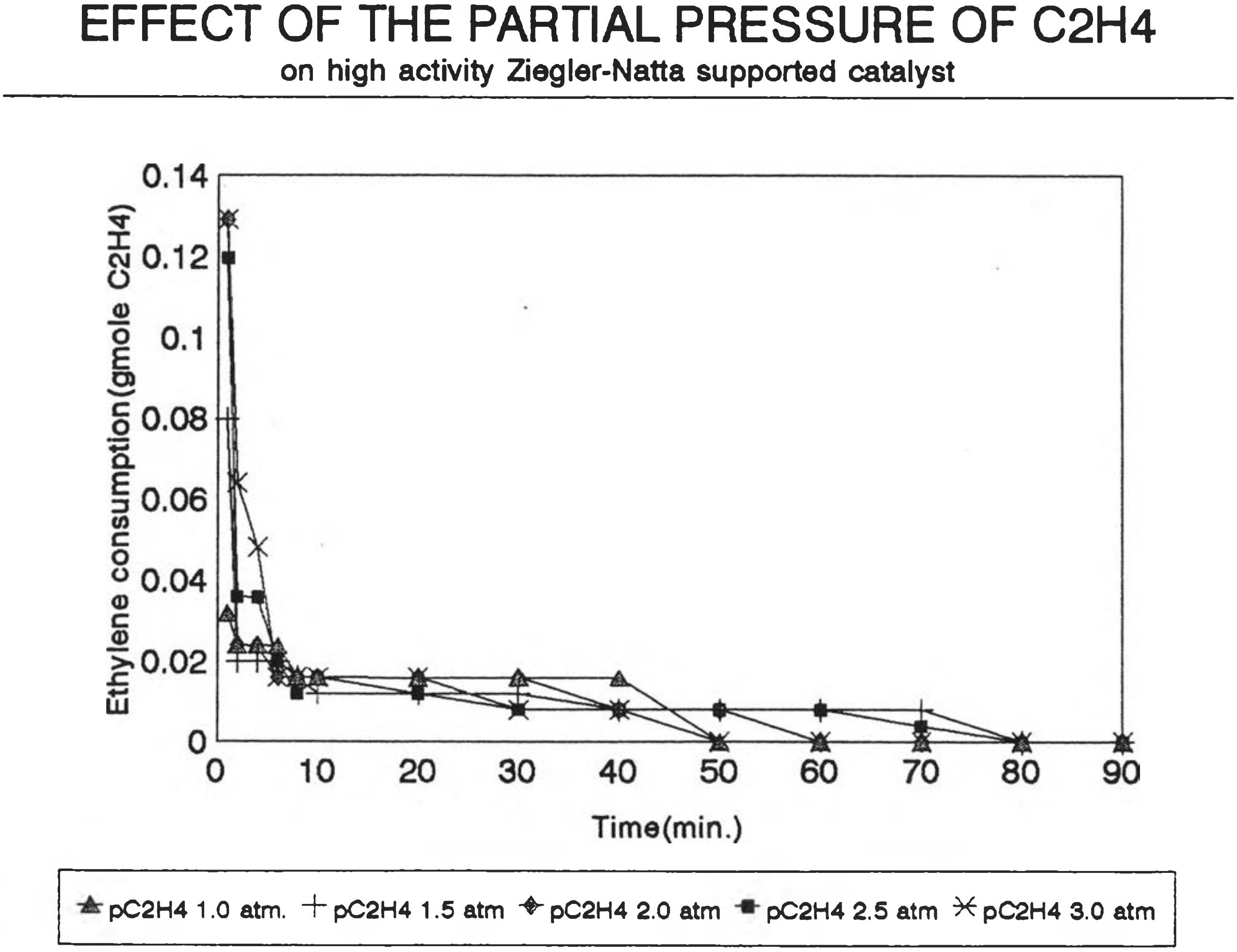


Figure 5.1 Ethylene Consumption versus Polymerization time curves at Various partial pressures of ethylene.

Polymerization conditions: [Ti] = 0.01780 moleTi/l,

Temperature = 85 ^0C,

TEA / Ti = 160,

Partial pressure of hydrogen = 1 atm,

Polymerization time = 1.5 hr.

Ethylene partial pressure of 1.0, 1.5, 2.0, 2.5, and 3.0 bar.

EFFECT OF THE PARTIAL PRESSURE OF C2H4

on high activity Ziegler-Natta supported catalyst

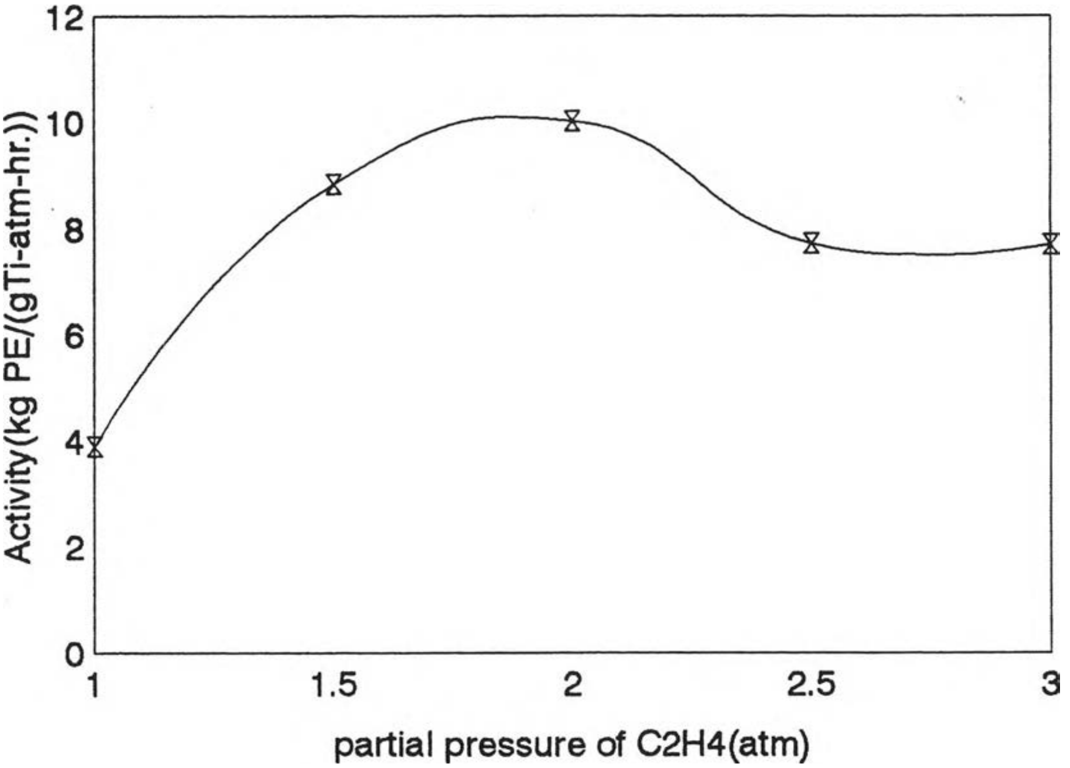


Figure 5.2 Catalyst Activity versus Partial presure of ethylene

Polymerization conditions:[Ti] = 0.01780 moleTi/l,
Temperature = 85 ^{0}C,
TEA / Ti = 160,
Partial pressure of hydrogen = 1 atm,
Polymerization time = 1.5 hr.
Ethylene partial pressure of 1.0, 1.5, 2.0, 2.5, and 3.0 bar.

The catalytic activity versus the pressure of ethylene indicated that the activity increased with the increasing of partial pressure of ethylene as showed in Fig. 5.2. When the partial pressure was 2.0 atm, the activity reached the maximum point. The activity would decrease beyond 2.0 atm.

Because the polymerization is an extremely exothermic reaction, the rapid growth rate produced a substantial amount of heat that may lead to the uncontrollable reaction in which it may cause explosion. In this consideration, the effective process control can overcome this problem. During the experiment, the temperature had been governed by feedback control configuration. The temperature offset occurred and the cooling water inside the reactor coil operated manually to minimize the temperature deviation.

The more rapid propagation took place, the less diffusion of monomer to the propagation site occurred. The polymerization rate was restricted by the mass transfer processes in the early duration. The decreasing rate was observed due 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 ethylene monomer to polymerize effectively. The illustrations from various characterization results of the polyethylene polymerization from high-activity Ziegler-Natta supported catalyst with the optimum condition showed in the following section.

From a practical point of view, a standard condition of 1.0 atm partial pressure of ethylene was investigated for further experiments because it showed a less effect of mass transfer limitation.

5.2 THE EFFECT OF TRIETHYLALUMINUM/ TITANIUM RATIO

The special characteristic of Ziegler-Natta catalyst is the activation by the certain type of alkyl aluminum as the cocatalyst. Afterwards, it is highly reactive to polymerize olefin more than its individual catalyst component. Many reactions occurred during the activation stage until the catalyst was ready to polymerize. The catalyst was a complex of $TiCl_4$ and the alkyl aluminum compound[73]. This complex was in equilibrium with its derivatives[74]. The catalytic activity should increase until it reaches the maximum point. Then, the cocatalyst still increased, the catalytic activity would decrease.

The ethylene consumption profile versus polymerization time as shown in Figure 5.3 and the catalytic activity versus TEA/ Ti molar ratio, Figure 5.4 were coincided to show a maximum activity at TEA/Ti molar ration of 160. The term of activity defined as gram of polyethylene produced from 1 gram-atom of titanium per 1.0 atm of ethylene partial pressure during 1 hour of polymerization time.

The higher increment in the ethylene consumption as a function of time found when the TEA / Ti ratio increased from 8 to 100 and the highest value was obtained at the ratio of 160. The reaction curve decreased after the ratio was above 160. Figure 5.4 showed the maximum point at the ratio of 160.

The influence of the cocatalyst ratio discussed as follows. The increase of cocatalyst ratio caused the catalytic activity to become higher in the exact interval before it reached the maximum value. The lower activity again obtained when this ratio was higher than 160 owing to the over-reduction of titanium active centers in lowering the oxidation state of titanium active centers[75].

The first point of TEA / Ti molar ratio used according to the previous thesis by Suwaree[67], in that the maximum activity occurred at the value of 8. It was assigned as the low activity catalyst, 1.0-5.0 kgPE/(gTi-atm-hr)[8]. In the experiment, the TEA /Ti gradually increased so as to obtain the high activity catalyst. Therefore, the high activity of the polymerization achieved at the higher TEA / Ti molar ratios within a shorter induction period than that of the unsupported catalytic polymerization.

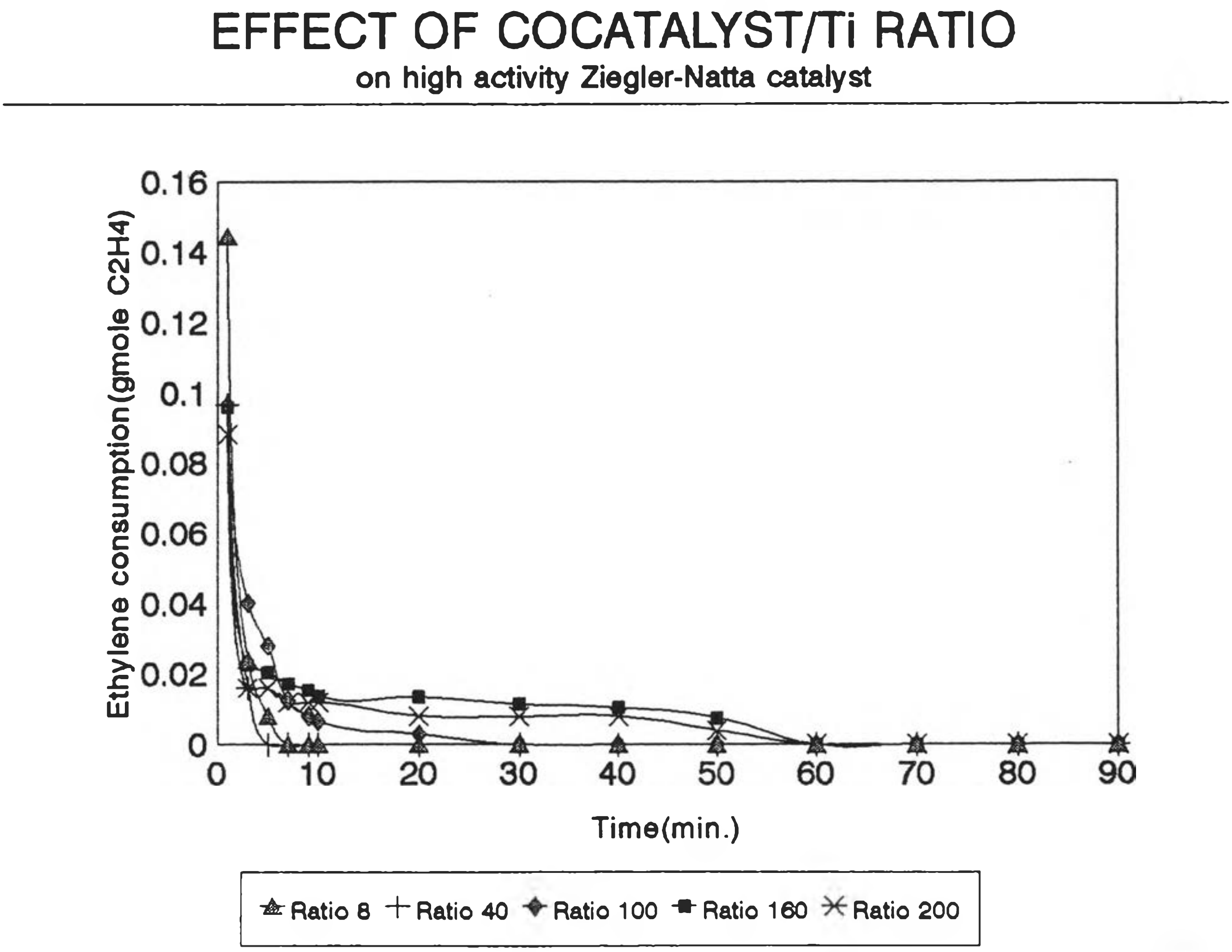


Figure 5.3 Ethylene consumption versus polymerization time curves at various TEA/Ti mole ratios.

Polymerization condition ; [Ti] = 1.068×10^{-4} mole / l,

Temperature = 85 ^{0}C,

Partial pressure of ethylene = 1 atm,

Partial pressure of hydrogen = 1 atm,

Polymerization time = 1.5 hr.

TEA / Ti mole ratios of 8, 40, 100, 160, 200, respectively.

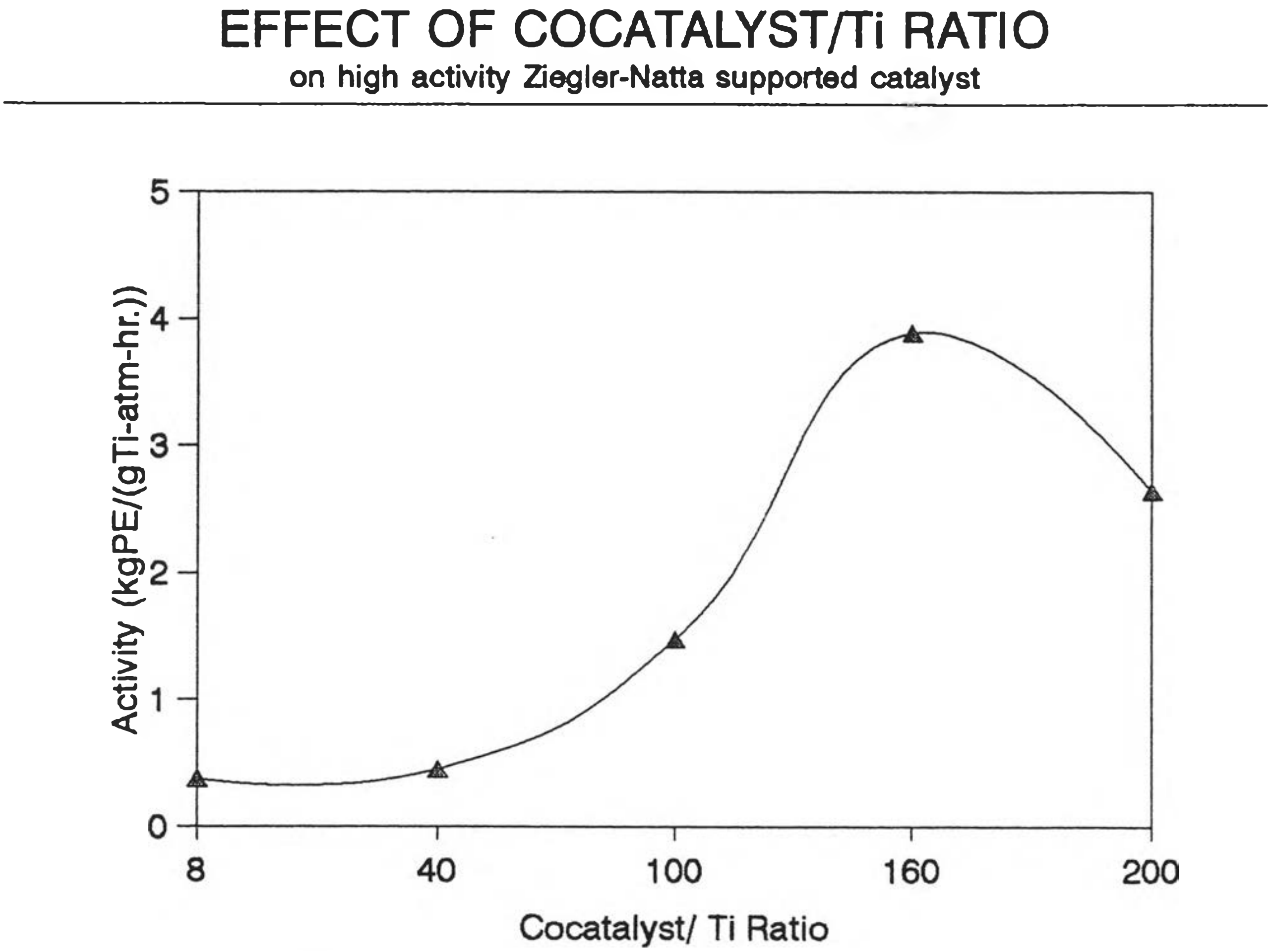


Figure 5.4 Catalytic activity at various TEA/Ti ratios with
Polymerization condition ; [Ti] = 1.068×10^{-4} mole / l,
Temperature = 85 ^{0}C,
Partial pressure of ethylene = 1 atm,
Partial pressure of hydrogen = 1 atm,
Polymerization time = 1.5 hr.
TEA / Ti mole ratios of 8, 40, 100, 160, 200, respectively.

A polymerization time of 1.5 hour was significant to investigate the whole polymerization curve. It was found that the ethylene consumption curve showed the characteristic curve as an abrupt ate and a decay type of polymerization curve. This was the character Ziegler-Natta supported catalyst for polymerization of ethylene from T

On the basis of the expe EA / Ti molar ratio of 160 and polymerization time of 1.5 hour wer urther investigation of the research work.

5.3 THE EFFECT OF HYDROGEN PARTIAL PRESSURE

In the sequence of experiments, the effect of the hydrogen partial pressure on the catalytic activity for ethylene polymerization was investigated. The ethylene polymerization occurred on the surface of the high-activity Ziegler-Natta supported catalyst. Because the polymerization was the heterogeneous catalytic reaction that occurred in the liquid phase of n-hexane. But the ethylene and hydrogen were in the gas phase, therefore, these two gases must diffuse into the n-hexane phase in order to react on the catalyst surface at the Ti supported active centers. The initiation then took place at the active centers after the coordination formation is completed. Then after initiation, the propagation progressed successively as long as the life-time of Ti active centers ability to polymerize ethylene .

The characteristic curves of ethylene consumption versus time in Figure 5.5 depicted the effect of hydrogen partial pressure. It was found that at high partial pressure of hydrogen gas caused the reaction to terminate faster than that at low partial pressure of hydrogen gas. Because of high partial pressure of hydrogen gas, it greatly over-reduced the titanium supported atoms to become the less active centers[77]. Whereas the surplus adsorbing hydrogen atoms remained on the surface, its function was the effective chain transfer agent to terminate polymer chains to obtain the lower molecular weight of polyethylene[78] and lower catalytic activity. At low partial pressure of hydrogen, it could properly activate the titanium supported atoms to polymerize the ethylene. The abrupt reaction reached the highest consumption of ethylene at the initial stage and then it decreased slowly.

Figure 5.6 showed the catalytic activity against hydrogen partial pressure of 1.0 atm in combination with various ethylene partial pressures. Therefore, the suitable condition, at hydrogen partial pressure of 1.0 atm and at ethylene partial pressure of 2.0 atm, was the most catalytic activity to polymerize ethylene on the high activity Ziegler-Natta supported catalyst.

Soon after the hydrogen molecules had diffused into n-hexane and adsorbed on the supported catalyst surface; it dissociated into 2 atoms on the surface of the catalyst as in Eq.5.1.

$$H_2 \xrightarrow{\text{DISSOCIATION}} 2H \qquad \text{Eq.5.1}$$

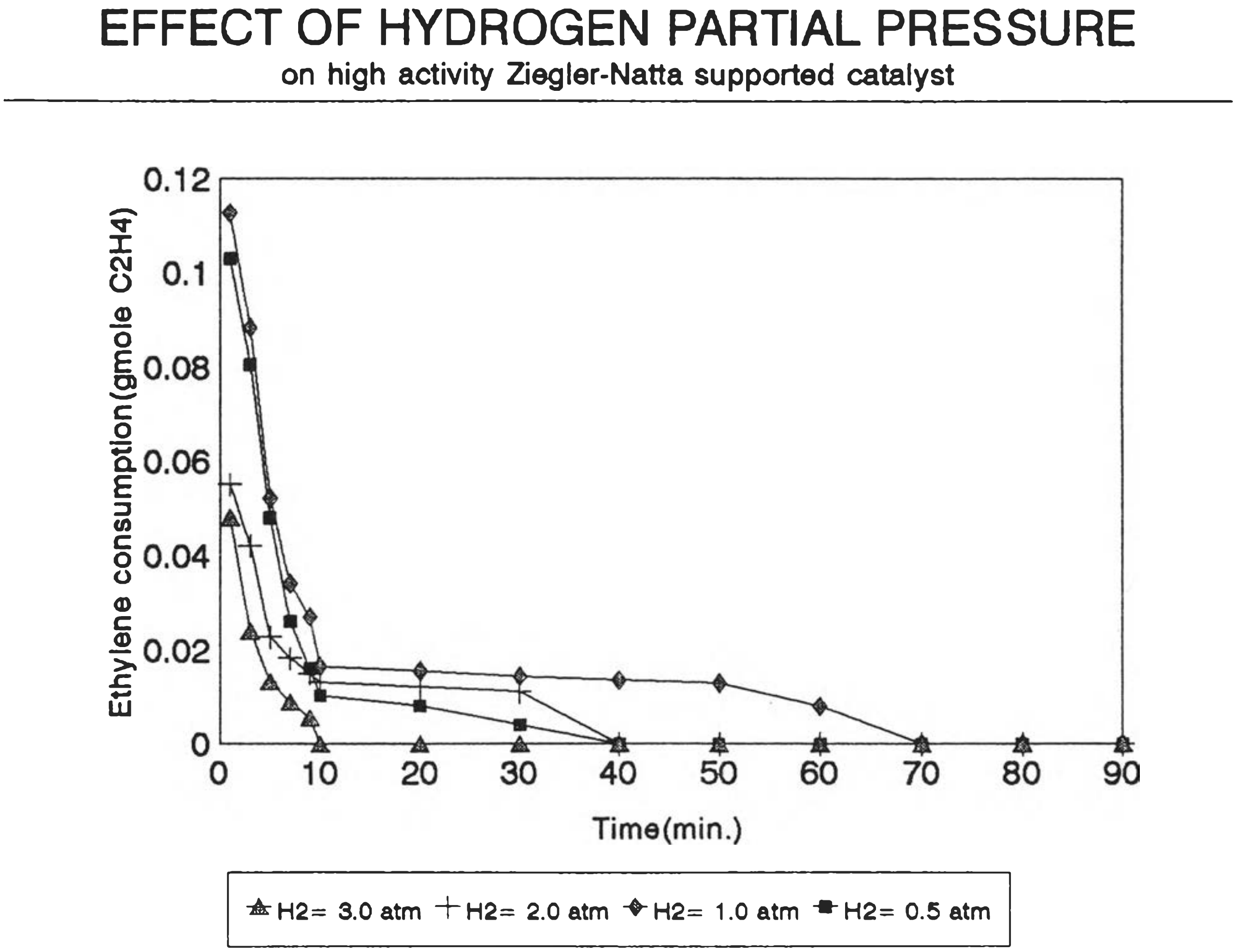


Figure 5.5 Ethylene consumption Versus polymerization time curves at various hydrogen partial pressures.

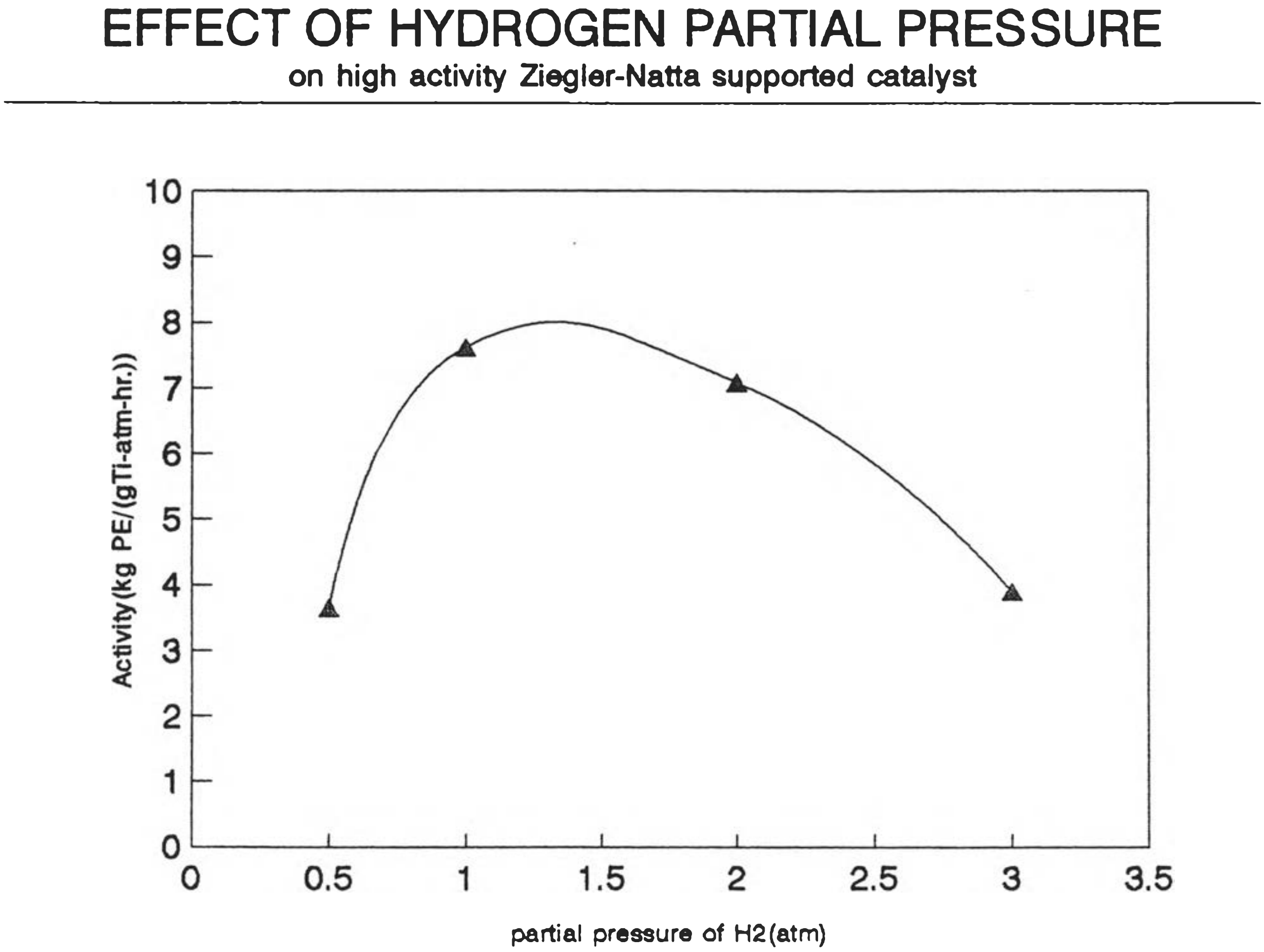
Polymerization condition [Ti] $=1.068 \times 10^{-4}$ mole / l,

Temperature = 85 ^{0}C,

Partial pressure of ethylene = 1.0 atm,

Polymerization time = 1.5 hr,

and partial pressure of hydrogen 0.5, 1.0., 2.0, 3.0 atm.



EFFECT OF HYDROGEN PARTIAL PRESSURE

on high activity Ziegler-Natta supported catalyst

Figure 5.6 Catalytic activity versus Partial pressure of Hydrogen at various hydrogen partial pressures.

Polymerization condition [Ti] =1.068x10^{-4} mole / l,

Temperature = 85 ^{0}C,

Partial pressure of ethylene = 1.0 atm,

Polymerization time = 1.5 hr,

and partial pressure of hydrogen 0.5, 1.0., 2.0, 3.0 atm.

The proper amount of adsorbed hydrogen atoms would then reduced the titanium supported atom to the active centers as in Eq. 5.2 [79]. But at high hydrogen partial pressures, it may propably further reduced the titanium supported atoms to the lower oxidation state. This lower oxidation state of titanium atom did not possess a high activity as that of the Ti(III) in the previous reaction. The over- reduction mechanisms of excess hydrogen could be established as the following Eq. 5.3.

$$H + TiCl_4 \xrightarrow{\text{REDUCTION}} TiCl_3 + HCl \qquad \text{Eq.5.2}$$

$$H + TiCl_3 \xrightarrow{\text{REDUCTION}} TiCl_2 + HCl \qquad \text{Eq.5.3}$$

Hydrogen is also known, among the research involving in the Ziegler-Natta supported catalytic polymerization, as the effective chain transfer in ethylene polymerization. The possible Eq.5.4 of the termination reaction by hydrogen is [80]

$$\text{M-(chain)} + H_2 \xrightarrow{\text{TERMINATION}} \text{M-H} + \text{(chain)-H} \qquad \text{Eq. 5.4}$$

It can occurred in case of the higher partial pressure of ethylene. The shorter saturated alkane would produce instead. The premature polyethylene was no sooner terminated through the same reaction after the primary insertion of ethylene as follows[81]:

$$\text{M-}CH_2CH_3 + CH_2{=}CH_2 \xrightarrow{\text{INSERTION}} \text{M-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 \qquad \text{Eq.5.5}$$

$$\text{M-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 + H_2 \xrightarrow{\text{TERMINATION}} \text{M-H} + CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \qquad \text{Eq. 5.6}$$

The scheme for the chain transfer reaction of the propagation species to the ethylene monomer was in Eq.5.7. Then it could propagate to the next propagation sites as in Eq.5.8.

$$\text{M-(chain)} + CH_2{=}CH_2 \xrightarrow{\text{CHAIN TRANSFER}} \text{M-}CH_2\text{-}CH_3 + \text{(chain)-H} \qquad \text{Eq.5.7}$$

$$\text{M-}CH_2CH_3 + CH_2{=}CH_2 \rightarrow \text{M-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 \xrightarrow{\text{PROPAGATION}} \qquad \text{Eq.5.8}$$

Hydrogen could also deactivate the active centers through the mechanism of hydrogen assisted deactivation as in [82].

5.4 THE EFFECT OF PERCENTAGE MOLE RATIO OF Fe/Ti MODIFICATION ON THE CATALYTIC ACTIVITY

The polymerization was carried out from the best selection of standard condition in the previous work at temperature of 85 ^0C. The concentration of titanium as the calculated Ti atom supported on the catalyst surface was 0.1068 mmole/l. The concentration of TEA was 17.09 mole / l. The partial pressures of C_2H_4 and H_2 were both at 1.0 atm. The above-mentioned paramaters was used to study the effect of iron(III) compound, Fe_2O_3, on the catalytic activity of Ziegler-Natta polymerization of ethylene.

As shown in Figure 5.7, the addition of iron compound (Fe_2O_3) to high activity Ziegler-Natta catalyst did affect the catalytic behavior. It seemed to be that a proper amount of (Fe_2O_3) increased the initial rate of polymerization and at this specific ratio of % Fe/Ti as a modification of Ziegler-Natta supported catalyst lowered the catalytic activity as shown in Figure 5.8.

The abruptly higher amount of ethylene consumption was found as the striking behavior from the previous characteristic of ethylene comsumption curve. The consumption was sharply decreased as the reaction proceeded. The modified Ziegler-Natta catalyst took a longer time to consume the ethylene gas than the pure Ziegler-Natta catalyst. The Fe_2O_3 modification of high-activity Ziegler-Natta supported catalyst had a lower activity than the conventional pure Ziegler-Natta catalyst. It was found that the ratio of %Fe/ Ti modification at 2-4 % could decrease the catalytic activity considerably as low as 10 %.

All phenomena occurring during the catalytic polymerization on Fe_2O_3 could be explained successively. An increase in the initial rate may infer to the larger amount active centers. Due to the formation of propagation site mechanisms, there still have definitive arguements. Among those machanisms, there are two reasonable proposals. First, it was called monometallic mechanism that was proposed by Cossee and Arlman[83-85]. There were numerous data telling about the influence of the cocatalyst on the activity and stereospecificity and on the molecular weight of polymer. Second, it was called bimetallic mechanism, Natta's model, it became more attractive to give the reasons to unravel the remaining problems. The bridge structure of Ti-R-Al was assigned as the active centers. These were supported by Fuji[86], Zahkarov et. al.[87], Balazs and co-worker[88].

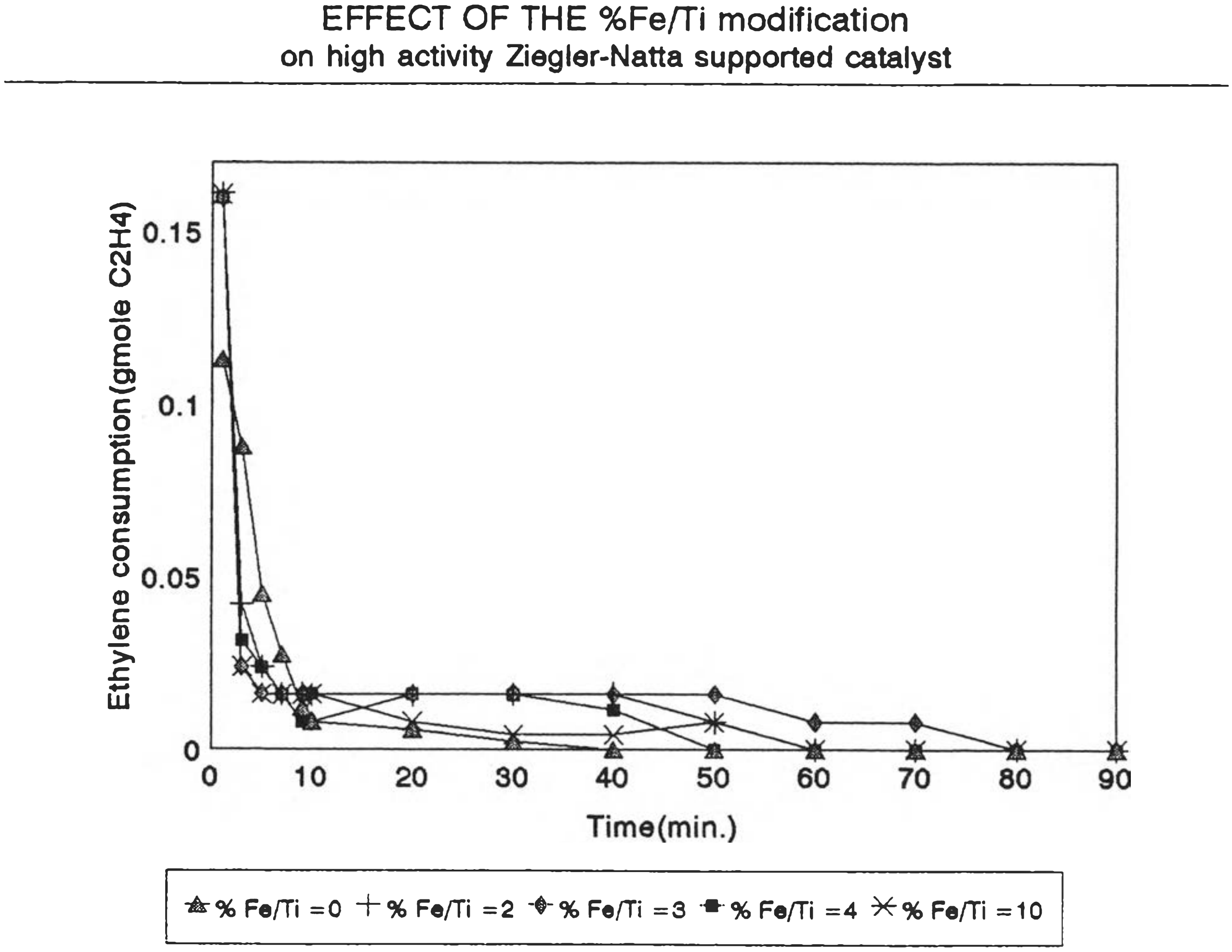


Figure 5.7 Ethylene consumption versus polymerization time curves at various mole ratios of %Fe/Ti modification

Polymerization condition: [Ti] = 1.068×10^{-4} mole / l,

Temperature = 85 ^{0}C,

Partial pressure of ethylene = 1.0 atm.,

Polymerization time = 1.5 hr.,

and %Fe/Ti 0, 2, 3, 4 10.

EFFECT OF THE %Fe/ Ti MODIFICATION

on high activity Ziegler-Natta supported catalyst

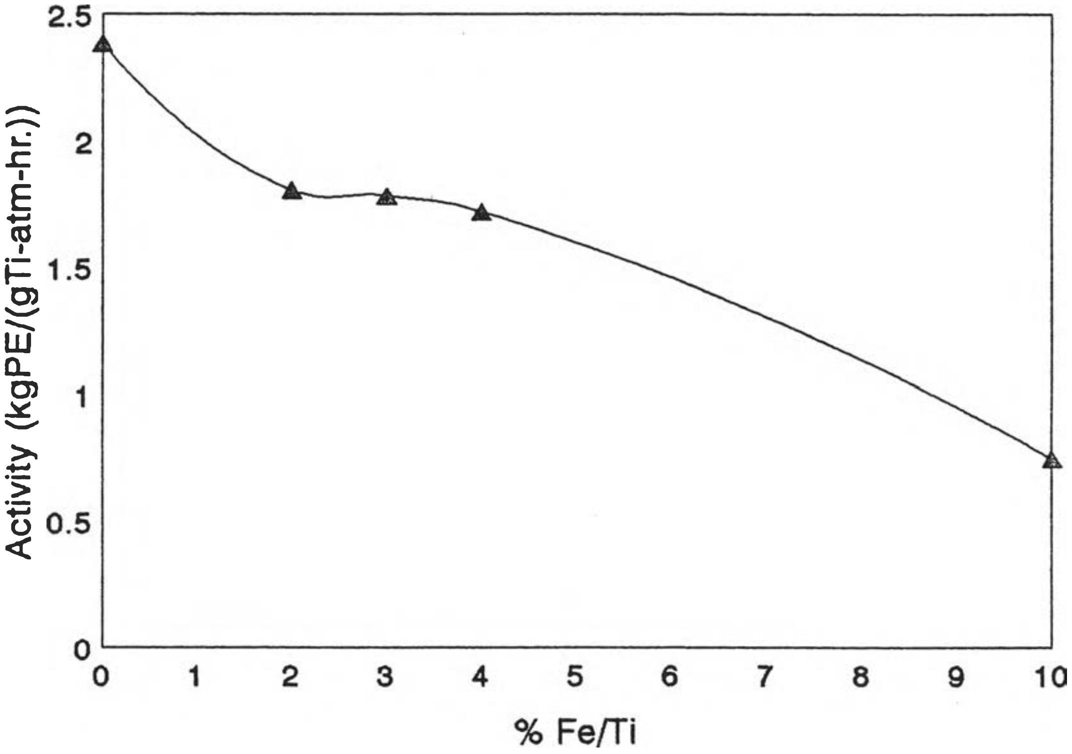


Figure 5.8 Catalytic Activity versus mole ratio of %Fe/Ti modification .

Polymerization condition: [Ti] = 1.068×10^{-4} mole / l,

Temperature = 85 ^{0}C,

Partial pressure of ethylene = 1.0 atm.,

Polymerization time = 1.5 hr.,

and %Fe/Ti 0, 2, 3, 4 10.

In this experiment, the amount of TEA used in high activity Ziegler-Natta supported catalyst was greatly increased more than that of the Ziegler-Natta unsupported catalyst. Triethylaluminium is the effective cocatalyst. The excess amount of TEA still adsorbed on the catalyst surface can easily react with the reduced Ti to a lower oxidation state[89,90]. But Chien [91] had found that Fe_2O_3 was an oxidizing agent. Therefore, the over-reduced Ti species could be re-oxidized to the suitable oxidation state by a redox process. The ferric ion could oxidize Ti as follows:

$$Ti^{2+} + 2Fe^{3+} \rightarrow Ti^{4+} + 2Fe^{2+} \qquad \text{Eq. 5.9}$$

$$Ti^{3+} + Fe^{3+} \rightarrow Ti^{4+} + Fe^{2+} \qquad \text{Eq. 5.10}$$

The behaviour of this high activity Ziegler-Natta supported catalyst system was used to polymerize ethylene resulting from the catalyst preparation method, the polymerization conditions and chemical interactions during each preparation step.

STEP 1 Adduct between $MgCl_2$ and Ethanol.

The predetermined amount of anhydrous $MgCl_2$ was solvated in ethanol. At an instant, the adduct between $MgCl_2$ and ethanol was formed.

$$MgCl_2 + 6\,EtOH \rightarrow MgCl_2.6EtOH \qquad \text{Eq.5.11}$$

The structure of the alcohol adduct was octahedral with ethanol molecules coordinating at each octahedral position[92]. Ethanol has an oxygen in the hydroxy group, as shown in Figure 5.9, so it aligned in the direction of O-Mg bond. In this step, the ethanol was added dropwise and stirred vigorously. The crystalline of magnesium chloride was also distorted and slided. Thus, a lot of defects, edges and distortions were formed. These imperfections would facilitate the immobilization of active centers[93,94].

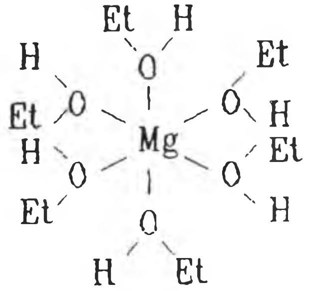
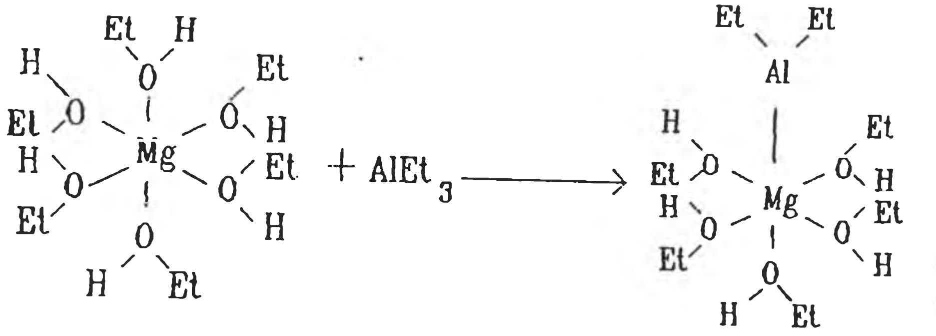


Figure 5.9 Alcohol adduct

STEP 2 Preparation of the reaction product

The alcohol adduct from step1 would react with TEA. Triethylaluminium molecules substituted the ethanol. They also killed the impurities and catalyst poisoning compounds. The reaction product was formed in this step.



Eq.5.12

Ethanol and triethylaluminum could react simultaneously. The exchange reaction was between ethoxy group on ethanol and ethyl group of TEA. The extent of exchange of ligand depened on the quantity of the ethanol existing in the system.

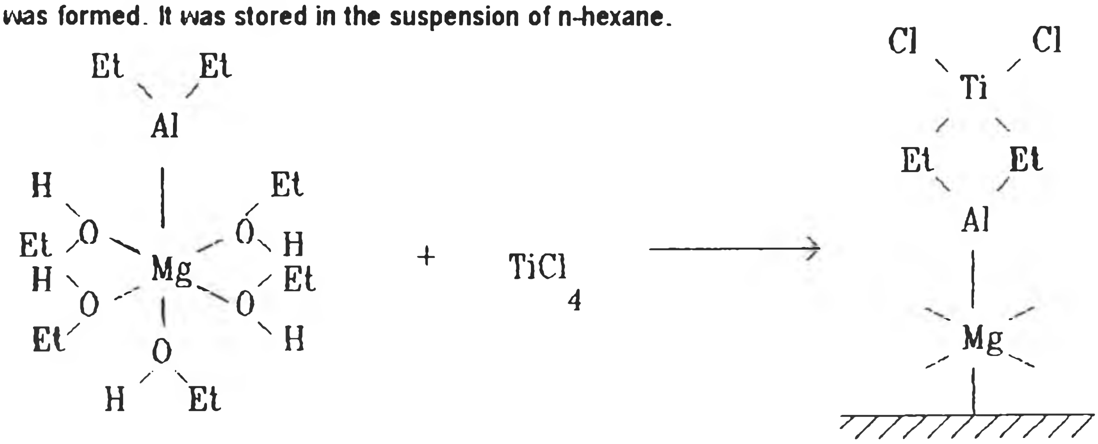
$C_2H_5OH + Al(C_2H_5)_3 \rightarrow Al(C_2H_5)_2(OC_2H_5) + C_2H_6$ Eq.5.13

$Al(C_2H_5)_2(OC_2H_5)+C_2H_5OH \rightarrow Al(C_2H_5)(OC_2H_5)_2 + C_2H_6$ Eq.5.14

$Al(C_2H_5)(OC_2H_5)_2 + C_2H_5OH \rightarrow Al(OC_2H_5)_3$ Eq.5.15

STEP 3 Impregnation of $TiCl_4$ on the reaction product surface

The reaction product would react with $TiCl_4$. The $TiCl_4$ was added dropwise and stirred vigorously for the effective impregnation of Ti atom on the surface. The Ti species would be impregnated on the surface of support by means of bimetallic bridge formation between the Ti–Mg. In this step, the transition metal catalyst component was formed. It was stored in the suspension of n-hexane.



STEP 4 The reaction between catalyst components

Before the polymerization was about to proceed; the transition metal catalyst component reacted with TEA. In this step, the polymerization took place in n-hexane after the active centers were formed. From step 1 to step 3, the product was not separated from hexane. Consequently, the product contained ethanol and the derivatives of the reaction between ethanol and TEA; ethanol and alkyl aluminium derivatives; ethanol and $TiCl_4$. The unexpected reactions were significant to disturb the function of catalyst system because of their coexistence and influences in the same system .

$EtOH + TiCl_4 \rightarrow TiCl_n(OEt)_{4-n}$ Eq.5.16

$EtOH + TiCl_3 \rightarrow TiCl_2(OEt)$ (as a surface Ti species) Eq. 5.17

$EtOH + AlEt_2Cl \rightarrow AlEt(OEt)Cl$ Eq. 5.18

TEA could solvate by ethanol having the following structures[95].

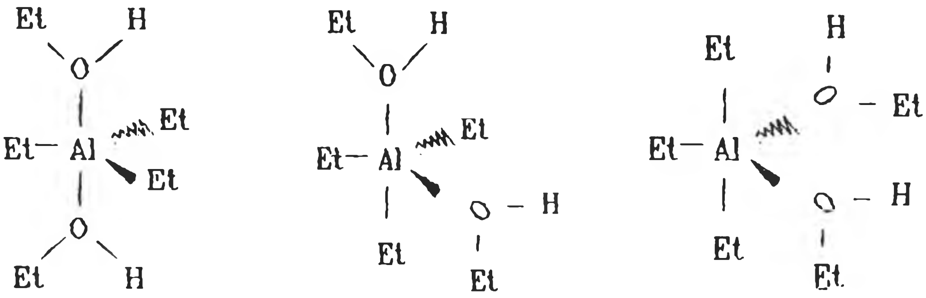


Figure 5.10 The structures of the products between ethanol and TEA.

The mechanism of active center formatiom could be expressed as followed.

$TiCl_4 + AlEt_3 \rightarrow EtTiCl_3 + Et_2AlCl$ Eq.5.19

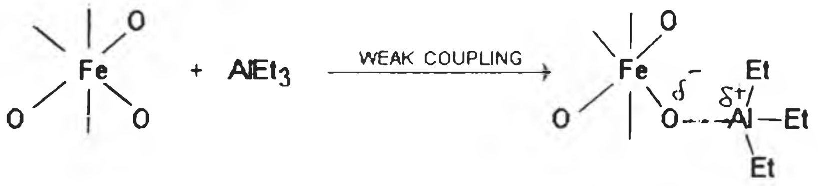
$EtTiCl3 \rightarrow TiCl_2 + Et$ Eq.5.20

However, scientists generally agree that the most active cocatalyst is triethylaluminum[96]. It provided more extensive alkylation and reduction of the intermediate; as a result of such reactions, β-$TiCl_3$ may occur. These further reductions process lead to the lower valence states of titanium [97].

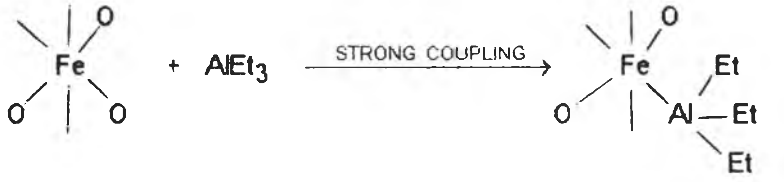
The proposal of Fe_2O_3 effect on the catalyst structure and behavior

The higher ethylene comsumption rate at the initial time could be speculated as the avaliablity of larger number of active centers. In other words, the freshness of the catalyst would initiate the polymerization sharply and then active centers were transformed to the less reactive centers. Therefore, it would oxidize Ti^{3+} and Ti^{2+} to Ti^{4}. After the oxidation of Ti species, Fe(III) reduced to Fe(II). Fe(II) might complex with $AlEt_3$ or/and aluminium alkyl derivatives. These complicated mechanisms produced two possible effects.

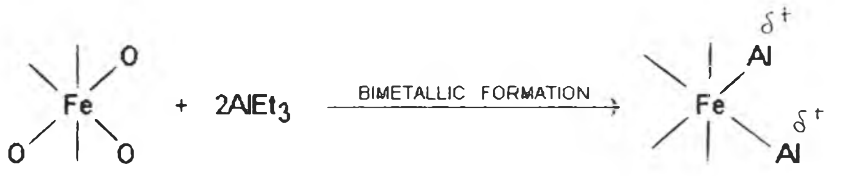
Effect 1. The complicated reaction between Fe_2O_3 and TEA or/and alkyl aluminum derivatives could reduce the amount and reactivity of alkyl aluminum compound to function as cocatalyst in the regular catalyst system. Such a effect lowered the catalytic activity. The reaction mechanism between the Fe-Al was[98-99]:



Eq. 5.21



Eq. 5.22



Eq. 5.23

Eq.5.21 was a weak coupling of Fe-Al. The ferric atom would react with TEA but the charge on Al was partially positive. Now alkyl aluminum compound had less reactivity to form active centers than the system without the Fe compound modification. From the proposal reactions in Eq.5.21-5.23, it would assume that TEA was decreased in both the reactivity and amount. The reactions of Eq.5.21-5.23 were the probable reasons for lowering catalytic activity in ethylene polymerizaion on high activity Ziegler-Natta supported catalyst.

Effect 2. Fe_2O_3 could form complexes with Al atom in the aluminium alkyl derivatives. The reaction between $TiCl_4$ and EtOH contained alkyl titanium alkoxides and various aluminum complexes as in Figure 5.11(a)-(d). They had some implication of reactions which resulted in the activity of polymerization behavior.

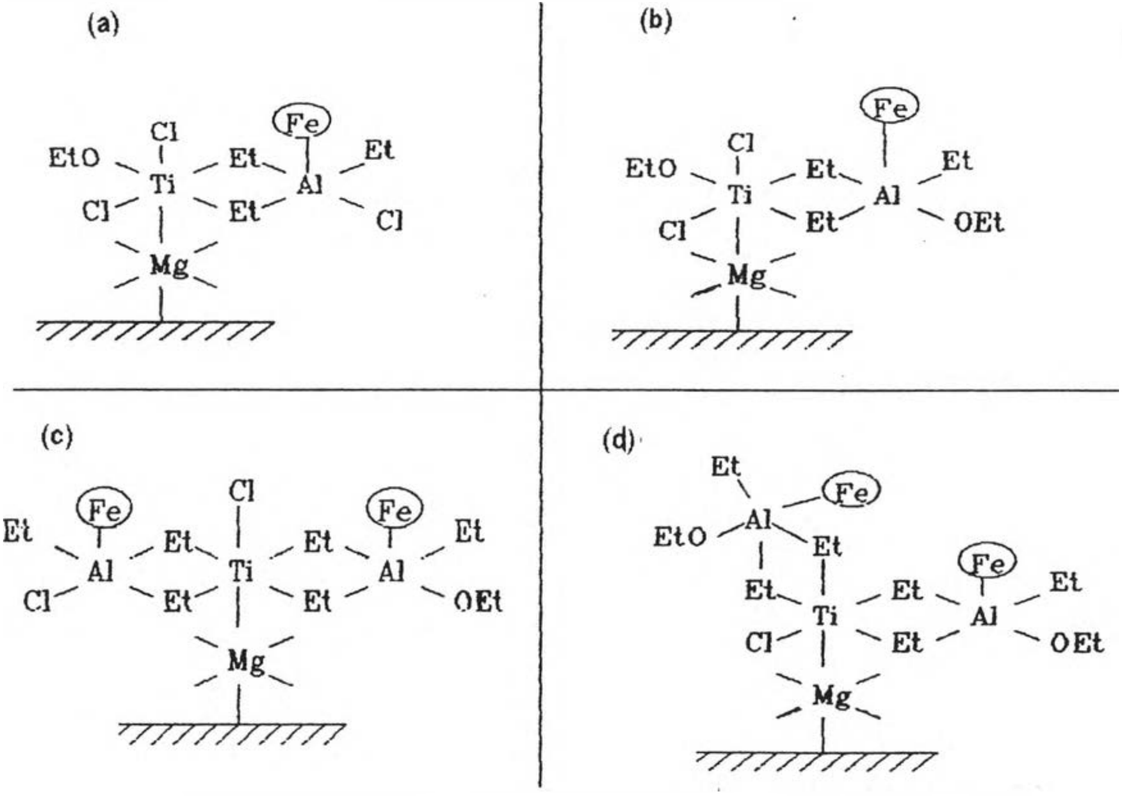


Figure 5.11 The proposal of structures of Fe in the catalyst complexes

All of the above-mentioned reactions and structures were found as that a wide variety of active center structures was formed. Tait[100] found the complexation reactions between active centers and alkylaluminum species; between active centers and donor molecules; between akylaluminum species and donor molecules. The reaction would control the relative numbers of potentially active centers.

In Figure 5.12, it showed the influence of the Fe on the catalytic behavior and clarified the longer time of ethylene comsumption. After the Fe incorporation in the active center structure, it had less mobility in the ethylene insertion process. Although the amount of ethylene consumption was higher than that of the Fe modified system but the polymer produced was lesser. This meant that Fe_2O_3 lowered the polymerization activity of the active centers by changing the electronic properties of alkylaluminium compound and the catalyst complexes. Fe_2O_3 could undergo some other side reactions such as dimerization, oligomerization. These could definitely decreased the amount of polyethylene.

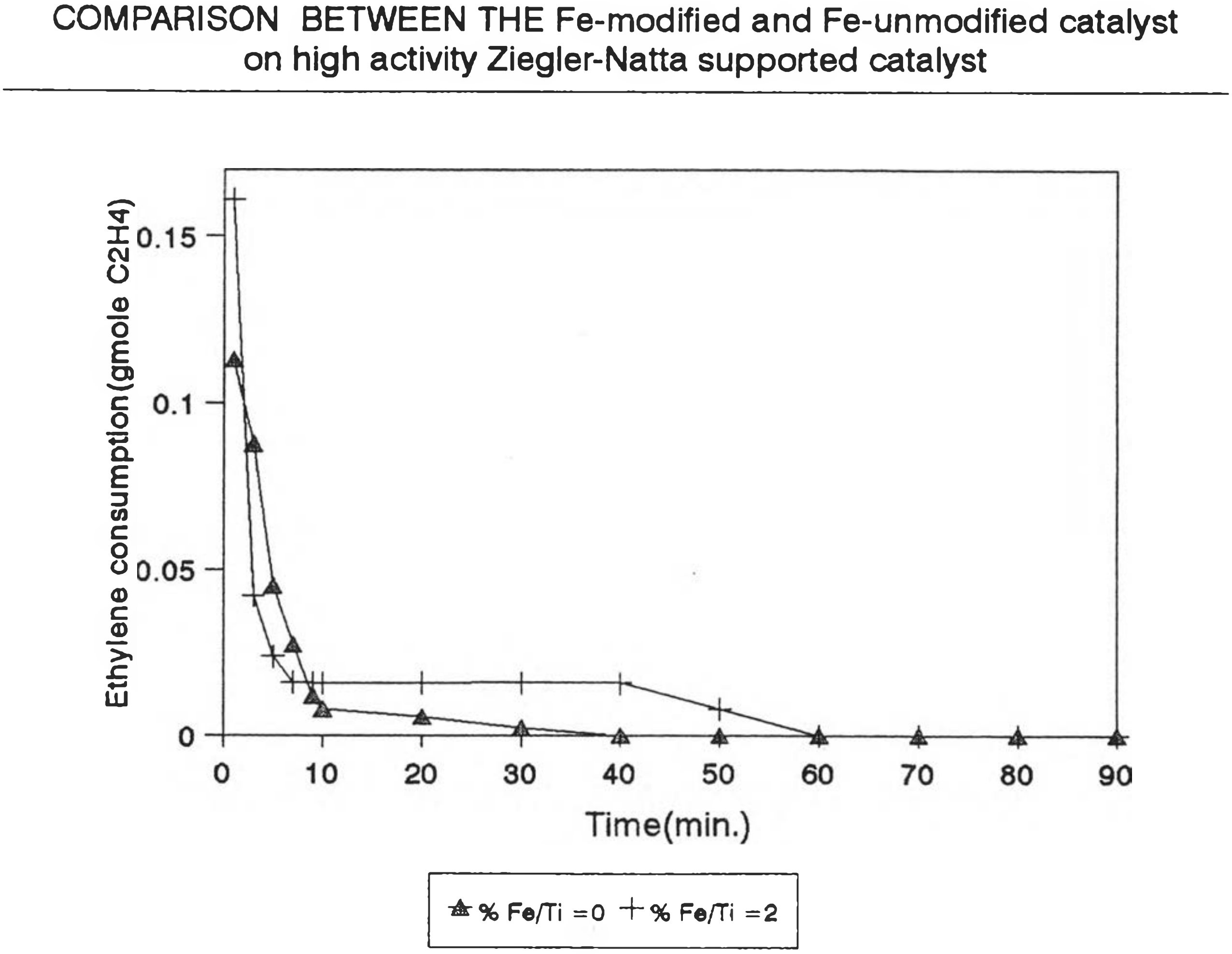


Figure 5.12 The influence of Fe_2O_3 on the catalyst behavior to consume ethylene

Polymerization condition: [Ti] = 1.068×10^{-4} mole / l,

Temperature = 85 ^{0}C,

Partial pressure of hydrogen = 1.0 atm.,

Polymerization time = 1.5 hr.,

5.5 CHARACTERIZATION OF POLYETHYLENE

5.5.1 Morphology of polyethylene

The polyethylene particles were subjected to Scanning Electron Microscope. It was found that all particles comprising of small particles bounded together as shown in Figure 5.13. The polyethylene from the high activity Ziegler-Natta supported catalyst had a larger particle size than those particles from Fe_2O_3 modification. The polyethylene particles of the Fe_2O_3 modification system were denser than that without Fe_2O_3 modification one.

The morphology of the catalyst and the subsequent polymer particles were closely related to the parent morphology of the support, $MgCl_2$ [101]. The macroscopical catalyst particles consisted of loosely bound agglomeration of small subparticles. The monomers diffused through the pores into the aggregate of subparticles. The polymerization took place at the active centers located on the surface, crystallizing the produced polymer. It became insoluble in the reaction medium, producing the encapsulation of catalyst particles.

Consequently, the pores were filled with polymer, leading to the fissuring, rupture, and expansion of the polymer particles. The diameters of the polymer particles grew to a factor or several times to size of the size of the catalyst particles[102].

The morphology of polyethylenes particle from Fe_2O_3 modified Ziegler-Natta catalytic polymerization were denser and smaller than that from the unmodified catalyst system. It was from the result of Fe_2O_3 interaction with TEA, ethanol, and Ti atoms supported on the catalyst surface. The function of Fe_2O_3 was the oxidant of the reduced titanium centers in the initiation step. Therefore, the rate was high at first and then decreased sharply. The Fe atom held titanium and TEA to form clusters. The outer layers of the particle underwent expansion less than the high activity Ziegler-Natta supported catalyst and this gave smaller polyethylene particles. The capability of controlling the polyethylene morphology was less effective in the Fe_2O_3 modified catalyst than the unmodified one.

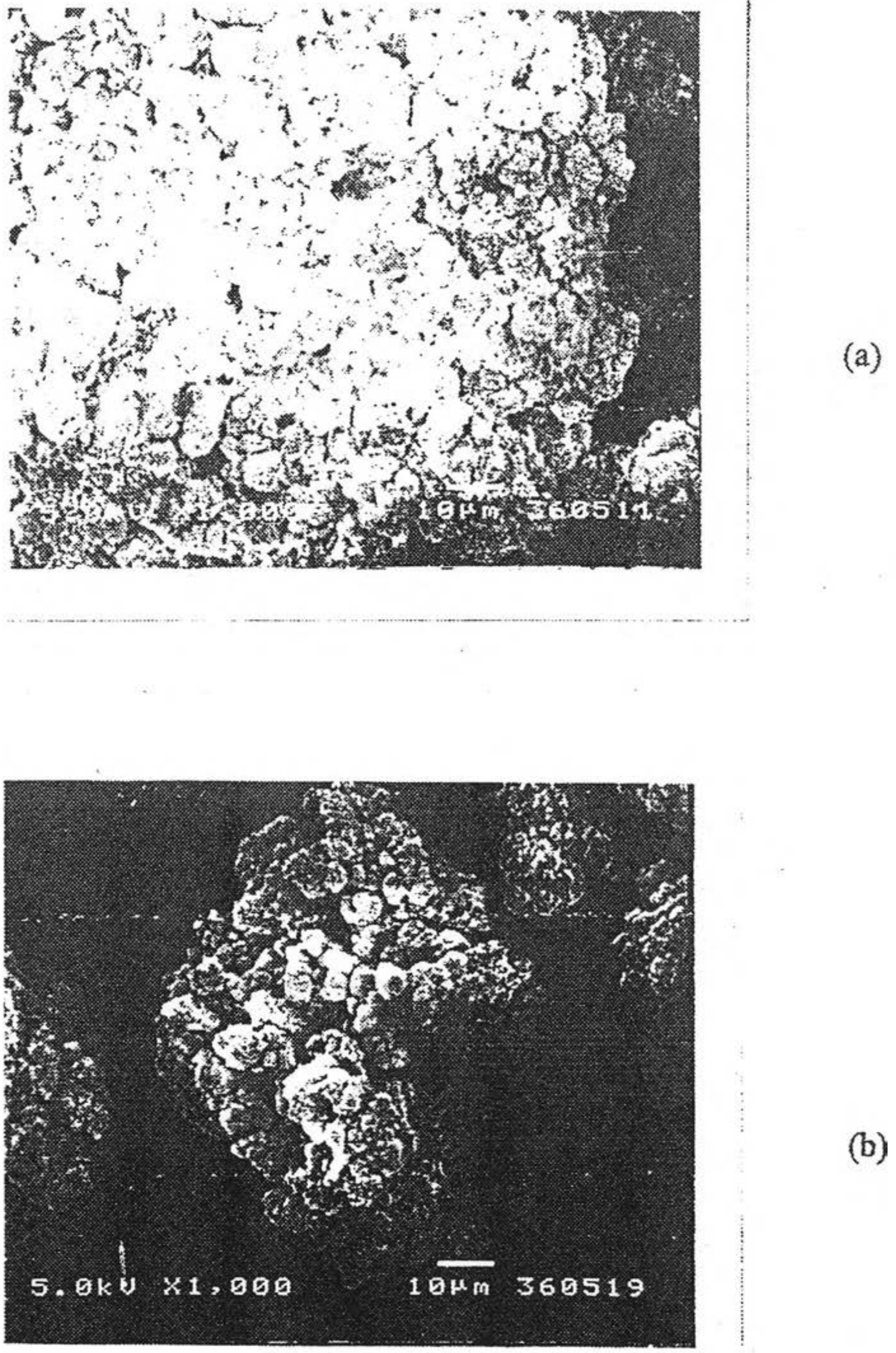


Figure 5.13 Scanning electron microscopes of polyethylenes

(a) PE produced from high activity Zigler-Natta supported catalyst,

(b) PE produced from Fe_2O_3 modified Ziegler-Natta supported catalyst.

But the catalyst without Fe_2O_3 modification produced the polyethylene particles with a spherical and bigger shape than Fe_2O_3 modified catalyst system did. This morphology are resulted from the high activity of titanium active centers. During polymerization, the particles of supported catlyst became fissure, rupture and expansion. Then, the inner part of active centers would expose to the polymerized ethylene. Therefore, the polyethylene particles were bigger and loosely bound.

Particles of polyethylene produced from Fe_2O_3 modified catalyst are of smaller size since the subparticles held more tightly. Because the polymer chains propagated at more active Ti centers then the chains grew rapidly. Due to the rapid deactivation process of the active centers, therefore, Fe_2O_3 initially interacted with Ti atoms in the catalyst complexes for a higher propagation rate. The ethylene consumption rate increased abruptly and decreased sharply, as well. The polymer chains did not propagate further and it formed a mass diffusion barrier for ethylene insertion. Fe_2O_3 could form clusters with titanium and it could deactivate the propagation to obtain polyethylene.

5.5.2 **Microstructure determination**

The infrared spectroscopic technique is the nondestructive method and it is sufficient to characterize the functional group of the sample especially for organic compound[103]. The infrared spectra of polyethylene produced from high activity Ziegler-Natta catalyst and from Fe_2O_3 modified Ziegler-Natta supported catalyst were shown in Figure 5.14 - 5.15, respectively. Assignments of the functional groups to wave number were given in Table 5.1 - 5.2, for the Ziegler-Natta system and the Fe_2O_3 modified system, respectively. The peak at 719 cm^{-1} contributed to the long series of $(-CH_2-)_n$ in the chains of polyetylene. The polyethylene from the Fe_2O_3 modified high activity Ziegler-Natta supported catalyst had higher % Transmittance than that from high activity Ziegler-Natta supported catalyst.

The wave number of 1368 cm^{-1} was the fingerprint of alkane and that of 1479 cm^{-1} was the bending mode of $-CH_2-/-CH_3-$. In addition of the wave number of 2849 and 2919 were the stretching mode of $-CH_2-/-CH_3-$. The IR spectra of both samples could assign to be polyethylene.

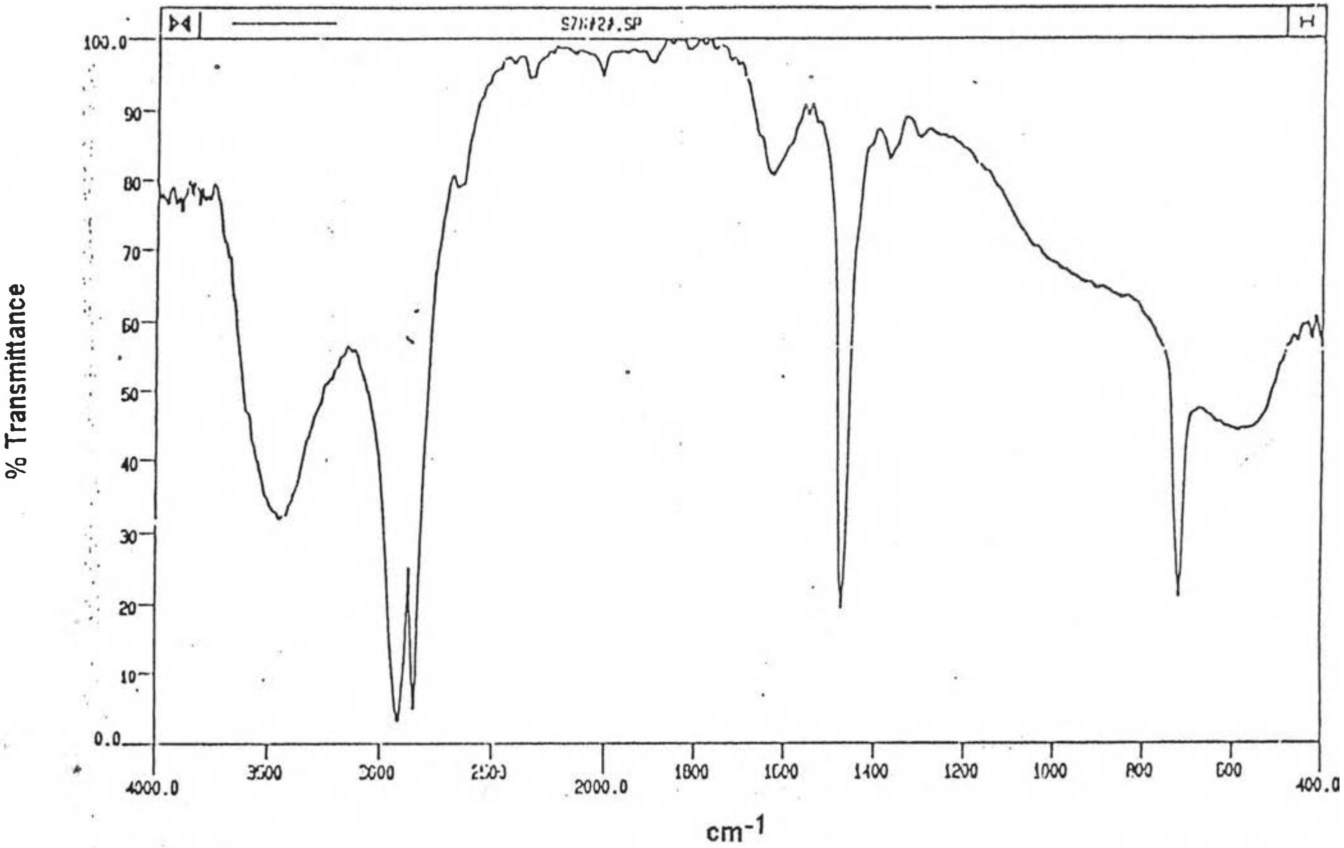


Figure 5.14 Infrared spectrum of polyethylene produced from High Activity Ziegler-Natta supported catalyst

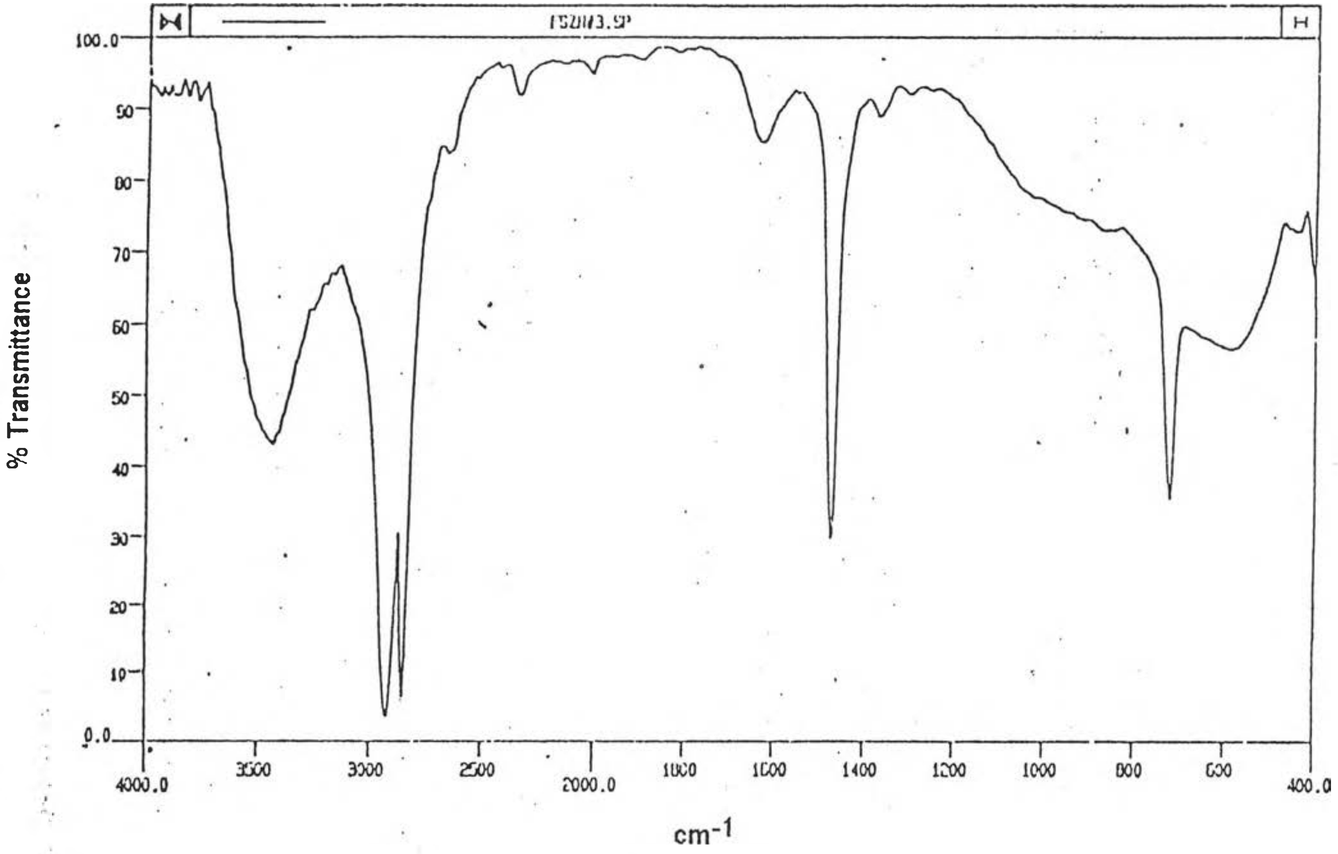


Figure 5.15 Infrared spectrum of polyethylene produced from Fe_2O_3 modified Ziegler-Natta supported catalyst.

Table 5.1 Identification of IR spectrum from PE
(High Activity Ziegler-Natta supported catalyst)

Wave no.(cm^{-1})	% T	Assignment
719	21	Long series of -(-CH_2-)$_n$
1303	86.17	Primary alcohol
1368	83.19	-CH_2-, -CH_3- finger print region
1479	19.51	-CH_2- bending
2849	4.76	-CH_2-, -CH_3- strectching
2919	3.10	
3450	31.98	-OH hydroxy group

Table 5.2 Identification of IR spectrum from PE
(Fe_2O_3 modified Ziegler-Natta supported catalyst)

Wave no.(cm^{-1})	% T	Assignment
719	35.61	Long series of -(-CH_2-)$_n$
1303	92.08	Primary alcohol
1368	83.19	-CH_2-, -CH_3- finger print region
1479	29.93	-CH_2- bending
2849	6.30	-CH_2-, -CH_3- strectching
2920	3.50	
3432	43.10	-OH hydroxy group

The other methods should carry out to compare the properties of polyethylene for the effect of Fe_2O_3 modification of the high activity Ziegler-Natta supported catalysts. The interesting methods are X-ray diffraction and Differential Thermal Analysis.

5.5.3 **Molecular weight determination by viscometry**

Polyethylenes obtained in both two catalyst systems were dissolved in decahydronapthalene(decalin). The temperature to dissolve was 140 ^0C. They would become clear solution within 4 hrs, but not longer than 6 hrs. The concentration range was from 0.10% to 0.50% w/v. The molecular weight determination by viscometry is convenient and more practical than the other methods.

Firstly, the flow time of decalin was measured. Second, the most dilute concentration was used to measure flow time. Afterwards, the next concentrated solution was used to measure flow time successively. The flow times of the solvent and the solution were used to calculate inherent viscosities, η_{inh}, and reduced viscositie, η_{red}. The limiting viscosity number, $[\eta]$, was obtained from Mark-Houwink-Sakarada equation.

$$[\eta] = K\,\overline{M}_v{}^{a}$$

From polyethylene; $K = 2.3\times10^{-4}$, and $a = 0.82$ were used[104].

After extrapolation, the limiting viscosity number $[\eta]$ of polyethylenes from both catalysts could obtain from Figure 5.16-5.17. The viscosity-average molecular weight of polyethylene from the high activity Ziegler-Natta supported catalyst was 53172 and that from the Fe_2O_3 modified Ziegler-Natta supported catalyst was 46669.

The higher $\overline{M}_v$ of polyethylene from that Fe_2O_3 unmodified catalyst clarified the effect of Fe_2O_3. The polymer chains became shorter, it meant that Fe_2O_3 had shortened the polymerization ability of titanium active centers. It could grow in the definite time before the catalyst deactivation. The molecular weight increased sharply at initial reaction, then decreased gradually which allowed oligomerization to occur.

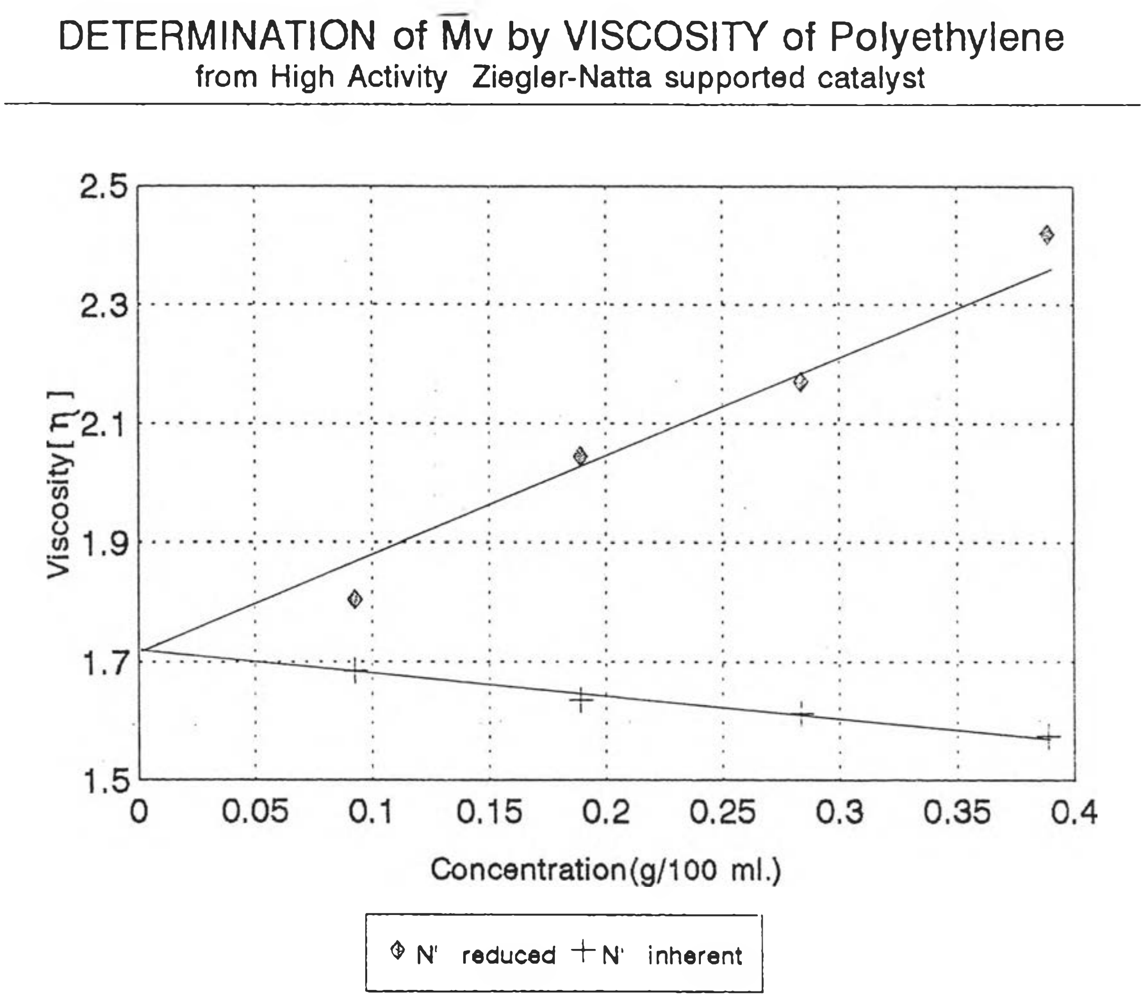


Figure 5.16 Inherent and reduced viscosities of polyethylene from High Activity Ziegler-Natta supported catalyst

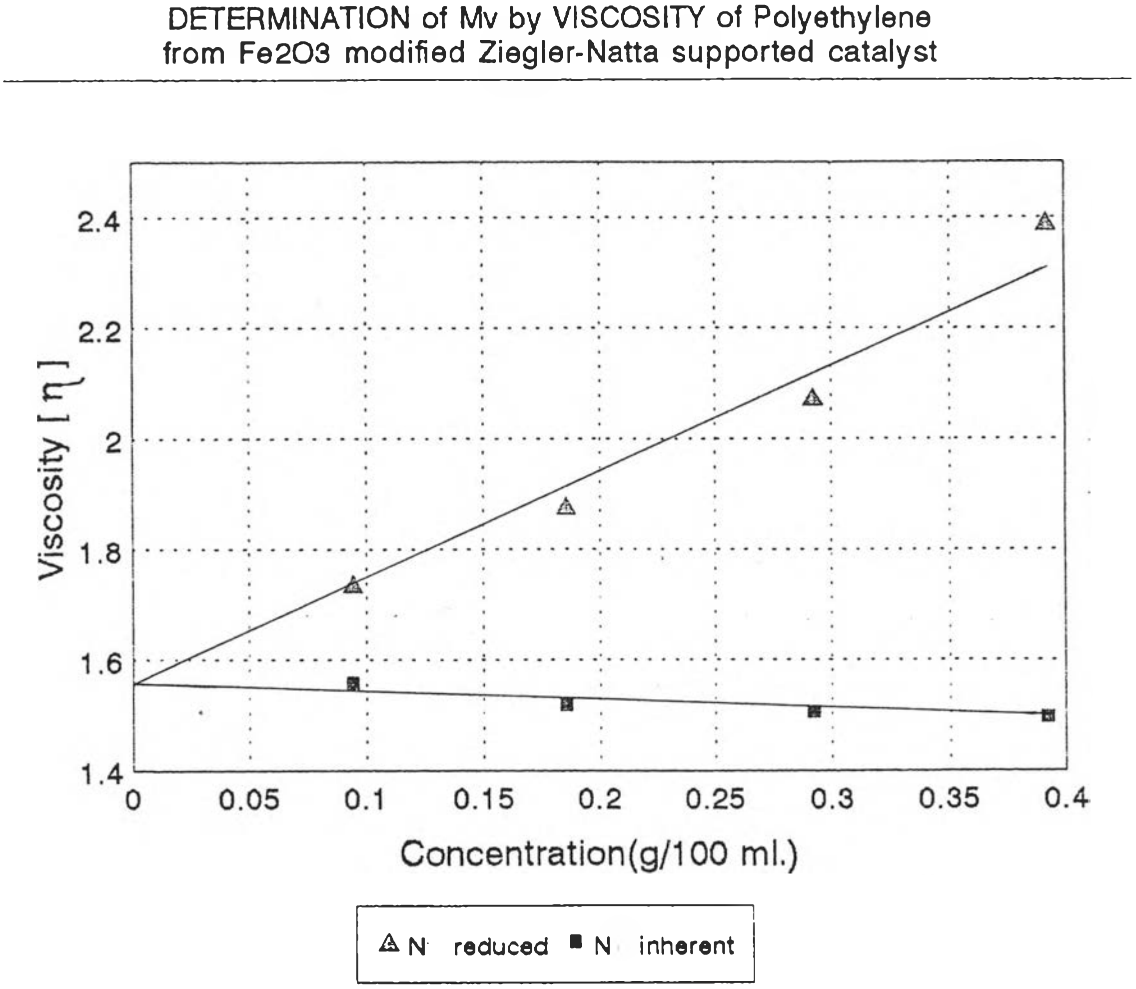


Figure 5.17 Inherent and reduced viscosites of polyethylene from Fe_2O_3 modified Ziegler-Natta supported catalyst.

Without Fe_2O_3, the propagation of ethylene could forward freely throughout its reaction time which was longer to terminate chains. These made the longer polyethylene chains than did the Fe_2O_3 modified catalyst.

5.5.4 **Flow Property**

The polyethylene produced from the high activity Zigler-Natta supported catalyst was molten in a Plastometer to determine melt flow index[105]. The temperature of the heater was set at 190 ^0C. The molten PE that flowed through the orifice was weighted as MI with 325 g loaded piston and as HLMI with 2160 g loaded piston. The MI and HLMI of polyethylene produced from the High Acitivity Ziegler-Natta supported catalyst were 0.47g and 2.45 g, respectively. The MI and HLMI of of polyethylene produced from Fe_2O_3 modified Ziegler-Natta supported catalyst were 1.67 g and 3.38 g, respectively.

The melt index of polyethylene from high activity Ziegler-Natta supported catalyst was smaller, it meant that the molecular weight of polyethylene was higher than that from Fe_2O_3 modified catalyst. It was the effect of Fe_2O_3 modification. In contrast, the melt index of polyethylene from the Fe_2O_3 modified catalyst was bigger, it meant that the molecular weight of polyethylene was smaller because of the less active to polymerize ethylene of titanium centers after Fe_2O_3 modification.

Table 5.3 **Melt index and Densities of PE**

Polymer	MI	HLMI	Density
PE from high activity supported catalyst	0.47	2.45	0.960
PE from Fe_2O_3 modified Ziegler-Natta supported catalyst	1.67	3.38	0.954

5.5.5 Density Determination

The gradient density column was set by the mixture of toluene and carbon tetrachloride[69]. Then the polyethylene chips were dropped and settled at the layer having the same density as the polymer density. The polyethylene produced from the high activity Ziegler-Natta supported catalyst had a density of 0.960 g/cm^{-3} while that from the Fe_2O_3 modified Ziegler-Natta supported catalyst had a density of 0.954 g/cm^{-3}. Both polyethylenes were high density polyethylene (HDPE)[105].

The density of polyethylene from the Fe_2O_3 unmodified catalyst was bigger than that from the Fe_2O_3 modified one. The polymer could propagate neatly and decreased the intermolecular volume. Because it had time to align the molecules during propagation. The polymers chains could pack tighter, then the density was higher than that from the Fe_2O_3 modification catalyst.

5.5.6 Crystallinity of polyethylene products.

The X-ray diffraction (XRD) pattern of polyethylene product from high activity Ziegler-Natta supported catalyst and from Fe-modified Ziegler-Natta supported catalyst both occurred at 21.5^0 and 23.8^0 as shown in Figure 5.18 - 5.19. Both peaks were in the same position but in different intensities. It indicated that both polyethylene products had the same crystal arrangment. The intensities of XRD peaks of polyethylene from high activity Ziegler-Natta supported catalyst had more intensities than that from Fe-modified catalyst. It meant that the crystallinity of polyethylene from high activity Ziegler-Natta supported catalyst had more crystallinity than that from Fe-modified catalyst. The higher crystallinity of polyethylene was obtained from unmodified Fe_2O_3 catalyst because ethylene propagated at titanium active centers step by step. The polymer chains can relax more to form crystallinity. But polyethylene from modified Fe_2O_3 catalyst has less crystallinity because of its higher activity to polymerize at the initial time of the reaction. In the latter case, titanium active centers could insert ethylene rapidly at the initial time of reaction so ethylene consumption increased suddenly; the rapid propagation did not provide chances for polyethylene to form crystallinity. The Fe_2O_3 modified catalyst also deactivated the polymerization ability of titanium centers quickly.

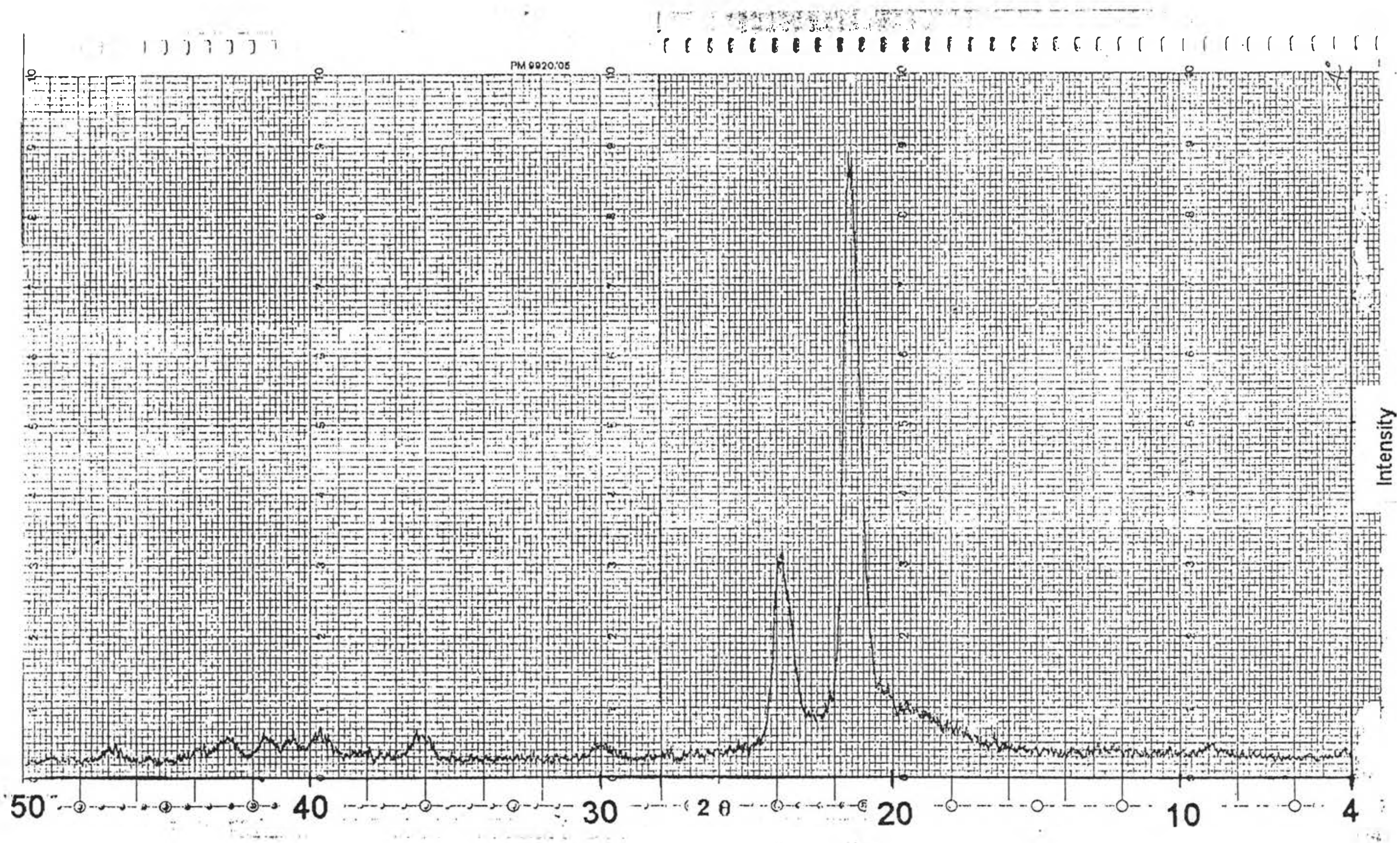


Figure 5.18 XRD of polyethylene produced from high activity Ziegler-Natta supported catalyst

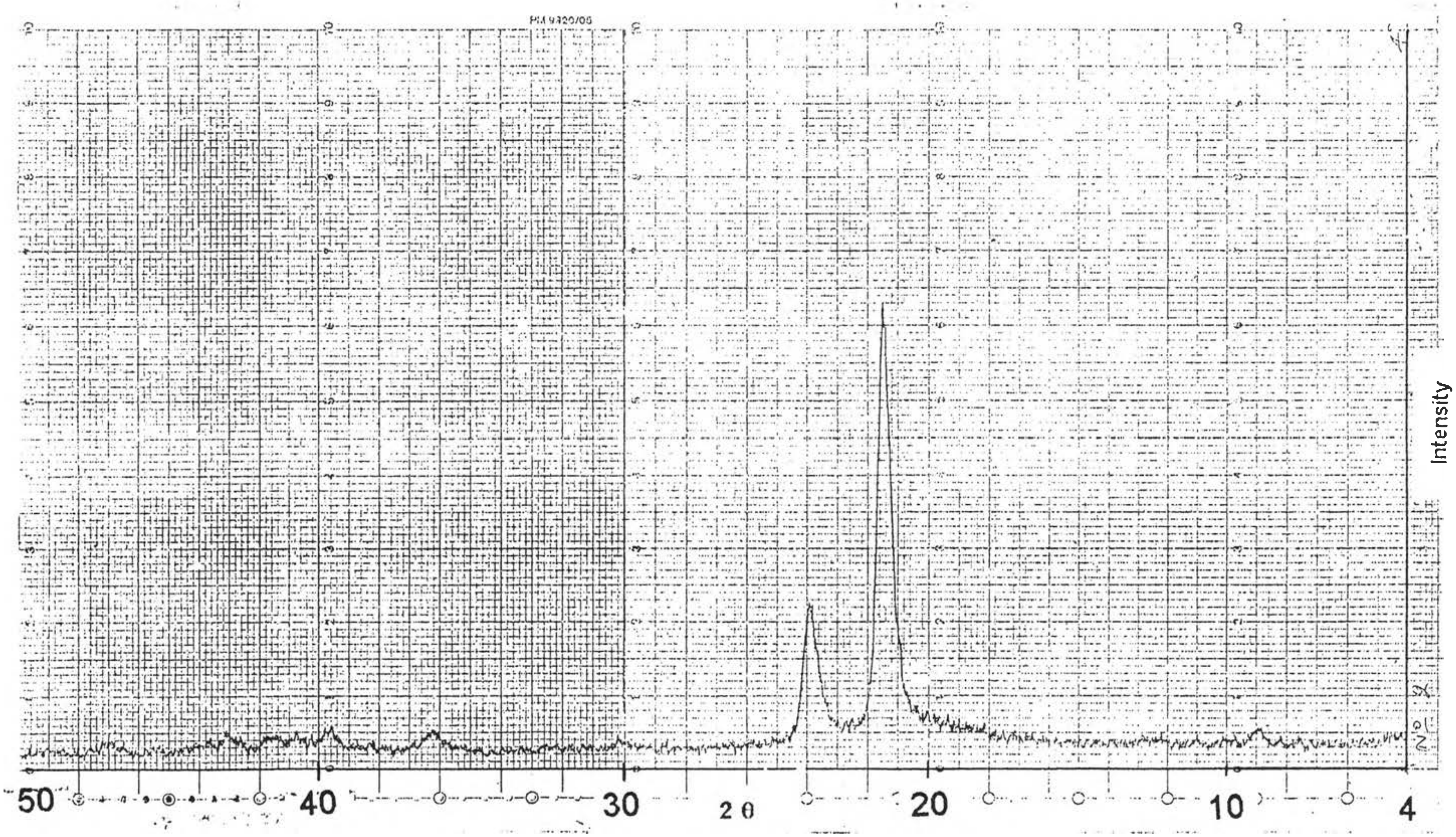


Figure 5.19 XRD of polyethylene produced from Fe_2O_3 modified Ziegler-Natta supported catalyst.

The Fe_2O_3 modified catalyst took shorter time to polymerize than did the unsupporterd system. But the decrease in activity brought about the oligomerization of ethylene instead at the final stage of reaction. So it produced oligomers subsequently during the catalyst deactivation. The ethylene balance in both catalysts in Table 5.4 showed the consistent effect. In Fe_2O_3 modified catalyst, the conversion of ethylene to polyethylene is 51.6 % while the Fe_2O_3 unmodified one 69.2 %.

It concluded that the additional effect of Fe_2O_3 decreased the crystallinity of polyethylene from XRD patterns.

5.5.7 **Differential Thermal Analysis (DTA) technique**

After polyethylene were heated to melt in Differential Thermal Analyzer (DTA) under the heating rate of 5 ^0C/ min. Figure 5.20 was the DTA thermogram of polyethylenes. Thermograms of both samples showed the crystal melting temperature at 138.6 ^0C and 136.6 ^0C. The former value was for polyethylene from high-activity Ziegler-Natta supported catalyst and the latter value was for that from Fe-modified Ziegler-Natta supported catalyst. The experiment used In(Indium) as reference with Tm 156 ^0C.

The melting temperature increased with increasing molecular weight and crystallinity[106]. As a consequence of DTA thermogram, polyethylene from high-activity Ziegler-Natta supported catalyst has higher molecular weight and more crystallinity than that from Fe-modified Ziegler-Natta supported catalyst. The results of crystallinity determinations from XRD and DTA were in tha same way, they showed that polyethylene from the high activity Ziegler-Natta supported catalyst had more crystallinity than that from Fe-modified one.

The presence of Fe_2O_3 in the high activity Ziegler-Natta supported catalyst could decrease the crystallinity and molecular weight of polyethylene.

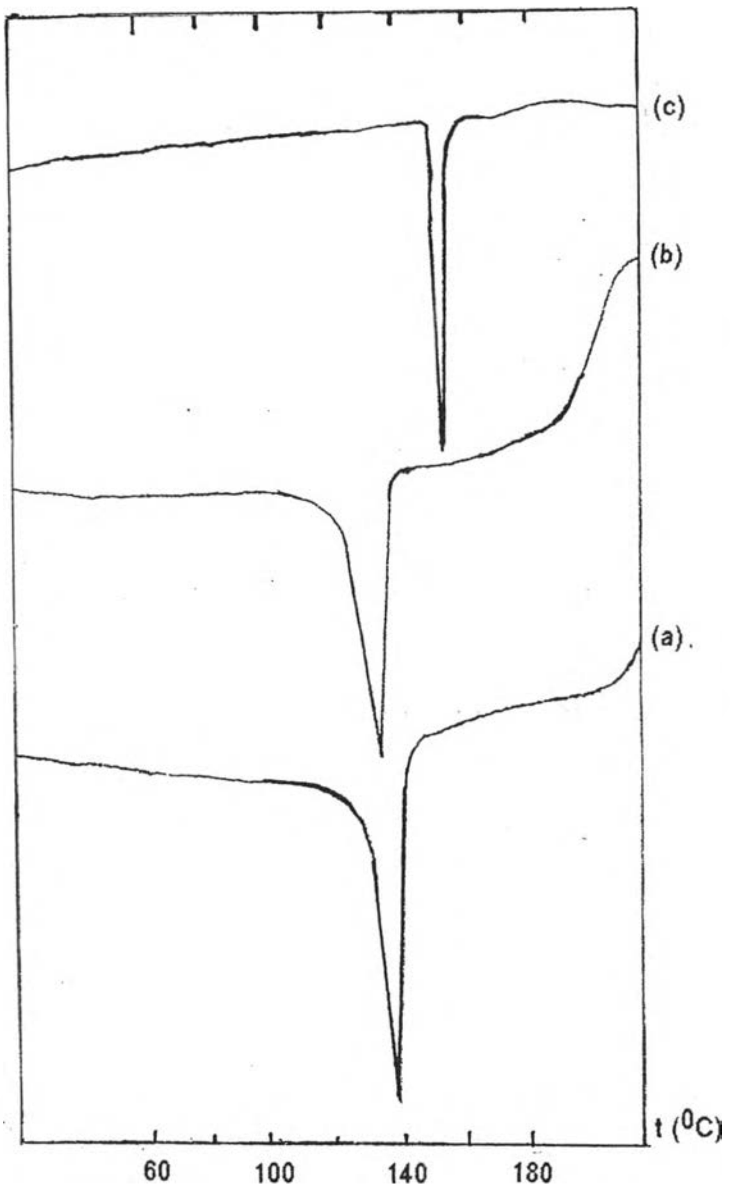


Figure 5.20 Differential Thermal Analysis of polyethylene

(a) PE from High Activity Ziegler-Natta supported catalyst

(b) PE from Fe_2O_3 modified Ziegler-Natta supported catalyst

(c) Indium metal

5.5.8 **Gel Permeation Chromatography of polyethylenes**

A molecular weight distribution represents the population of molecule that constitute a polymer. The shape of this distribution is a reflection of the polymerization geometries under which this polymer produced. As the geometries of polymerization are changed so will the molecular weight distribution. One of the accepted technique to describe, or quantitate a molecular weight distribution is the determination of its moments, or average molecular weights. Because the molecular weight averages are statistical parameters, it is advantangeous to have the distribution, too.

Gel Permeation Chromatography can provide four average molecular weights values, Mn, Mv, Mw, Mz. And polydispersity comes from the ratio of Mw / Mn. Both the average molecular weight and molecular weight distribution have the relationship to physical properties. The GPC chromatogram of the two polyethylene samples are shown in Figure 5.21. It was found that the addition of Fe decreased the Mn, Mv, Mw, Mz and the polydispersity. The GPC result also supported the previous results of the characterization method.

Melt index can be related to Mw[107]. The polyethylene from the high activity Ziegler-Natta supported catalyst has Mw of 557099 which is higher than that from Fe modified Ziegler-Natta supported catalyst with Mw of 388773. So this occurs in the same way the lower Mw the higher Melt index is obtained.

The results of Mv from Mark-Houwink-Sakarada Equation was in the same way as the result from GPC in Table 5.5. Mv from GPC of polyethylene from the high activity Ziegler-Natta supported catalyst was higher than that from Fe modified Ziegler-Natta supported catalyst. The intervension of Fe in the catalyst decreased Mv of polyethylene. And the two GPC chromatograms had nearly the same pattern. The polydispersity of polyethylene from the high activity Ziegler-Natta supported catalyst was 10.04 and the another one from the Fe modified Ziegler-Natta supported catalyst was 9.02. The addition of Fe_2O_3 to the catalyst decreased the polydispersity and average molecular weight.

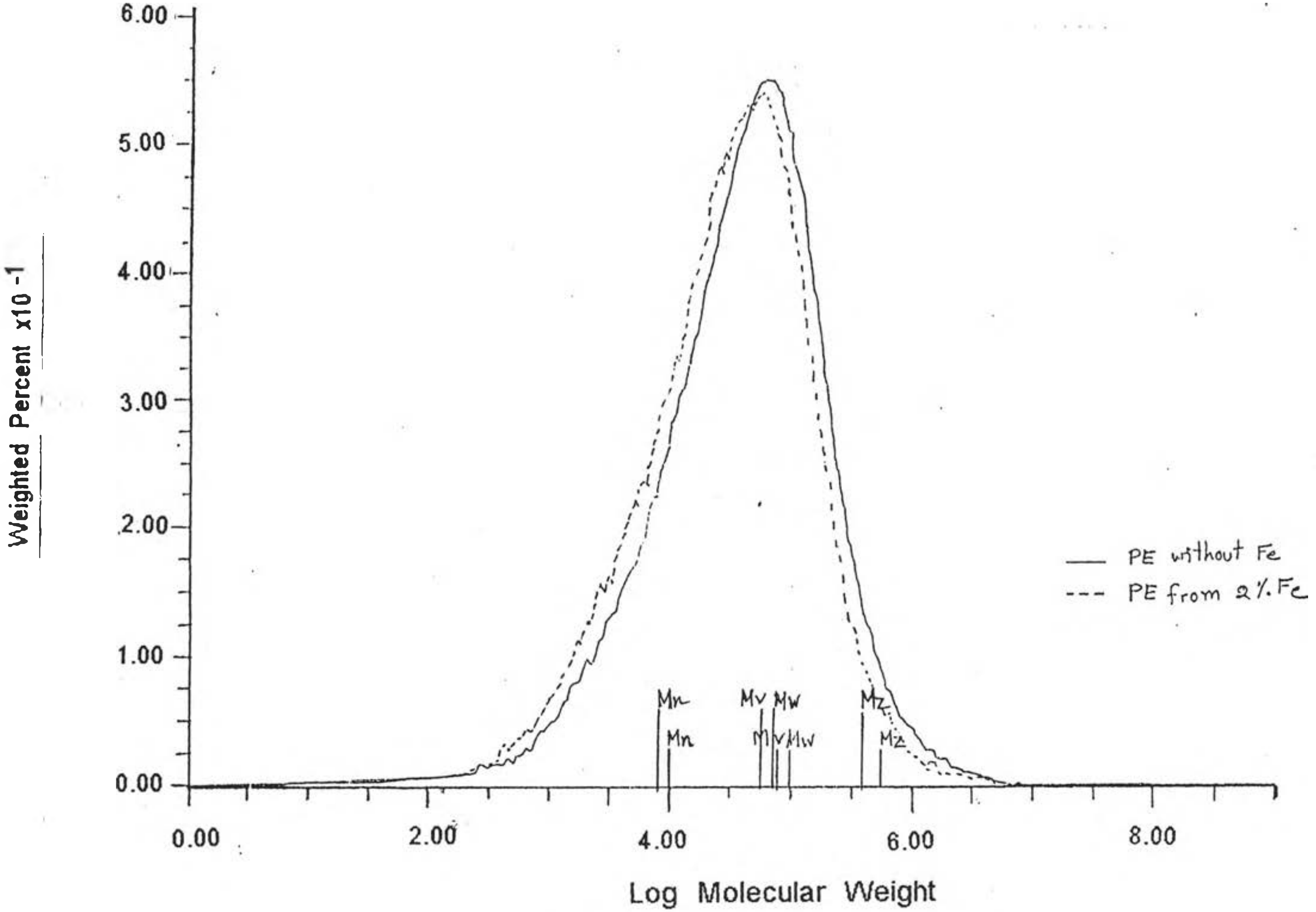


Figure 5.21 Gel Permeation Chromatography of polyethylenes

Table 5.4 Ethylene balance to the ethylene consumption to polyethylene

Catalyst	C_2H_4 consumption (gmole)	PE product (g)	% Conversion $C_2H_4 \rightarrow$ PE
High Activity Ziegler-Natta supported catalyst	0.273	5.29	69.2
Fe_2O_3 modified Ziegier-Natta supported catalyst	0.330	4.78	51.6

Table 5.5 Average molecular weight and Polydispersity

	Mn	Mv	Mw	Mz	Polydispersity*
PE from High Activity Ziegler-Natta supported catalyst	9772	74488	98079	557099	10.04
PE from Fe_2O_3 modified Ziegler-Natta supported catalyst	8143	56625	73489	388773	9.02

* Polydispersity = Mw / Mn.