CHAPTER IV
RESULTS AND DISCUSSION

The results of this thesis are shown and discussed in this chapter in connection with information from the published literature and handbook. The influence of cyclohexylmethyldimethoxysilane(CHMDMS) concentration on ethylene propylene random copolymer properties are depicted in Figure 4.1 to Figure 4.6 while the influence of ethylene content are described in Figure 4.7 to Figure 4.12. The experimental data of the present study are summarized in the Appendix.

4.1 Effect of Ethylene Content

4.1.1 Effect of Ethylene Content on Isotactic Index

From Figure 4.1, it can be seen that the addition of ethylene causes a decreasing rate of isotactic index for all different CHMDMS concentrations. The maximum value of isotactic index is observed for polymer without ethylene. Isotactic index decreases when ethylene content in the copolymer increases. The different slopes of the four lines in Figure 4.1 show that as the ethylene content increases, an increasing of CHMDMS/Ti in the catalyst system can retard the declination of copolymer isotacticity.

In this experiment, it is thought that ethylene monomer helps to create new active sites. As a consequence, the new active sites promote a growing chain with out specific polymerization to ethylene or propylene. So the increasing of ethylene will result in the decreasing of isotactic index.

Moore(1996) explained that “when propylene is copolymerized with small amounts of ethylene in Ziegler-Natta catalyst systems, its polymerization rate is increased. This behavior may be accounted for by

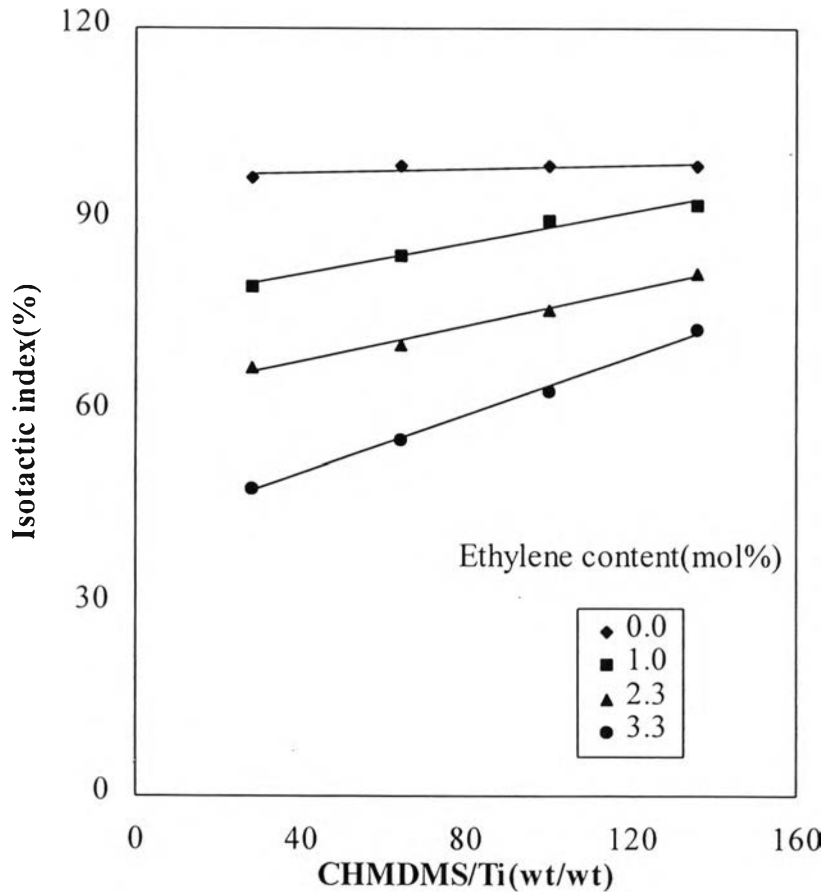

Figure 4.1 Effect of ethylene content on isotactic index.

assuming that propylene insertion in the Ti-carbon bond is easier when an ethylene unit is bonded to the transition metal, or that the ethylene insertion after a regioirregular propylene insertion reactivates a dormant site."

4.1.2 Effect of Ethylene Content on Melting Temperature

Ethylene is the most common comonomer with propylene for producing random copolymer. This copolymer provides a lower melting point, usually for the heat-sealable layer on the laminated film. As shown in Figure 4.2, at any constant CHMDMS/Ti used(i.e., 28, 64, 100, 136 wt/wt), the melting temperature decreases with the increase of ethylene content and its value is nearly the same at each ethylene contents. So it can be considered that the reduction in melting temperature is mainly related to the ethylene content in copolymer. It is interesting to note here that by having 3.3mol% of ethylene, the copolymer's melting temperature reduces to about melting temperature of high density polyethylene. Moreover, an insignificant changed in melting temperature distribution with an increase in ethylene is observed as shown in Table 2.6.

Moore(1996) described that the introduction of a comonomer into the polymeric chain created a discontinuity that sharply reduced the crystallization and resulted in a reduction of melting temperature.

4.1.3 Effect of Ethylene Content on Crystallization Temperature

Below an ethylene content 2.3 mol%, the increase in amount of ethylene does not affect the crystallization temperature. So the discontinuity in the copolymer chain may have only a small effect on crystallization. However, above an ethylene content 2.3 mol%, the crystallization temperature tends to decrease with increasing ethylene content. This phenomenon can be explained that at a high enough amount of ethylene, the discontinuity in copolymer chains will affect polymer crystallization as illustrated in Figure 4.3. In addition, insignificant effect on crystallization temperature distribution can be seen in Table 2.6.

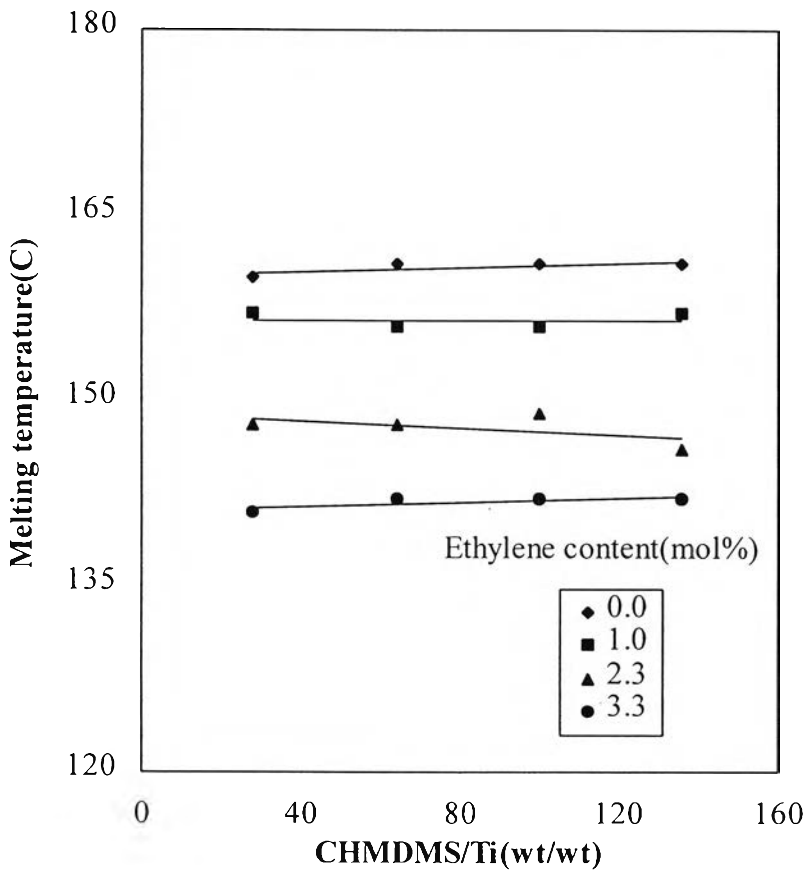

Figure 4.2 Effect of ethylene content on melting temperature.

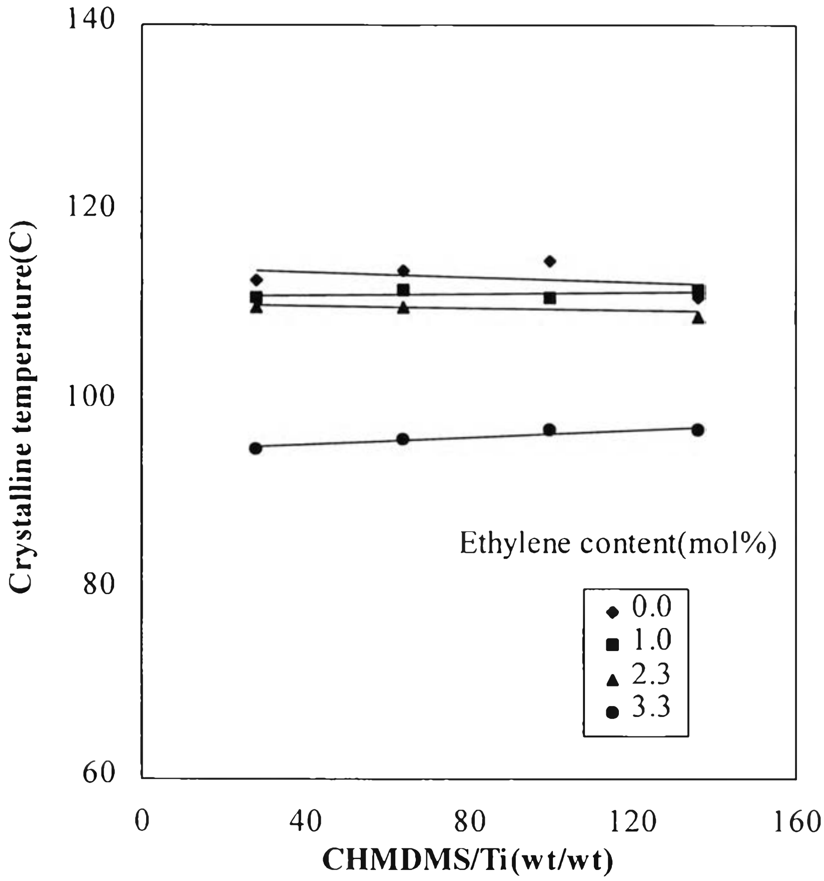

Figure 4.3 Effect of ethylene content on crystallization temperature.

Table 2.6 Effect of ethylene content on melting temperature and crystallization temperature distribution.

CHMDMS/Ti (wt/wt)	ethylene content (%mol)	Tm(C)			Tc(C)		
		started	peak	ended	started	peak	ended
28	0.0	93	160	156	112	113	56
28	1.0	95	157	158	114	111	56
28	2.3	92	148	165	113	110	54
28	3.3	95	141	162	113	95	53
64	0.0	109	161	160	125	114	63
64	1.0	106	156	160	123	112	63
64	2.3	106	148	160	125	110	63
64	3.3	110	142	157	123	96	63
100	0.0	127	161	167	127	115	68
100	1.0	123	156	165	126	111	68
100	2.3	123	149	165	126	111	68
100	3.3	118	142	165	126	97	68
136	0.0	133	161	170	128	111	63
136	1.0	129	157	170	125	112	63
136	2.3	137	146	170	126	109	63
136	3.3	137	142	169	126	97	63

4.1.4 Effect of Ethylene Content on Polymer Molecular Weight

The GPC results of weight average molecular weight, number average molecular weight, polydispersity are presented in Figure 4.4, Figure 4.5, and Figure 4.6, respectively.

It can be concluded that polymer produced with an addition of ethylene from 0.0 to 2.3 mol% have the same quality in terms of weight average molecular weight, number average molecular weight, and polydispersity. However, at an ethylene content of 3.3 mol%, the weight average molecular weight increases while the number average molecular weight decrease and this results in broader polydispersity.

Adding enough amount of ethylene can prolong polymerization leading to longer chain, i.e. higher MW as well as produce more amount of polymer chains.

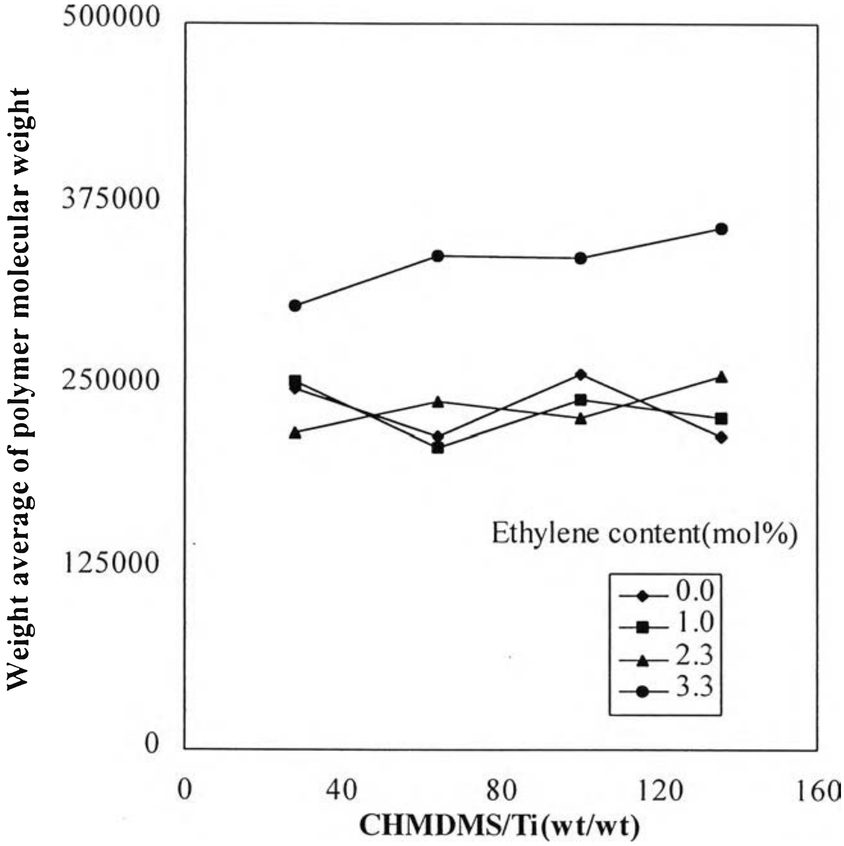

Figure 4.4 Effect of ethylene content on weight average of polymer molecular weight.

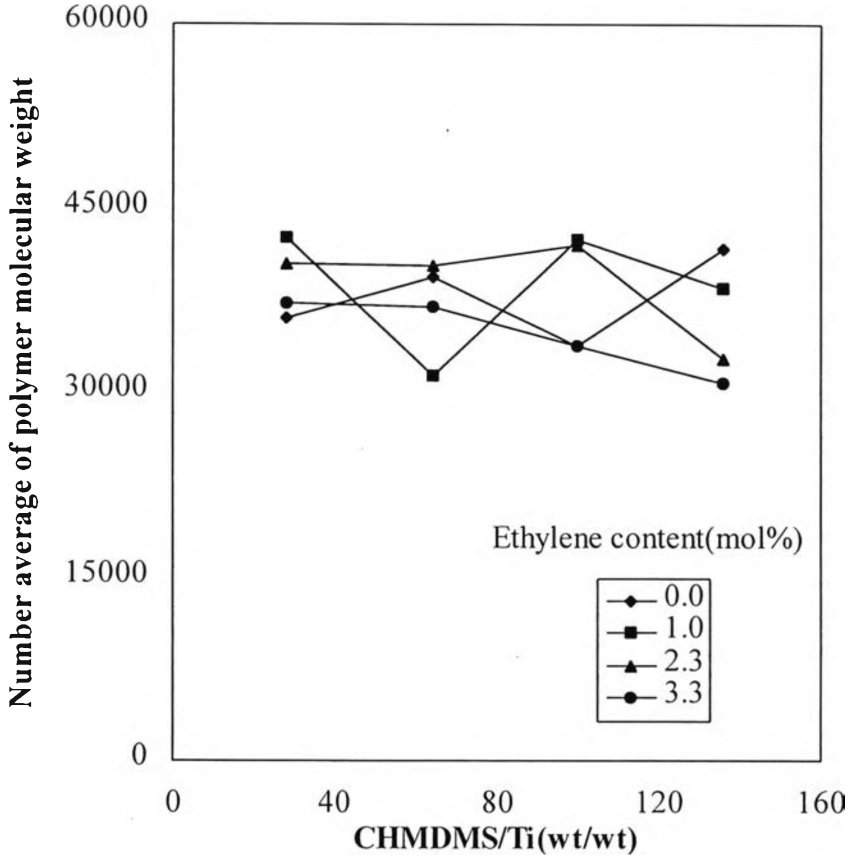

Figure 4.5 Effect of ethylene content on number average of polymer molecular weight.

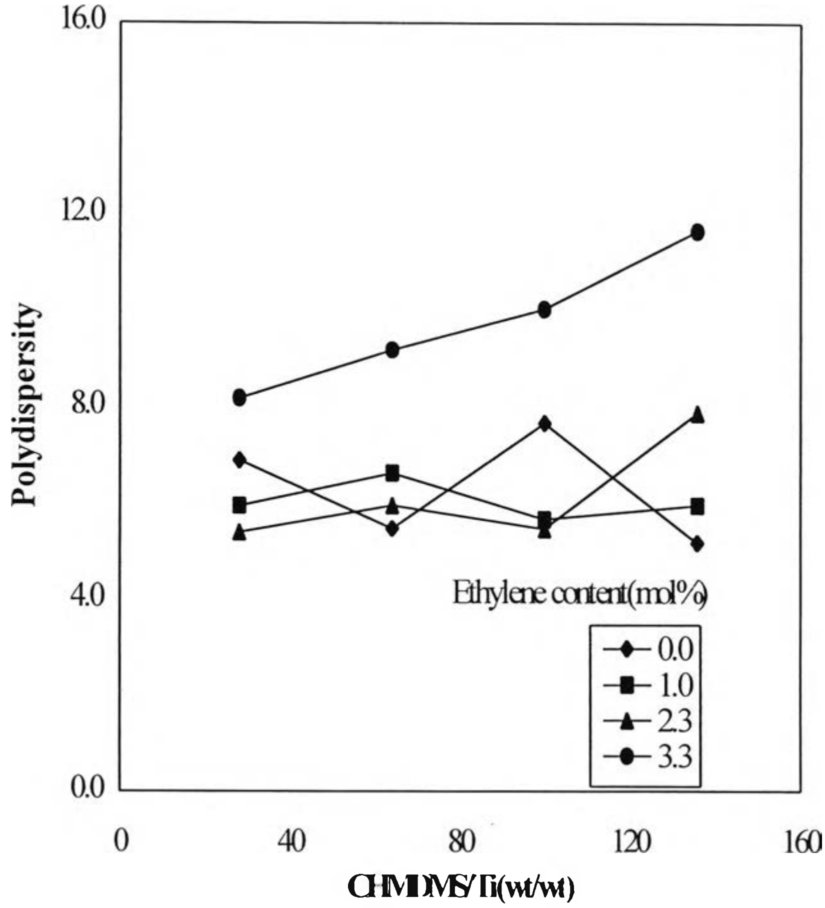

Figure 4.6 Effect of ethylene content on polydispersity.

4.2 Effect of Cyclohexylmethyldimethoxysilane(CHMDMS) Concentration

4.2.1 Effect of CHMDMS Concentration on Isotactic Index

The effect of CHMDMS concentration is investigated by changing cyclohexylmethyldimethoxysilane per titanium in weight ratio (CHMDMS/Ti) from 28 to 136. Figure 4.7 shows that an increase in CHMDMS/Ti in copolymerization results in increasing polymer isotacticity. Xu *et al.*(1997) used DPDMS (diphatalatedimethoxysilane) as an external electron donor on homopolymer and found the same result of an increasing isotactic index.

As discussed in the effect of ethylene, the amount of CHMDMS added will interact with the new active sites and produce more isotactic polymer.

4.2.2 Effect of CHMDMS Concentration on Melting Temperature

The independence of melting temperature of copolymer on CHMDMS/Ti is illustrated in Figure 4.8. At every level of ethylene content in the copolymer, the melting temperature remains constant although CHMDMS/Ti ratio is changed. It is possible that the effect of CHMDMS/Ti on stereoregularity cause a tiny effect on melting temperature. In the contrary, Table 2.7 shows an decrease in CHMDMS/Ti results in increasing of melting temperature distribution. So the amorphous phase of copolymer has been increased as the donor decreases.

4.2.3 Effect of CHMDMS Concentration on Crystallization Temperature

The effects of CHMDMS/Ti on crystalline temperature looks similar to melting temperature. Figure 4.9 shows that the crystalline temperature does not change with increases of CHMDMS/Ti. From Table 2.7 it can be seen that the crystallization temperature distribution is same but started Tc and ended Tc are reduced when CHMDMS/Ti below 64 wt/wt.

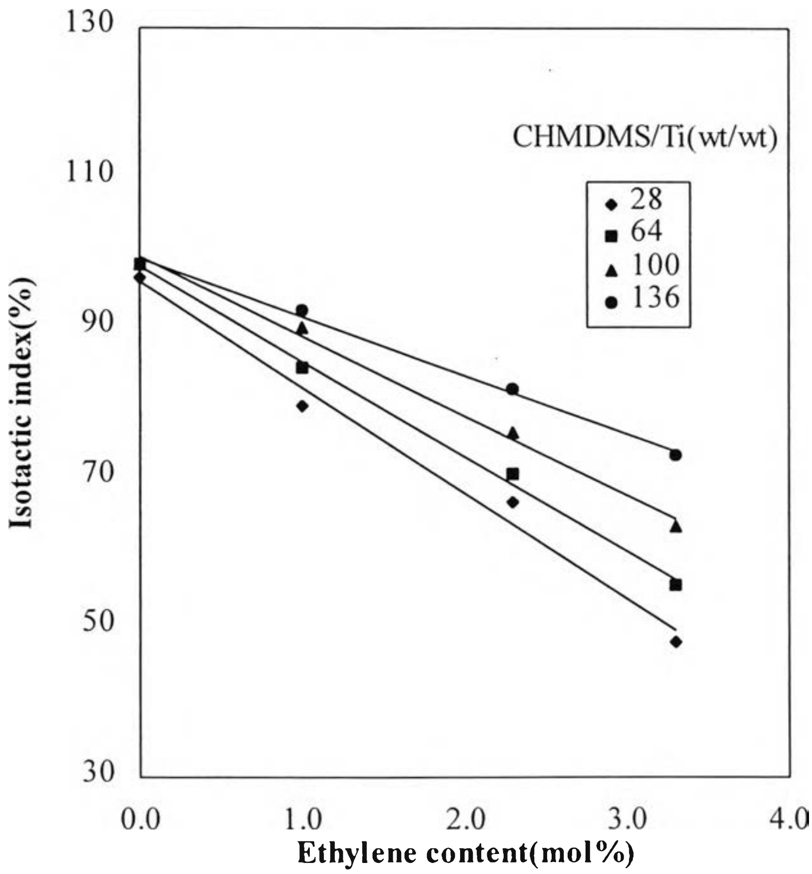

Figure 4.7 Effect of CHMDMS concentration on isotactic index.

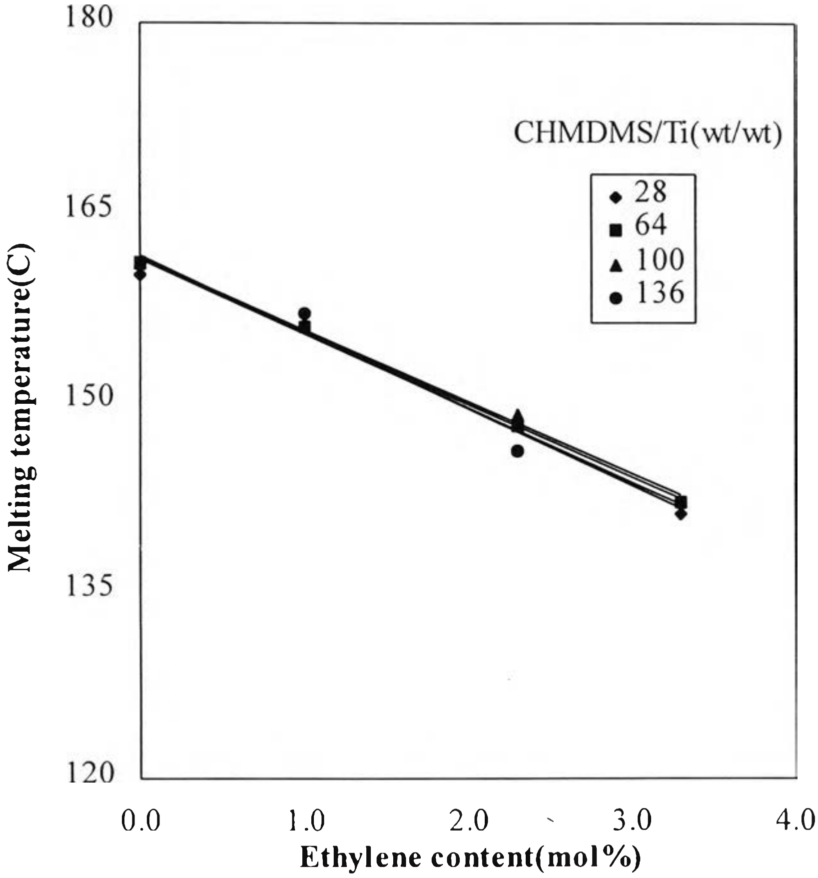

Figure 4.8 Effect of CHMDMS concentration on melting temperature.

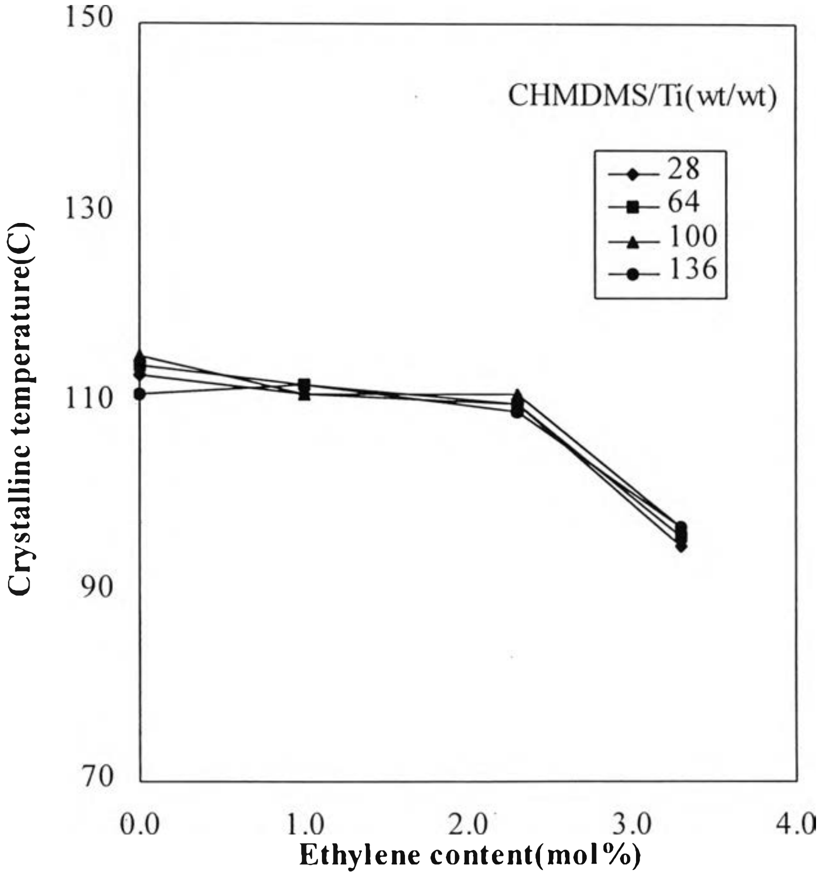

Figure 4.9 Effect of CHMDMS concentration on crystallization temperature.

Table 2.7 Effect of CHMDMS concentration on melting temperature and crystallization temperature distribution.

ethylene content	CHMDMS/Ti	Tm(C)			Tc(C)		
(%mol)	(wt/wt)	started	peak	ended	started	peak	ended
0.0	136	133	161	170	128	111	63
0.0	100	127	161	167	127	115	68
0.0	64	109	161	160	125	114	63
0.0	28	93	160	156	112	113	56
1.0	136	129	157	170	125	112	63
1.0	100	123	156	165	126	111	68
1.0	64	106	156	160	123	112	63
1.0	28	95	157	158	114	111	56
2.3	136	137	146	170	126	109	63
2.3	100	123	149	165	126	111	68
2.3	64	106	148	160	125	110	63
2.3	28	92	148	165	113	110	54
3.3	136	137	142	169	126	97	63
3.3	100	118	142	165	126	97	68
3.3	64	110	142	157	123	96	63
3.3	28	95	141	162	113	95	53

4.2.4 Effect of CHMDMS Concentration on Polymer Molecular Weight

Figure 4.10, Figure 4.11, and Figure 4.12 are resulted from GPC for weight average molecular weight, number average molecular weight, and polydispersity. From these results, the discussion can be divided into two parts as follow:

For ethylene contents below 2.3 mol%, the addition of CHMDMS/Ti has not affected to weight average molecular weight, number average molecular weight, and polydispersity. So the properties of the polymer in term of molecular weight do not change when CHMDMS/Ti increases.

For the ethylene content above 2.3 mol%, the weight average molecular weight increases while the number average molecular weight decreases with increasing CHMDMS/Ti. These two effects result in a broader molecular weight distribution and therefore polydispersity. This may result from the discontinuity of monomer insertion in the polymeric chain. When the ethylene content is high enough, an increase of CHMDMS/Ti that affects polymer stereoregularity can disturb polymerization by modifying more amounts of catalyst and result in high molecular weight of the copolymer.

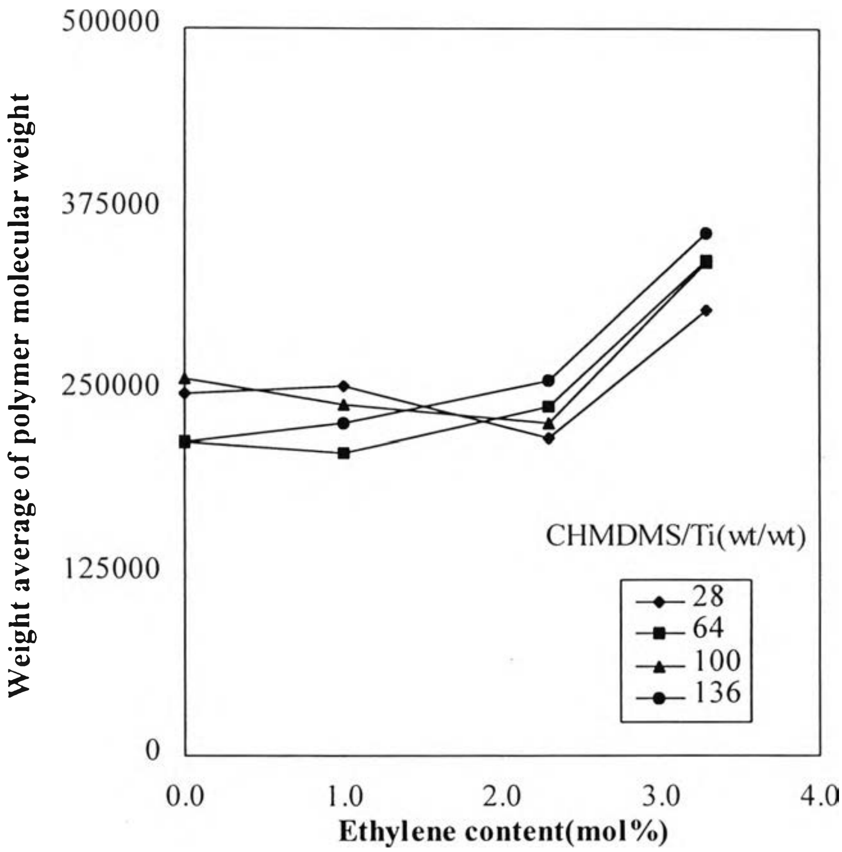

Figure 4.10 Effect of CHMDMS concentration on weight average of polymer molecular weight.

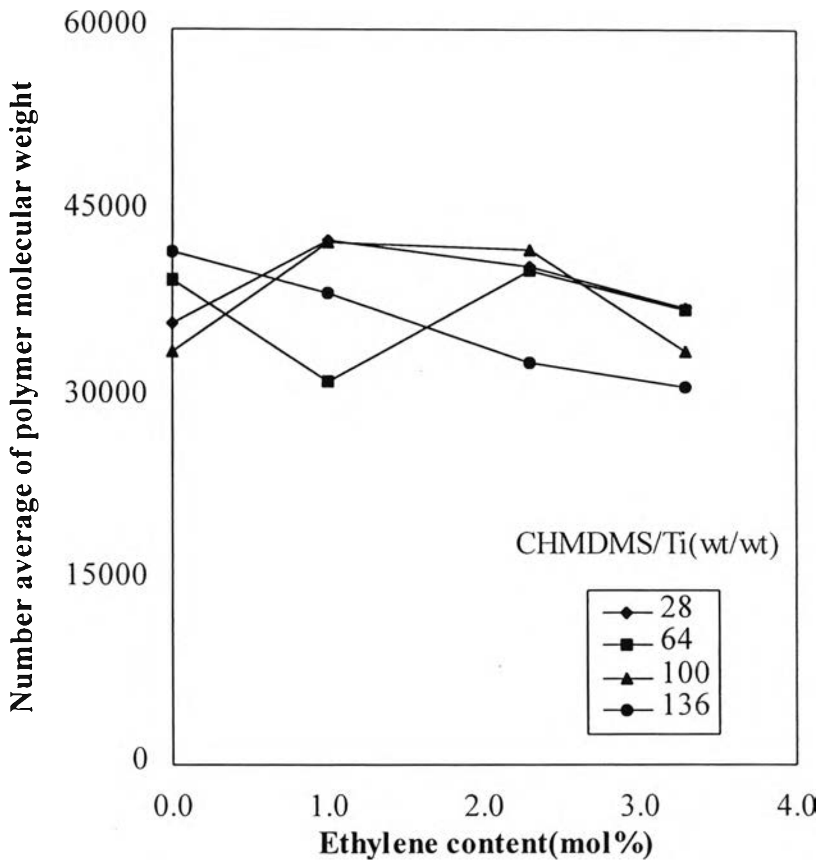

Figure 4.11 Effect of CHMDMS concentration on number average of polymer molecular weight.

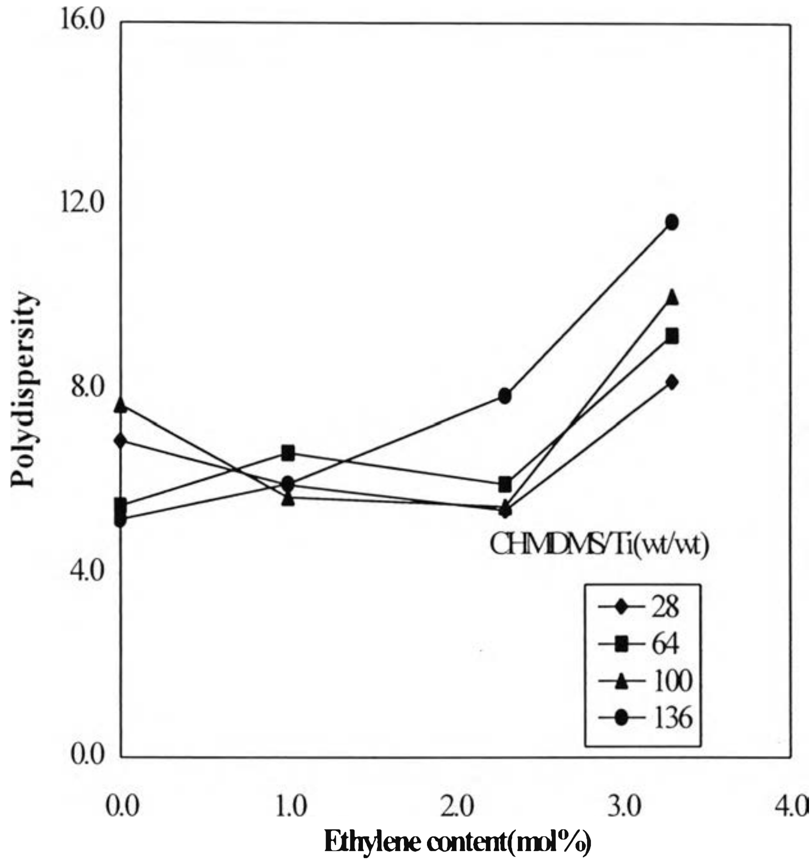

Figure 4.12 Effect of CHMDMS concentration on polydispersity.