

CHAPTER IV

RESULTS AND DISCUSSION

The purpose of this work is to study copolymerization of ethylene and norbornene using metallocene catalyst system in the presence of methylaluminoxane (MAO) as a cocatalyst. This chapter provides information about some preliminary results concerning the reaction conditions such as molar ratios of $[Al]_{MAO}/[Zr]$, catalyst concentrations $[Zr]$, polymerization temperatures, norbornene concentrations, different types of metallocene catalysts and characteristics of copolymers obtained.

4.1 Influence of reaction conditions on catalytic activity of ethylene and norbornene copolymerization

4.1.1 The effect of $[Al]_{MAO}/[Zr]$ molar ratio

The effect of $[Al]_{MAO}/[Zr]$ molar ratio was investigated using racemic-ethylenebis(indenyl)zirconium dichloride ($rac\text{-Et}[\text{Ind}]_2\text{ZrCl}_2$) catalyst in the presence of methylaluminoxane (MAO) as a cocatalyst. The molar ratio of $[Al]_{MAO}/[Zr]$ ranged between 750 to 4000. The copolymerization was performed in toluene at 40°C using ethylene consumption of 6 psi or 0.018 mole (pressure within reactor 50 psi), 0.1 M of norbornene and zirconium concentration 5.0×10^{-5} M with total solution volume 30 ml. The results of the influence of $[Al]_{MAO}/[Zr]$ molar ratios on the catalytic activity are shown in Table 4.1 and Figure 4.1.

Figure 4.1 illustrated the variation in catalyst activity for different amount of the cocatalyst, the activity of the catalyst increased with increasing the amount of cocatalyst. The most significant increase of catalyst activity occurred when $[Al]/[Zr]$ molar ratio was increased from 1000 to 2000. No significant increase in the catalyst activity was observed with increasing $[Al]/[Zr]$ molar ratio from 2000 to 4000. The increase of cocatalyst concentration in the polymerization medium may cause an augmentation in the number of active site. However, larger amounts of MAO ($[Al]/[Zr] = 4000$) were not able to increase significantly the capacity of activation of the metallocene and thus the catalyst activity was not strongly influenced. It might be concluded that the maximum number of active sites was attained at an $[Al]/[Zr]$ molar

ratio between 2000 to 4000. The further increase of $[Al]/[Zr]$ molar ratio higher than 4000 may result in slightly increase of catalyst activity but in much less proportional gain and will result in higher amount of Al residual in the polymer produced.

Table 4.1 Catalytic activity at different $[Al]_{MAO}/[Zr]$ molar ratios^a

$[Al]_{MAO}/[Zr]$ molar ratio	Polymerization time (sec)	Yields (g)	Catalytic activity (kg Copolymer/mol Zr.h)	Catalytic activity (kg Ethylene/mol Zr.h)
750	362	0.49	3248	3314
1000	305	0.46	3260	3934
2000	226	0.71	7540	5310
3000	223	0.76	8180	5381
4000	220	0.79	8727	5455

^aCopolymerization condition : $[Zr]=5.0 \times 10^{-5}$ M, 40°C, 0.018 mole of ethylene consumption, 0.1 M of norbornene, total volume=30 ml.

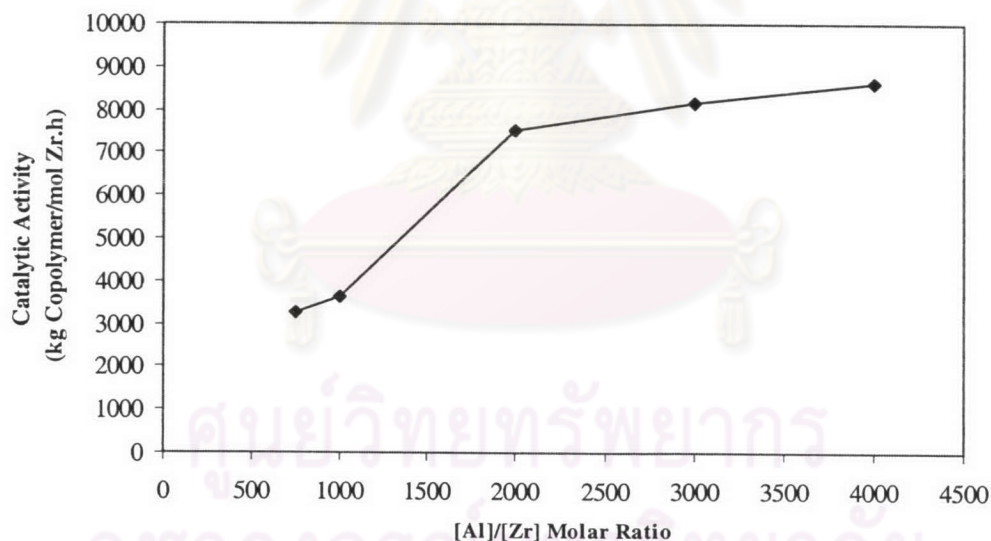


Figure 4.1. Catalytic activity at different $[Al]_{MAO}/[Zr]$ molar ratios

Ruchatz and Fink (1998) reported that at low MAO concentrations ($[Al]/[Zr] \approx 690$), the polymerization activity dropped rapidly toward zero. This behavior is possibly caused by impurities. MAO can be consumed by impurities due to its scavenging behavior. They found that the ethylene reaction rate cannot be

further increased by increasing the ratio of [Al]/[Zr]. Even at [Al]/[Zr] molar ratios of 4000 the reaction rate was not higher than at an [Al]/[Zr] molar ratio of 2000.

4.1.2 The effect of catalyst concentration

The effect of catalyst concentration was studied using *rac*-Et[Ind]₂ZrCl₂ catalyst and MAO as a cocatalyst. The catalyst concentrations were tested in the range between 3.3×10^{-5} M to 10.0×10^{-5} M. The copolymerization was carried out in toluene at 40°C using ethylene consumption of 6 psi or 0.018 mole (pressure within reactor 50 psi), 0.1 M of norbornene with [Al]_{MAO}/[Zr] molar ratio of 1000 and total solution volume 30 ml. The results for the effect of catalyst concentrations on the catalytic activity are shown in Table 4.2 and Figure 4.2.

Table 4.2 Catalytic activity of different catalyst concentrations^b

Catalyst concentration ($\times 10^5$) M	Polymerization time (sec)	Yields (g)	Catalytic activity (kg Copolymer/mol Zr.h)	Catalytic activity (kg Ethylene/mol Zr.h)
3.3	628	0.10	573	2866
5.0	305	0.46	3620	3934
6.7	263	0.56	3833	3422
8.3	268	0.52	2794	2687
10.0	285	0.56	2358	2105

^bCopolymerization condition : [Al]_{MAO}/[Zr]=1000, 40°C, 0.018 mole of ethylene consumption, 0.1 M of norbornene, total volume=30 ml

Table 4.2 and Figure 4.2 revealed that the catalyst activity increased with increasing catalyst concentrations up to 6.7×10^{-5} M, then decreased with higher catalyst concentration.

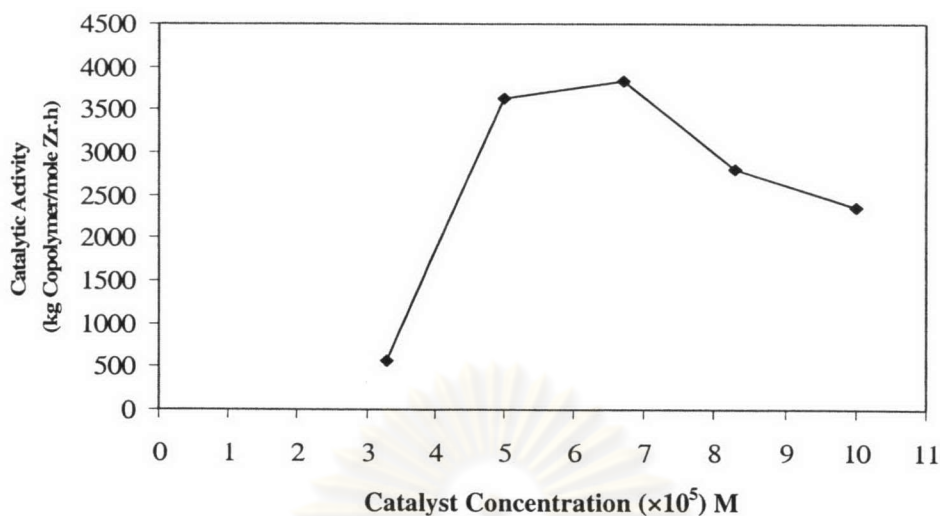
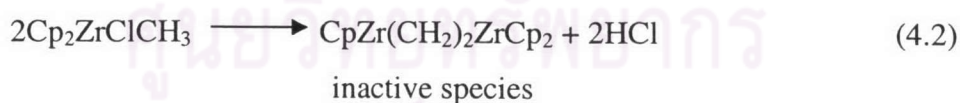
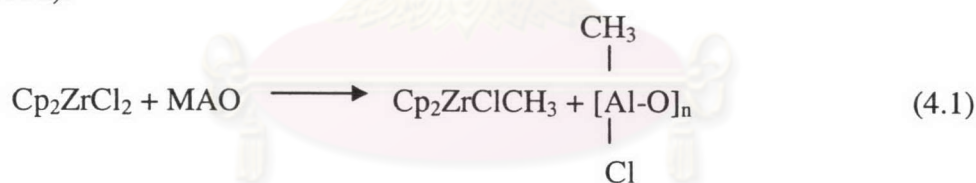


Figure 4.2. Catalytic activity of different catalyst concentrations

The change of [Zr] concentration should not result in the different nature of the active species formed. Only the number of active species should be increased according to the [Zr] concentration. However, at higher concentration of [Zr] the dimerization of the active zirconium complexes can occur resulting in the catalyst deactivation, which is illustrated in equation 4.1 and 4.2 (Keii and Soga, 1990; Chien and He, 1991).



Young *et al.* (2003) reported that the catalyst activity increased with increasing of catalyst concentration in lower catalyst concentration regime and decreased in the higher catalyst concentrations due to the site competition effect. The optimal catalyst concentration value for catalyst activity is about 7×10^{-6} mol/l.

4.1.3 The effect of polymerization temperatures

The effect of polymerization temperatures was investigated in the range of 40°C to 90°C. The copolymerization were performed in toluene using rac-Et[Ind]₂ZrCl₂/MAO catalyst, ethylene consumption 6 psi or 0.018 mole (pressure within reactor 50 psi), 0.1 M of norbornene and total solution volume 30 ml. The catalyst concentration and [Al]_{MAO}/[Zr] molar ratio were fixed at 6.7×10⁻⁵M and 1000, respectively. Table 4.3 and Figure 4.3 illustrate the results for the effect of polymerization temperatures on the catalytic activity.

Table 4.3 Catalytic activity of different polymerization temperatures^c

Temperature (°C)	Polymerization time (sec)	Yields (g)	Catalytic activity (kg Copolymer/mol Zr.h)	Catalytic activity (kg Ethylene/mol Zr.h)
40	263	0.56	3833	3422
50	259	0.57	3961	3475
60	256	0.67	4710	3516
70	250	0.70	5040	3600
80	224	0.80	6429	4018
90	195	0.79	7255	4615

^cCopolymerization condition : [Zr]=6.7×10⁻⁵M, [Al]_{MAO}/[Zr]=1000, 0.018 mole of ethylene consumption, 0.1 M of norbornene, total volume=30 ml

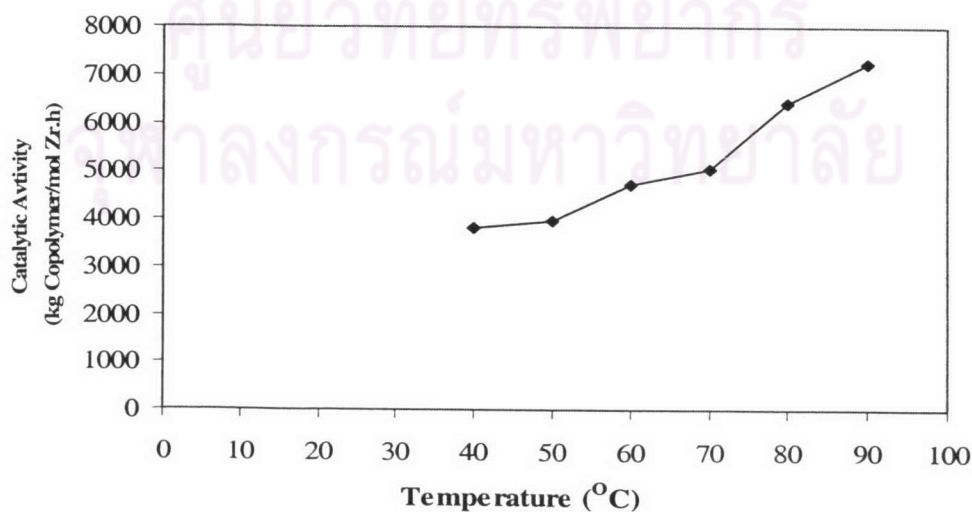
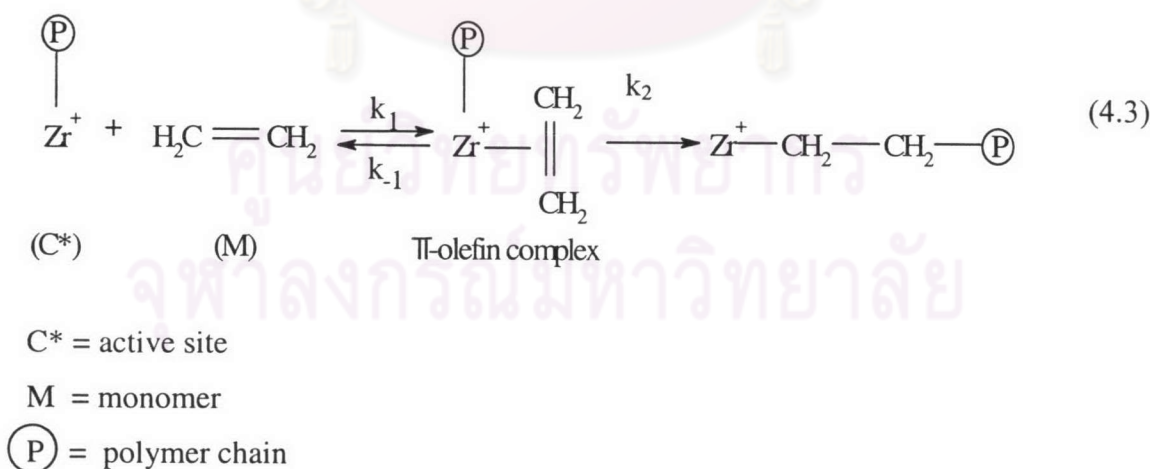


Figure 4.3. Catalytic activity of different polymerization temperatures

Figure 4.3 presented the variation in catalyst activity for difference polymerization temperatures in the range of 40°C to 90°C, the activity of the catalyst slightly increase by increasing the polymerization temperature from 40°C to 50°C. However, a further increase in temperature to 90°C resulted in increased activities almost linearly. Generally, the average molecular weight of the polymer produced with metallocene catalyst system decreases with increasing polymerization temperature therefore, there are not necessary to proceed copolymerization at higher temperature.

Jeong *et al.* (2003) reported that the activity increased by increasing the polymerization temperature from 30°C to 70°C at a constant pressure, a further increase in temperature to 100°C resulted in a slight decreased in catalyst activity. The latter result is due to decreased ethylene solubility, which supersedes the positive effect on reactivity (Berhström and Seppälä, 1997).

In general, the rate of a chemically controlled reaction increases with increasing temperatures due to an increased rate constant. In Ziegler-Natta catalysis, a widely accepted mechanism of propagation involves the initial formation of a π -complex of an olefin with the catalyst metal, followed by chain migratory insertion (Tsai and Chien, 1994).



At low polymerization temperatures, the π -olefin complex is more stable; its lifetime is longer than the period of insertion. At high temperatures, the complex readily dissociates (dos Santos *et al.*, 1999). The increasing of the activity with the increase of reaction temperature may be attributed to the process of activated insertion

and the activity is expected to decrease with further increase of reaction temperature because of a shift of equilibrium to the dissociation of the π -complex (Tsai and Chien, 1994).

4.1.4 The effect of different types of catalyst

The effect of different types of catalyst for ethylene and norbornene copolymerization was investigated by using seven types of catalyst such as *rac*-Et[Ind]₂ZrCl₂, (*n*-BuCp)₂ZrCl₂, Cp₂ZrCl₂, Cp₂TiCl₂, CpTiCl₃, Cp*TiCl₃ and Cp*TiMe₃ at the similar polymerization conditions. The copolymerization were performed in toluene at 50°C using ethylene consumption of 6 psi or 0.018 mole (pressure within reactor 50 psi), 0.1 M of norbornene, catalyst concentration of 6.7×10^{-5} M and [Al]_{MAO}/[Zr] or [Al]_{MAO}/[Ti] of 1000 with total solution volume 30 ml. The results for the effect of different catalysts on the catalytic activity are shown in the Table 4.4 and Figure 4.4. The structure of metallocene catalysts using in this investigation are presented in Figure 4.5.

Table 4.4 Catalytic activity of different types of catalyst^d

Type of catalyst	Polymerization time (sec)	Yields (g)	Catalytic activity (kg Copolymer/ mol Zr.h)	Catalytic activity (kg Ethylene/ mol Zr.h)
<i>rac</i> -Et[Ind] ₂ ZrCl ₂	259	0.57	3961	3475
(<i>n</i> -BuCp) ₂ ZrCl ₂	316	0.41	2335	2848
Cp ₂ ZrCl ₂	488	0.40	1476	1844
Cp ₂ TiCl ₂	647	0.41	1141	1391
CpTiCl ₃	n.p.	n.p.	n.p.	n.p.
Cp*TiCl ₃	n.p.	n.p.	n.p.	n.p.
Cp*TiMe ₃	n.p.	n.p.	n.p.	n.p.

^dCopolymerization condition : [Zr]= 6.7×10^{-5} M, [Ti]= 6.7×10^{-5} , [Al]_{MAO}/[Metal]=1000, 50°C, 0.018 mole of ethylene consumption, 0.1 M of norbornene, total volume=30 ml, n.p.= can not copolymerized

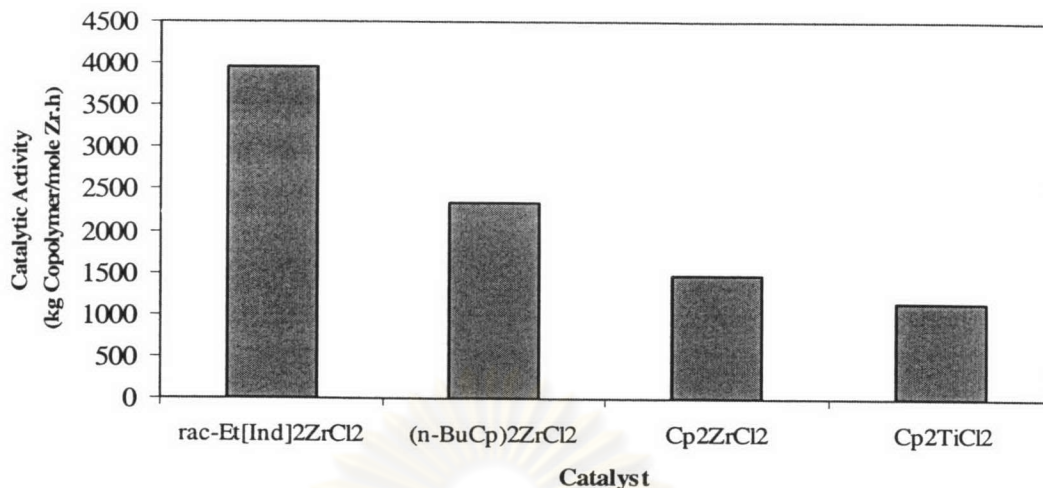


Figure 4.4. Catalytic activity of different catalysts

Table 4.4 and Figure 4.4 displayed the order of the catalytic activity for different catalysts was $\text{rac-Et[Ind]}_2\text{ZrCl}_2 > (\text{n-BuCp})_2\text{ZrCl}_2 > \text{Cp}_2\text{ZrCl}_2 > \text{Cp}_2\text{TiCl}_2$ respectively. The high activity for bulky norbornene was due to the electronic effect and the minimum steric hindrance on the reaction site (B.G.Jeong *et al.*, 2003).

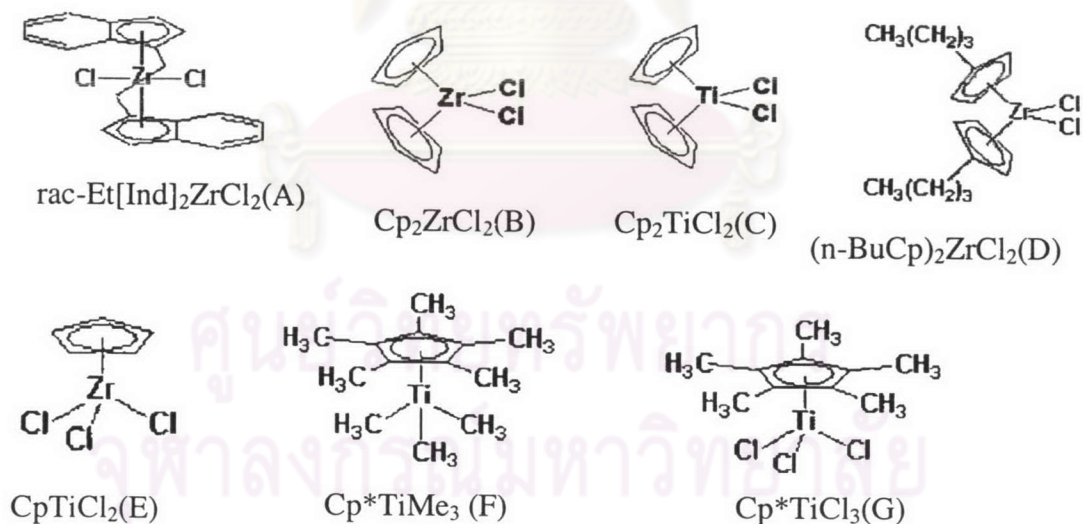
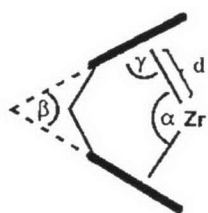


Figure 4.5. The structure of metallocene catalysts

The different monomer reactivities in the copolymerizations with $\text{rac-Et[Ind]}_2\text{ZrCl}_2$ (Catalyst A) and Cp_2ZrCl_2 (Catalyst B) should be due to a difference of electronic nature of the coordinate ligand. The catalyst A shows a somewhat smaller γ angle and a larger β angle and longer $d(\text{Zr-C}_{\text{cp}})$ than those of the catalyst C (See

scheme 1). This difference means that the coordination space of the catalyst A is wider than that of the catalyst C. Another possibility is a distortion of indenyl ligands of catalyst A forms either right-handed or left-handed ring helix as reported by Kaminsky *et al.* (1995).



Where α = angle of cp-Zr-cp' (cp,cp' =centroids of the Cp rings)
 β = angle between Cp planes
 γ = angler between Cp plane and cp-Zr bond
 d = length of cp-Zr

Scheme 1. Bond length and bond angle of a zirconocene catalyst (Naga and Imanishi, 2002)

The activity of $(n\text{-BuCp})_2\text{ZrCl}_2$ (Catalyst D) is higher than catalyst B could be explained on the basis of an alternating polyinsertion mechanism involving two heterotopic coordination sites. The coordination site hindered by the bulky *n*-Bu group in the β -position on the Cp ligand exclusively permits ethylene coordination/insertion where as both ethylene and norbornene can be coordinated/inserted on the other site (Arndt and Beulich, 1998, 1999; Hasan *et al.*, 2002). The activity of catalyst B is higher than Cp_2TiCl_2 (Catalyst C) due to the atomic radius of Zr is larger than that of Ti, resulting in the wider coordination space of catalyst B than catalyst C.

There are significant steric and electronic differences between catalyst C and CpTiCl_3 (Catalyst E). For these reasons one might expect marked differences in polymerization behaviors for catalysts of the two compounds.

However, half metallocene catalysts such as CpTiCl_3 , Cp^*TiCl_3 and Cp^*TiMe_3 can not be proceeded copolymerization of ethylene and norbornene. Since the ordinary half-sandwich catalysts such as CpTiCl_3 , Cp^*TiCl_3 , $\text{Cp}^*\text{Ti}(\text{OMe})_3$ and $(\text{Ind})\text{TiCl}_3$ are know to be efficient catalyst precursor for syndiospecific styrene polymerization which are less active for homopolymerization of norbornene therefore, they are not suitable for copolymerization ethylene and norbornene (Kaminsky *et al.*, 1997; Chien *et al.*, 1993).

4.1.5 The effect of norbornene concentrations

The effect of norbornene concentrations was studied with different norbornene concentration in the range of 0.03 M to 0.2 M. Copolymerization of ethylene and norbornene with zirconocene catalysts; $\text{rac-Et[Ind]}_2\text{ZrCl}_2$ and Cp_2ZrCl_2 was carried out in toluene at 50°C using ethylene consumption of 6 psi or 0.018 mole (pressure within reactor 50 psi), catalyst concentration of 6.7×10^{-5} M and $[\text{Al}]_{\text{MAO}}/[\text{Zr}]$ of 1000 with total solution volume 30 ml. The results for the effect of norbornene concentrations on catalytic activity are presented in Table 4.5 and Figure 4.6. The copolymerization activity profiles at different norbornene concentrations for both zirconocene catalyst systems were recorded and illustrated in Figures 4.7-4.8.

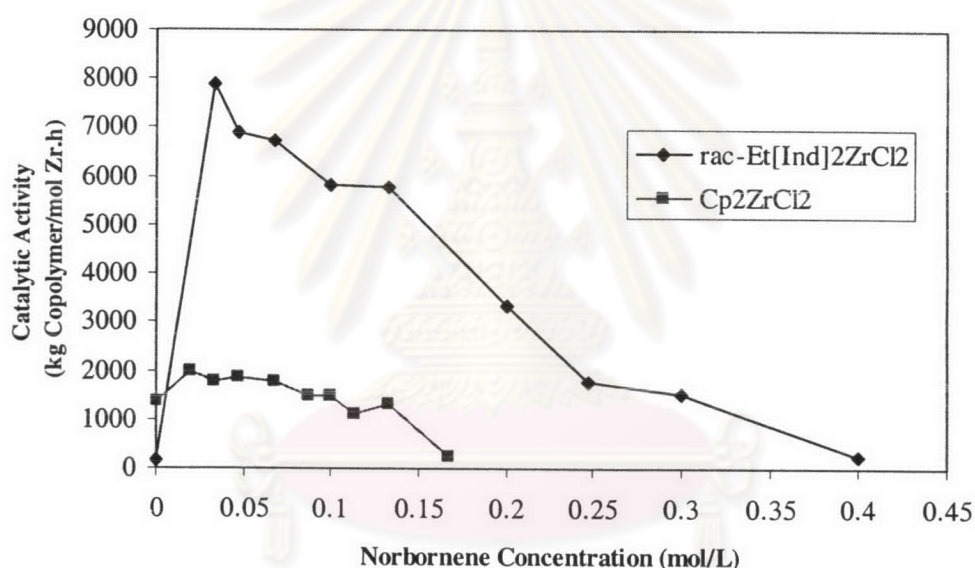


Figure 4.6. Catalytic activity of different norbornene concentrations with $\text{rac-Et[Ind]}_2\text{ZrCl}_2$ and Cp_2ZrCl_2 catalysts system

Table 4.5 and Figure 4.5 illustrated the catalytic activity of ethylene and norbornene copolymerization was higher than ethylene homopolymerization and decreased with increasing norbornene concentrations for both zirconocene catalyst systems. The addition of small amounts of norbornene results in a large increase in the copolymerization rate. Kravchenko and Waymouth (1998) suggested that it is likely the result of the activation of dormant catalyst sites by comonomer. Another type of activation effect has been observed for ethylene polymerization upon addition of small amounts of an α -olefin comonomer, which usually referred to as a

“comonomer effect”. Some explanations have been forwarded to explain this phenomenon, including the “trigger” mechanism (Naga *et al.*, 1997) and improved rates of diffusion due to the solubilization of active centers by incorporation of comonomer (Koivumaki and Seppala, 1993). The decreased activity for *rac*-Et[Ind]₂ZrCl₂ is higher than that for Cp₂ZrCl₂. The reason of a decrease in rates at higher amounts of norbornene may be due to the coordination of norbornene to the catalytic sites, which reduces the ethylene insertion and/or propagation. In addition, Bergstrom *et al.* (1997) suggested that high amounts of norbornene seemed to deactivate the active sites of the catalyst. The activity profiles (Figures 4.6-4.7) became broader with increasing norbornene concentration. All activity profiles showed a period of activation followed by deactivation. Deactivation rates were more sensitive to norbornene concentration than activation rates; that is, there was a higher activation energy for the deactivation process(es) than for the activation process(es) of the catalytic sites. The concentration of comonomer also affected the rates of activation and deactivation. The deactivation rate at higher amounts of norbornene was higher than the deactivation rate at lower norbornene concentration. For comparison, the reaction curves using Cp₂ZrCl₂ indicated that the catalyst system deactivated more rapidly than *rac*-Et[Ind]₂ZrCl₂ catalyst system for all low norbornene concentrations.

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Table 4.5 Catalytic activity of difference norbornene concentrations with rac-Et[Ind]₂ZrCl₂ and Cp₂ZrCl₂ catalysts system^c

Norbornene concentration		rac-Et[Ind] ₂ ZrCl ₂					Cp ₂ ZrCl ₂				
mol/L	mole (×10 ³)	Polymerization time (sec)	Yields (g)	Catalytic activity* (kg Copolymer/mol Zr.h)	Catalytic activity* (kg Ethylene/mol Zr.h)	Polymerization time (sec)	Yields (g)	Catalytic activity (kg Copolymer/mol Zr.h)	Catalytic activity (kg Ethylene/mol Zr.h)		
0	0	4140	0.45	196	217	523	0.39	1342	1720		
0.020	0.5	-	-	-	-	270	0.30	2000	3333		
0.033	1.0	160	0.70	7875	5625	292	0.29	1786	3082		
0.047	1.5	185	0.70	6811	4865	299	0.31	1867	3010		
0.067	2.0	190	0.71	6726	4737	302	0.30	1788	2980		
0.087	2.5	-	-	-	-	380	0.31	1469	2368		
0.100	3.0	223	0.72	5812	4036	488	0.40	1476	1844		
0.113	3.5	-	-	-	-	492	0.31	1134	1829		
0.133	4.0	236	0.76	5796	3813	513	0.38	1333	1754		
0.167	5.0	-	-	-	-	1458	0.21	259	617		
0.200	6.0	420	0.78	3342	2143	-	-	-	-		
0.247	7.5	523	0.52	1790	1721	-	-	-	-		
0.300	9.0	605	0.51	1517	1487	-	-	-	-		
0.400	12.0	1740	0.53	265	517	-	-	-	-		

^cCopolymerization condition : [Zr]=6.7×10⁻³M, [Al]/[Zr]=1000, 50°C, 0.018 mole of ethylene consumption, total volume=30 ml, * = activated catalyst by MAO in glove box

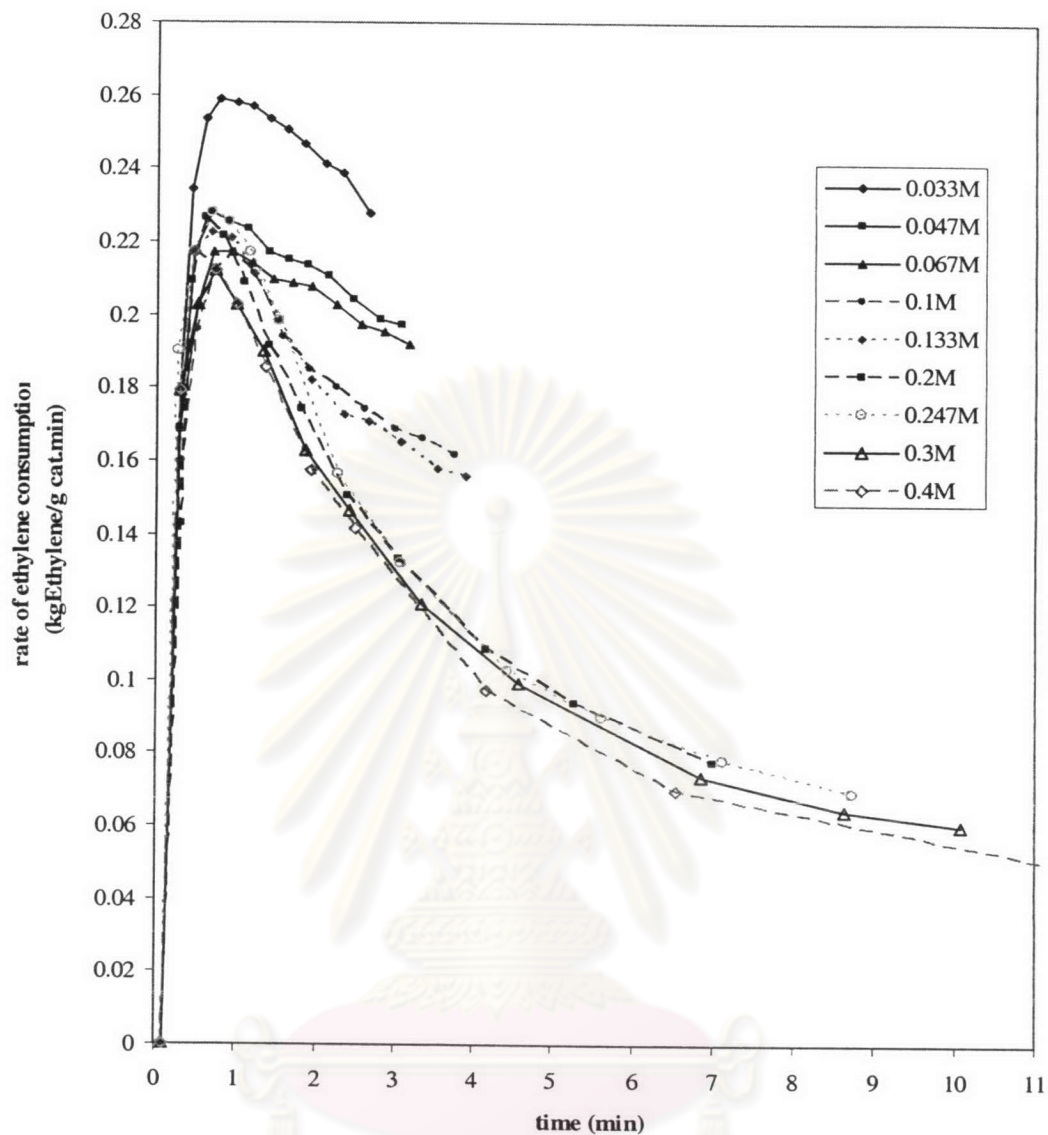


Figure 4.7. Activity profiles for ethylene and norbornene copolymerization with different norbornene concentrations in $\text{rac-Et}[\text{Ind}]_2\text{ZrCl}_2$ catalyst system

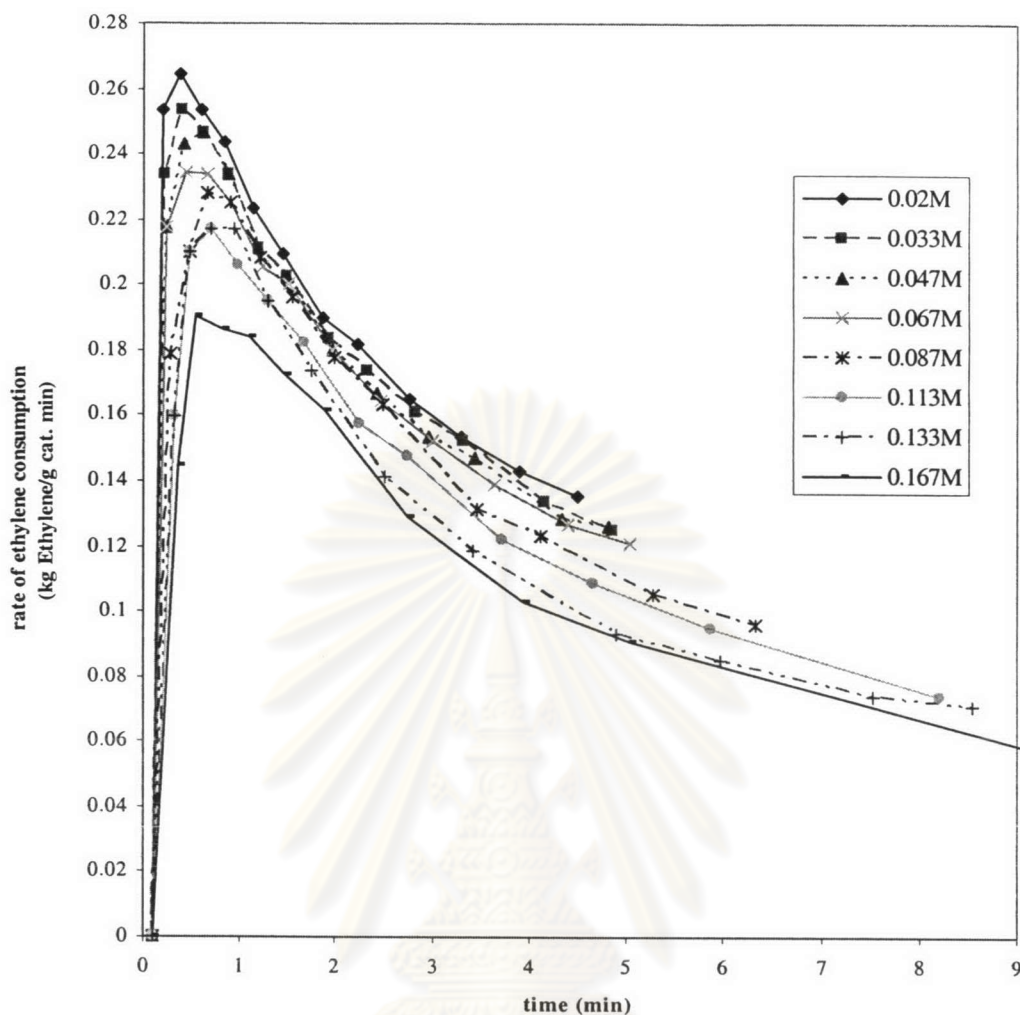


Figure 4.8. Activity profiles for ethylene and norbornene copolymerization with different norbornene concentrations in Cp_2ZrCl_2 catalyst system

4.1.6 The effect of polymerization times and solvents

The effect of polymerization times was investigated in the range of 15 min to 120 min using $\text{rac-Et}[\text{Ind}]_2\text{ZrCl}_2/\text{MAO}$ catalyst system. The copolymerization of ethylene and norbornene was performed in aromatic solvent (toluene and Xylene) or aliphatic solvent (1-hexane, 1-heptane and 1-decane) at 50°C using 0.3 M of norbornene and total solution volume 30 ml. The catalyst concentration and $[\text{Al}]_{\text{MAO}}/[\text{Zr}]$ molar ratio were fixed at $6.7 \times 10^{-5}\text{M}$ and 1000, respectively. Table 4.6 presented the results for the effect of polymerization times on the catalytic activity and norbornene incorporation in the copolymer chain were determined by ^{13}C -NMR spectrometer.

Table 4.6 Catalytic activity and norbornene content in the copolymer chain of different solvents and polymerization times^f

Solvent	Polymerization time (min)	Yields (g)	Catalytic activity* (kg Copolymer/mol Zr.h)	Catalytic activity* (kg Ethylene/mol Zr.h)	NB in the Copolymer (mol%)
Toluene	15	1.34	2677	1660	15.7
	30	1.66	1660	1010	16.0
	60	1.79	894	625	14.1
	90	1.99	667	486	n.d.
	120	2.06	515	385	12.5
	15	0.81	1622	1160	17.5
Xylene	30	1.22	1227	830	15.7
	60	1.97	985	685	14.8
	90	2.04	680	500	n.d.
	120	2.17	542	418	14.1
1-Hexane	n.p.	n.p.	n.p.	n.p.	n.p.
1-Heptane	n.p.	n.p.	n.p.	n.p.	n.p.
1-Decane	n.p.	n.p.	n.p.	n.p.	n.p.

^fCopolymerization condition : $[Zr]=6.7 \times 10^{-5} M$, $[Al]_{MAO}/[Zr]=1000$, $50^{\circ}C$, $0.3 M$ of norbornene, total volume=30 ml , n.d. = not determined, n.p. = can not copolymerized
 * = catalyst not identical to Table 4.5.

Table 4.6 presented the influence of different polymerization times and solvents (toluene or xylene) on the catalytic activity and norbornene incorporation in the polymer chain. For both systems, the catalytic activity decreased with increasing the polymerization times. The effect of different solvents on a decrease of norbornene content in the copolymer when increasing the polymerization time was not observed. One explanation could be due to a mass transfer limitation of ethylene when increasing the polymerization times. The observation that the catalytic activity of ethylene and norbornene copolymerization which performed in toluene higher than xylene for shorter polymerization time, however, norbornene content in the copolymer chain which performed in xylene was higher than that performed in toluene. However, ethylene and norbornene copolymerization was not proceeded in the system which used aliphatic solvents (1-hexane, 1-heptane, 1-decane). The solubility parameter and polarity of aromatic hydrocarbon are higher than aliphatic hydrocarbon (see Table 4.7). The use of an aliphatic hydrocarbon as the polymerization milieu is the low solubility of the catalyst components due to the low polarity of the solvent (Britto *et al.*,2001)

Table 4.7 Solubility parameter of organic compounds

Solvent Type	Solubility Parameter (J/cm ³)*
Toluene	18.346
Xylene	17.838
1-Hexane	14.988
1-Heptane	15.208
1-Decane	15.538

*from data for the heat of vaporization at ambient conditions, the values apply at 25°C (Yaws,1999)

The change in the fraction of crystalline PE with increasing reaction times implies that the concentration of catalytic sites responsible for the formation of the crystalline PE decreased with time; such a transformation has been suggested by Estrada and Hamielec (1994). This decrease can be due to the rapid deactivation of these sites or to the transformation of these sites to sites which incorporated norbornene more readily. It should be pointed out that the norbornene concentration

at the end of the longer run was less than the norbornene concentration at the end of the shorter runs; therefore, the fraction of ethylene homopolymer formed increased with increasing reaction times.

Bergström and Seppälä (1997) observed that by decreasing the polymerization time, the average norbornene content in the reaction mixture for ethylene/norbornene copolymerization must be higher for shorter polymerization time due to the ethylene content also decreased as the polymerization proceeded. The polymer/toluene solution is rather viscous and a decreased mass transfer of ethylene. Furthermore, Bergström *et al.* (2000) expected that the increasing concentration of copolymer in the solution at the same time decreased the solubility of ethylene so that the monomer ratio did not change significantly as a function of time. They found the phenyl groups of phenylnorbornene (PN) are of two types, endo- and exo-substituents, one can assume two types of active sites whose relative concentrations change as a function of time for ethylene/PN copolymerization with $\text{rac-Et[Ind]}_2\text{ZrCl}_2$ /MAO catalyst system.

4.2. Characteristics of copolymer produced with different catalysts

4.2.1. Thermal properties of copolymer and norbornene insertion

The influence of different metallocene catalysts on the thermal properties and norbornene content in ethylene and norbornene copolymers were presented in Table 4.8. The incorporation of norbornene in the copolymer chain was determined by ^{13}C -NMR. The melting temperatures (T_m) of copolymer were evaluated by Differential Scanning Calorimeter (DSC). The ^{13}C -NMR spectrums and DSC curves of the copolymer are also shown in Appendix A and B respectively.

The results displayed in Table 4.7 indicated that the melting temperature (T_m) with increasing the norbornene incorporation in the copolymers. The glass transition temperature (T_g) of ethylene and norbornene depends on the composition of ethylene and norbornene in the copolymer. In general, the norbornene content in the copolymer increases of the glass transition temperature as the copolymer also increases (Bergström and Seppälä, 1997; Bergström *et al.*, 1997; B.-G. Jeong *et al.*,

2003). However, in this investigation this phenomena was not achieved perhaps due to much lower norbornene content in the copolymer chain.

Table 4.8 Melting temperature and norbornene content in the copolymer chain of various metallocene catalysts^f

Type of catalyst	Catalytic activity (kg Copolymer/molZr.h)	T _m (°C)	χ (%)	NB in the Copolymer (mol%)
rac-Et[Ind] ₂ ZrCl ₂	3278	66.4	8.2	7.6
(n-BuCp) ₂ ZrCl ₂	2335	108.0	24.3	2.4
Cp ₂ ZrCl ₂	1476	103.5	20.9	4.7
Cp ₂ TiCl ₂	1161	119.8	36.5	1.6

^fCopolymerization condition : [Zr]=6.7×10⁻⁵M, [Ti]=6.7×10⁻⁵, [Al]_{MAO}/[Zr]=1000, 50°C, 0.018 mole of ethylene consumption, 0.1 M of norbornene, total volume=30 ml

The order of the norbornene contents in the copolymer was rac-Et[Ind]₂ZrCl₂ > Cp₂ZrCl₂ > (n-BuCp)₂ZrCl₂ > Cp₂TiCl₂ catalysts. The highest norbornene content in the copolymer was obtained using rac-Et[Ind]₂ZrCl₂ catalyst due to the wide coordination space of zirconium resulting from the electronic effect and the less steric nature of the ligand structure. The catalytic activity of (n-BuCp)₂ZrCl₂ catalyst was higher than that of Cp₂ZrCl₂ catalyst, however, lower norbornene content in the copolymer was obtained. It could be explained that ethylene preferred coordinated/inserted on the coordination site hindered by the bulky n-Bu group whereas both ethylene and norbornene can be inserted on the other site.

4.2.2 Morphology

The morphologies of ethylene and norbornene copolymer obtained with rac-Et[Ind]₂ZrCl₂, (n-BuCp)₂ZrCl₂, Cp₂ZrCl₂ and Cp₂TiCl₂ catalysts were observed by scanning electron microscopy technique as shown in Figures 4.9-4.12.

The relationship between norbornene incorporation in the copolymers from Table 4.8 and morphologies found that copolymers with lower norbornene content in the copolymer were untidy wrinkle were show in Figures 4.9 and 4.10. It can be seen that with higher norbornene content. in the copolymer, higher uniform

particle were obtained (Figure 4.11). The agglomeration from ethylene and norbornene coordination are occurred when increasing norbornene content in the copolymer obtained from the copolymer produced with $\text{rac-Et}[\text{Ind}]_2\text{ZrCl}_2$ catalyst system (Figure 4.12).

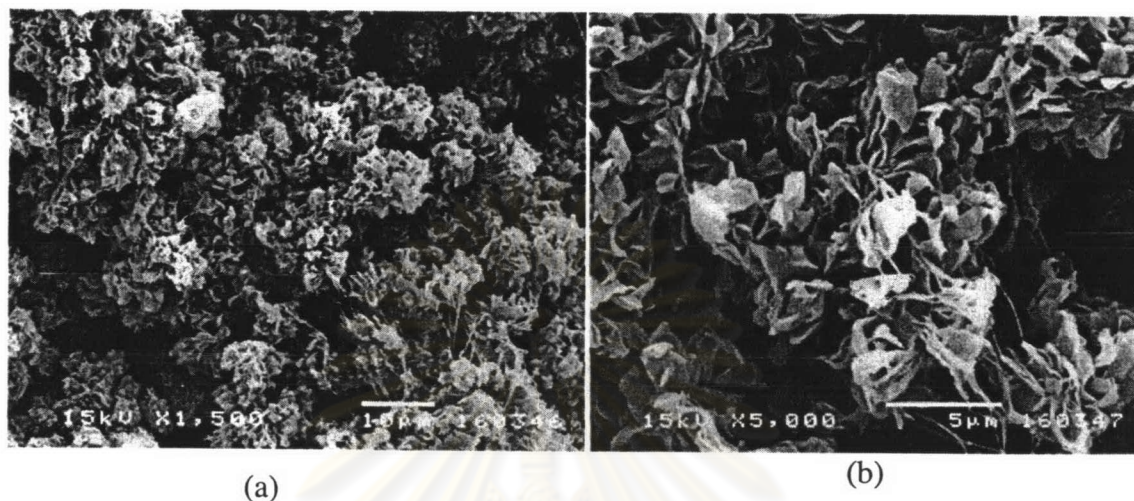


Figure 4.9. Scanning electron microscope image of ethylene and norbornene copolymer produced with $(\text{n-BuCp})_2\text{ZrCl}_2$ (a) $\times 1500$ (b) $\times 5000$ (Copolymerization condition : $[\text{Zr}] = 6.7 \times 10^{-5} \text{M}$, $[\text{Al}]_{\text{MAO}}/[\text{Zr}] = 1000$, 50°C , 0.018 mole of ethylene consumption, 0.1 M of norbornene)

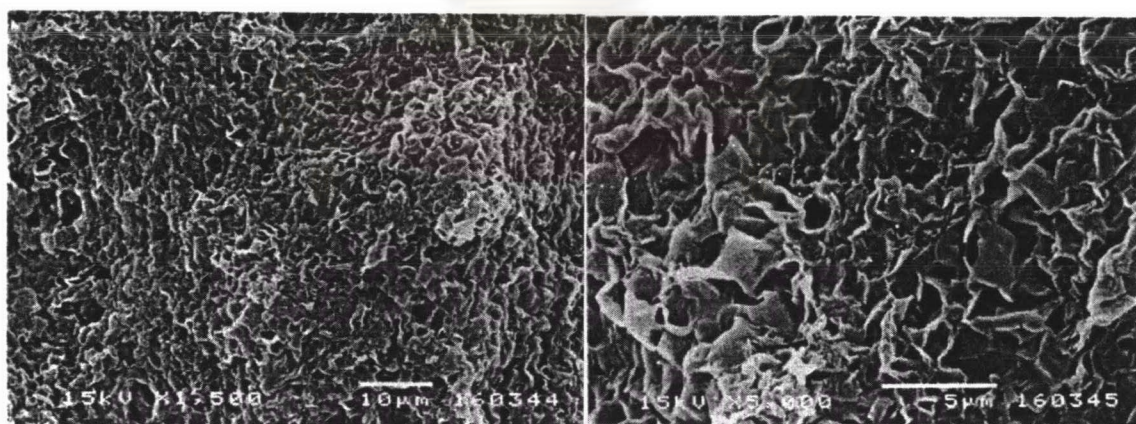


Figure 4.10. Scanning electron microscope image of ethylene and norbornene copolymer produced with Cp_2TiCl_2 (a) $\times 1500$ (b) $\times 5000$ (Copolymerization condition : $[\text{Zr}] = 6.7 \times 10^{-5} \text{M}$, $[\text{Al}]_{\text{MAO}}/[\text{Zr}] = 1000$, 50°C , 0.018 mole of ethylene consumption, 0.1 M of norbornene)

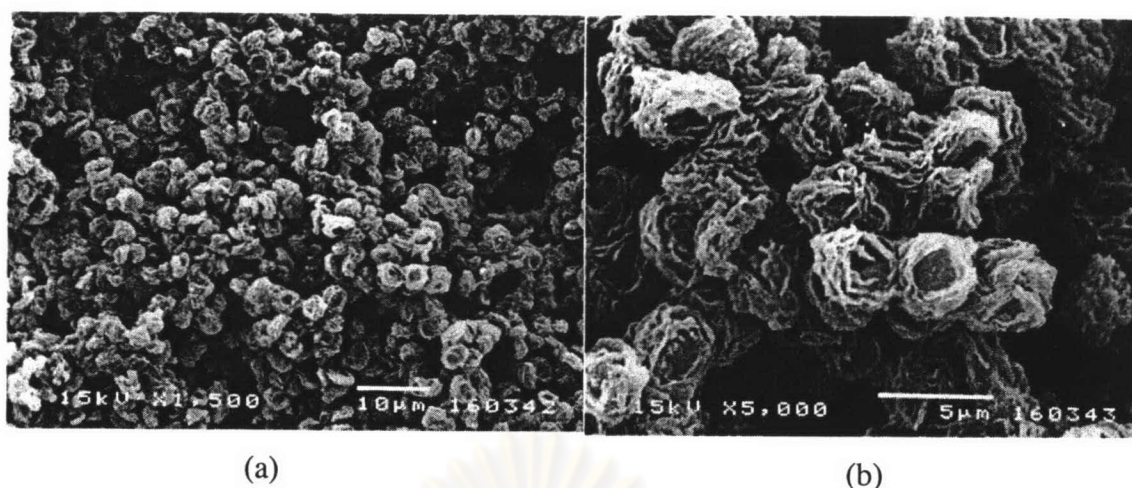


Figure 4.11. Scanning electron microscope image of ethylene and norbornene copolymer produced with Cp_2ZrCl_2 (a) $\times 1500$ (b) $\times 5000$
(Copolymerization condition : $[\text{Zr}] = 6.7 \times 10^{-5} \text{M}$, $[\text{Al}]_{\text{MAO}}/[\text{Zr}] = 1000$, 50°C , 0.018 mole of ethylene consumption, 0.1 M of norbornene)

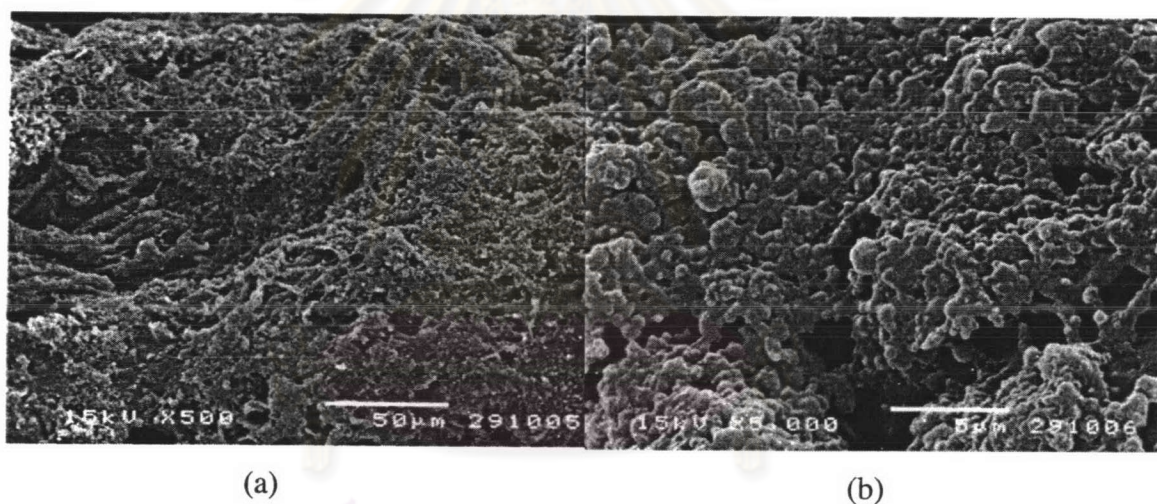


Figure 4.12. Scanning electron microscope image of ethylene and norbornene copolymer produced with $\text{rac-Et}[\text{Ind}]_2\text{ZrCl}_2$ (a) $\times 500$ (b) $\times 5000$
(Copolymerization condition : $[\text{Zr}] = 6.7 \times 10^{-5} \text{M}$, $[\text{Al}]_{\text{MAO}}/[\text{Zr}] = 1000$, 50°C , 0.018 mole of ethylene consumption, 0.1 M of norbornene)

4.3. Characteristics of copolymer produced with different norbornene concentrations

4.3.1 Norbornene insertion in copolymer chain

The norbornene content in the ethylene and norbornene copolymers produced with $\text{rac-Et}[\text{Ind}]_2\text{ZrCl}_2$ catalyst system in the presence of MAO as a

cocatalyst with different norbornene concentrations in the polymerization mixture determined by ^{13}C -NMR were illustrated in Table 4.9. The ^{13}C -NMR spectra are also shown in Appendix A. The results suggested that the copolymer had a random distribution of comonomer insertion.

Table 4.9 Norbornene content in the copolymer chain at different norbornene concentrations^g

Norbornene Concentration		Yields (g)	Catalytic Activity (kg Copolymer/mol Zr.h)	NB in the Copolymer (mol%)
mol/L	mole ($\times 10^3$)			
0	0	0.45	196	0
0.033	1.0	0.70	7875	5.3
0.047	1.5	0.70	6811	5.5
0.067	2.0	0.71	6726	7.4
0.100	3.0	0.72	5812	7.6
0.133	4.0	0.76	5796	11.8
0.200	6.0	0.78	3342	12.7
0.247	7.5	0.52	1790	15.5
0.300	9.0	0.51	1517	15.6
0.400	12.0	0.53	265	17.5

^gCopolymerization condition : $[\text{Zr}] = 6.7 \times 10^{-5} \text{M}$, $[\text{Al}]_{\text{MAO}}/[\text{Zr}] = 1000$, 50°C , 0.018 mole of ethylene consumption, total volume=30 ml

From Table 4.9 it can be seen that higher norbornene concentrations in the polymerization mixture, the higher norbornene content in the copolymer chain. Furthermore, the yields decreased at higher norbornene content in the copolymers may be oligomer can occurred in polymer milieu.

Figures 4.13 and 4.14 presented IR spectra of residual from copolymerization medium which were insoluble and soluble in hexane, respectively. The results revealed that norbornene which can not be consumed in copolymerization was in the insoluble part and ethylene in oligomer formed with short chain polymers was in the soluble part resulted in the peak of C=C (cyclic) and C-H aliphatic (or CH_2 ,

CH₃-stretching) were clearly observed at 1680-1560 cm⁻¹ and 2850-2920 cm⁻¹, respectively (Amon and Phetsom, 1991).

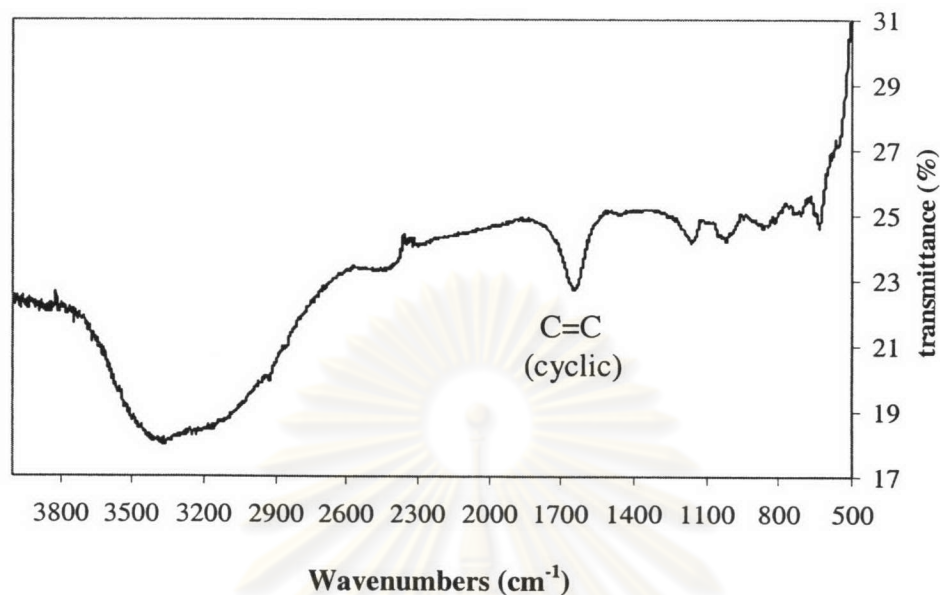


Figure 4.13 Infrared spectrum of residual from copolymerization medium in the insoluble part in hexane

Copolymerization condition : [Zr]= 6.7×10^{-5} M, [Al]_{MAO}/[Zr]=1000, 50°C, 0.133 M of norbornene, 0.018 mole of ethylene consumption, total volume=30 ml

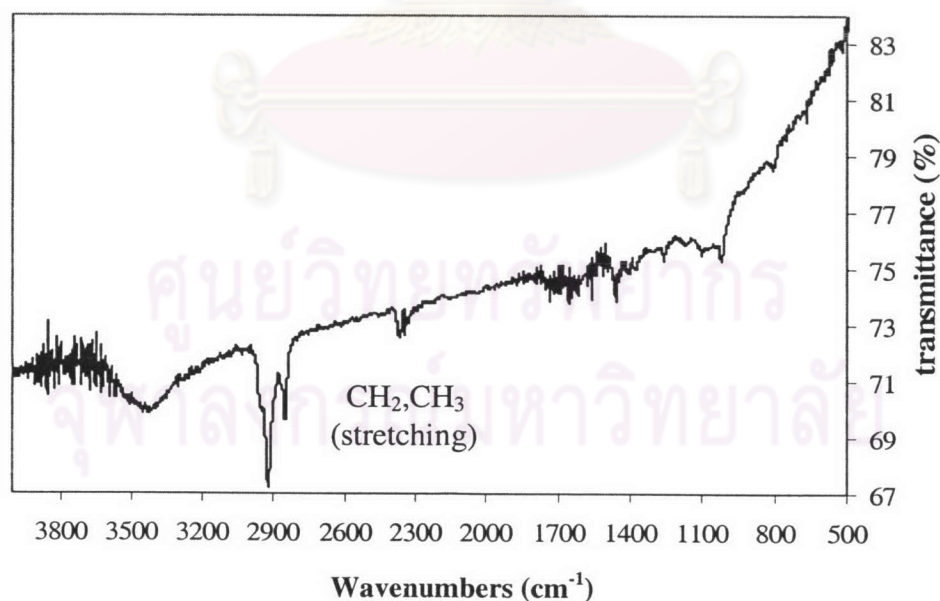


Figure 4.14 Infrared spectrum of residual from copolymerization medium in the soluble part in hexane

Copolymerization condition : [Zr]= 6.7×10^{-5} M, [Al]_{MAO}/[Zr]=1000, 50°C, 0.133 M of norbornene, 0.018 mole of ethylene consumption, total volume=30 ml

On the other hand, yields increased at lower norbornene content in the copolymer. The weights of obtained copolymer higher than total weight of ethylene and norbornene. Table 4.10 revealed that for all copolymers the percent of ash in the products were small and not difference. Percent ash determined by TGA. The results indicated that the contamination of Al metal in obtained copolymers had been small amount and not difference. When investigated the swelling of copolymers in methanol and toluene, the weight of copolymer before and after immersed in methanol are not difference. However, the weight of copolymers after immersed in toluene higher than before. The results indicated that the contamination of hydrocarbon from solvent resulting in the weight of obtained copolymer higher than total weight of ethylene and norbornene.

Table 4.10 The copolymer swelling and ash content in ethylene and norbornene copolymer^h

Norbornene Concentration		Yields (g)	Catalytic Activity (kg Copolymer/mol Zr.h)	% Ash	% Swelling (in toluene)
mol/L	mole ($\times 10^3$)				
0	0	0.45	196	4.3	4.8
0.033	1.0	0.70	7875	3.1	9.1
0.047	1.5	0.70	6811	3.5	10.2
0.067	2.0	0.71	6726	4.1	17.5
0.100	3.0	0.72	5812	4.5	14.2
0.133	4.0	0.76	5796	6.3	5.7
0.200	6.0	0.78	3342	7.8	7.7
0.247	7.5	0.52	1790	6.0	7.2
0.300	9.0	0.51	1517	2.3	6.7
0.400	12.0	0.53	265	1.7	8.2

^hCopolymerization condition : $[Zr]=6.7 \times 10^{-5} M$, $[Al]_{MAO}/[Zr]=1000$, $50^\circ C$, 0.018 mole of ethylene consumption, total volume=30 ml

4.3.2 Morphology

The morphologies of ethylene and norbornene copolymer obtained with $\text{rac-Et[Ind]}_2\text{ZrCl}_2$ catalyst at low and high norbornene concentrations (from Table 4.9) were observed using scanning electron microscopy technique and also compared with homopolymer of ethylene as shown in Figures 4.15-4.24.

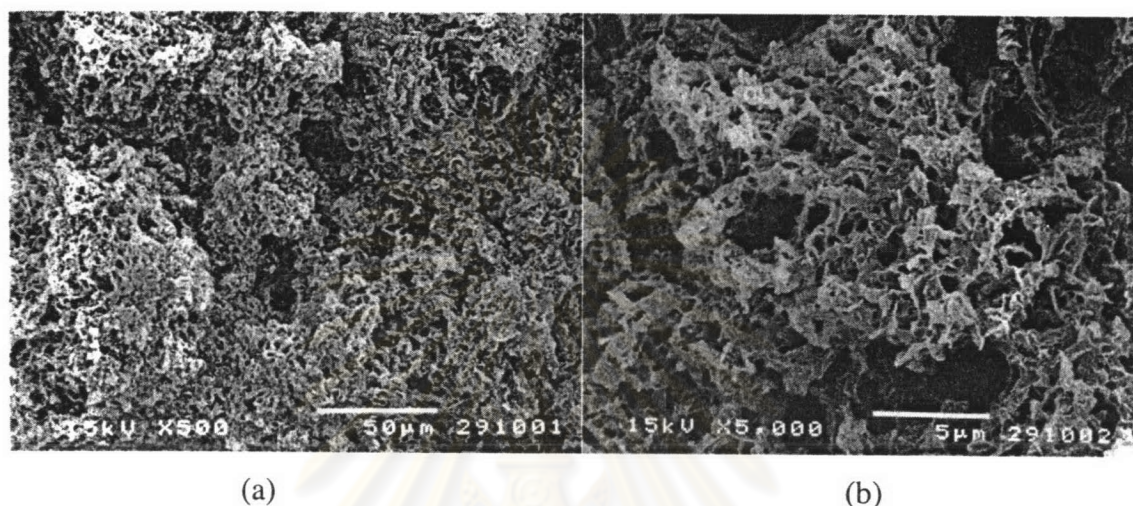


Figure 4.15. Scanning electron microscope image of homopolymer of ethylene (a) $\times 500$ (b) $\times 5000$ (Copolymerization condition : $[\text{Zr}] = 6.7 \times 10^{-5} \text{M}$, $[\text{Al}]_{\text{MAO}}/[\text{Zr}] = 1000$, 50°C , 0.018 mole of ethylene consumption)

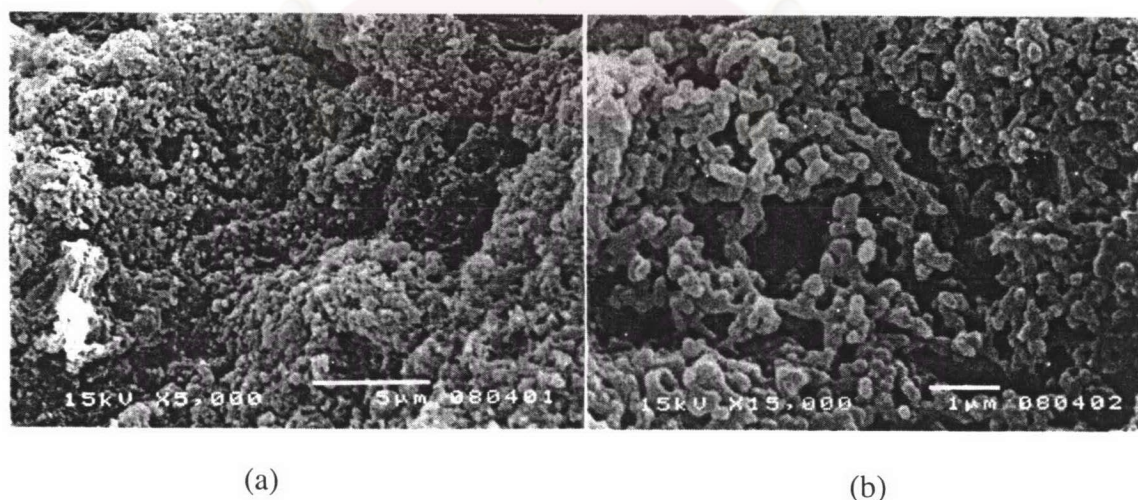


Figure 4.16. Scanning electron microscope image of ethylene and norbornene copolymer (a) $\times 5000$ (b) $\times 15000$ (Copolymerization condition : $[\text{Zr}] = 6.7 \times 10^{-5} \text{M}$, $[\text{Al}]_{\text{MAO}}/[\text{Zr}] = 1000$, 50°C , 0.018 mole of ethylene consumption, 0.033 M of norbornene)

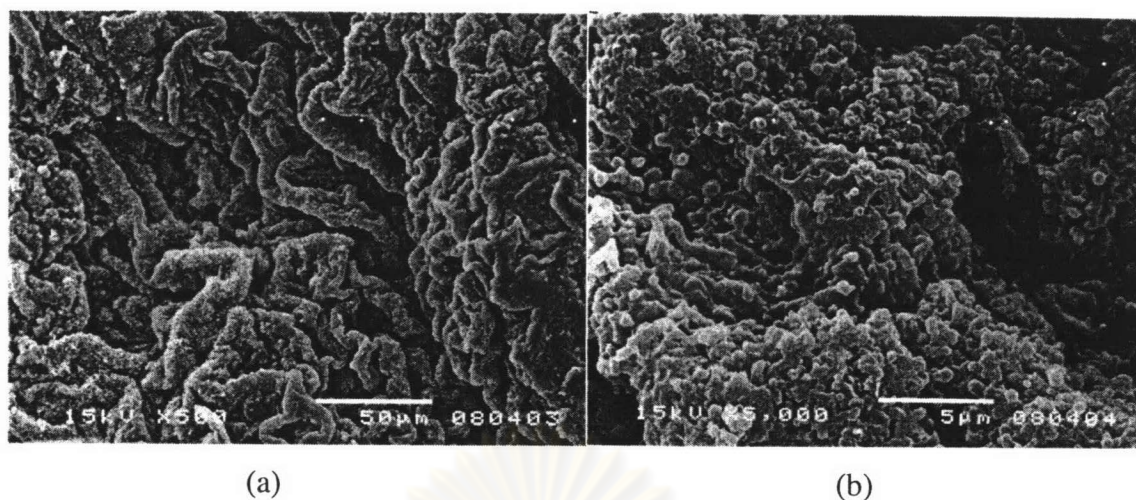


Figure 4.17. Scanning electron microscope image of ethylene and norbornene copolymer (a) $\times 500$ (b) $\times 5000$ (Copolymerization condition : $[\text{Zr}] = 6.7 \times 10^{-5} \text{M}$, $[\text{Al}]_{\text{MAO}}/[\text{Zr}] = 1000$, 50°C , 0.018 mole of ethylene consumption, 0.047 M of norbornene)

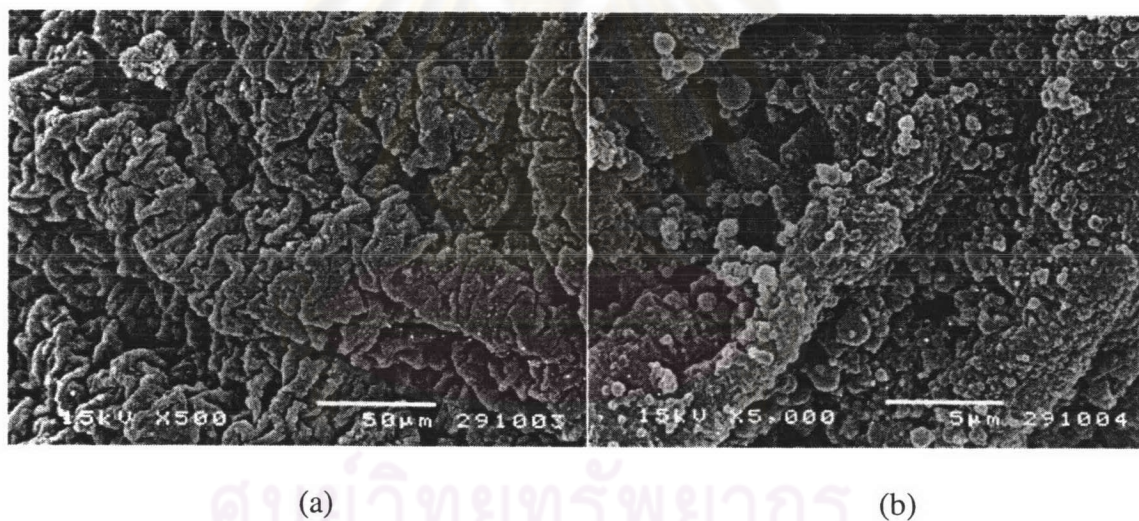


Figure 4.18. Scanning electron microscope image of ethylene and norbornene copolymer (a) $\times 500$ (b) $\times 5000$ (Copolymerization condition : $[\text{Zr}] = 6.7 \times 10^{-5} \text{M}$, $[\text{Al}]_{\text{MAO}}/[\text{Zr}] = 1000$, 50°C , 0.018 mole of ethylene consumption, 0.067 M of norbornene)

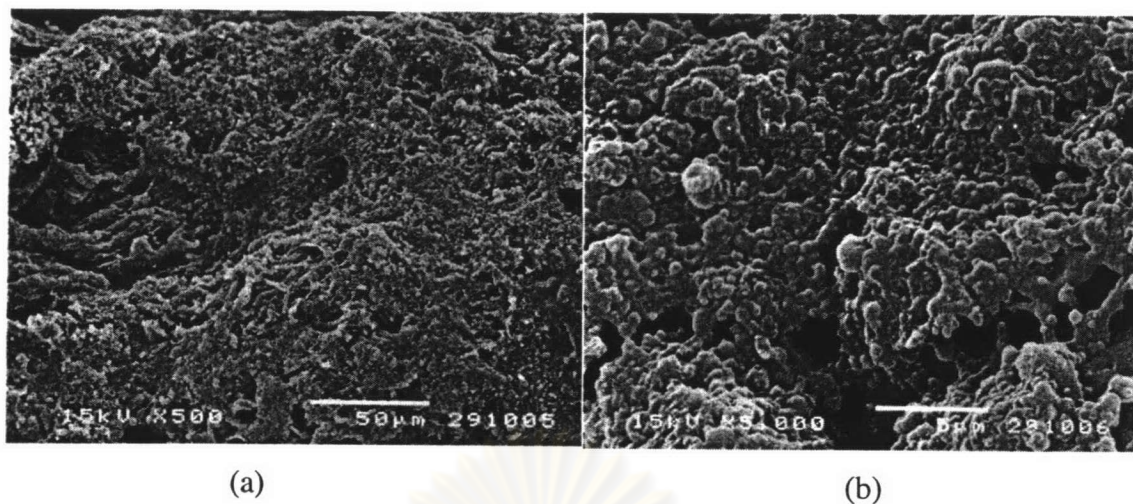


Figure 4.19. Scanning electron microscope image of ethylene and norbornene copolymer (a) $\times 500$ (b) $\times 5000$ (Copolymerization condition : $[\text{Zr}] = 6.7 \times 10^{-5} \text{M}$, $[\text{Al}]_{\text{MAO}}/[\text{Zr}] = 1000$, 50°C , 0.018 mole of ethylene consumption, 0.1 M of norbornene)

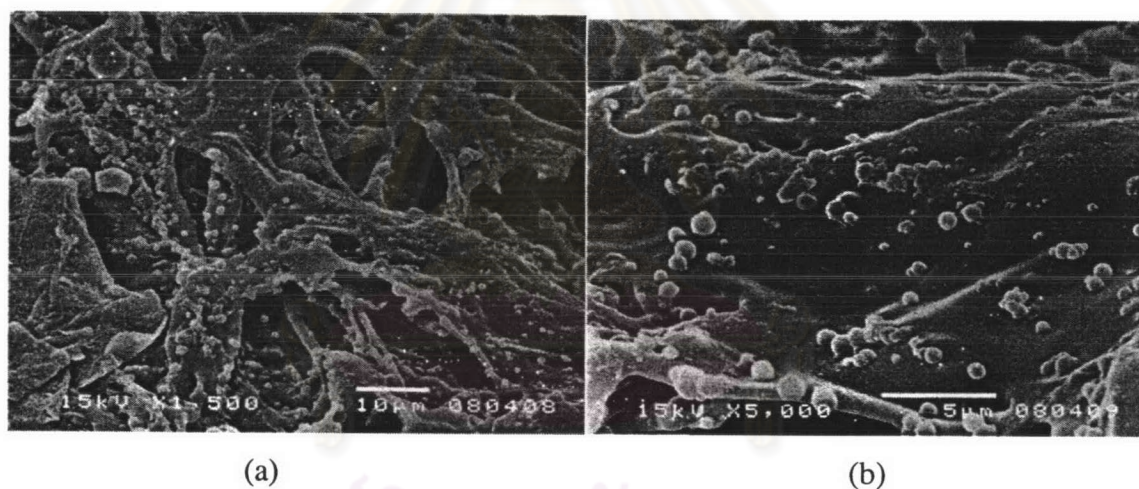


Figure 4.20. Scanning electron microscope image of ethylene and norbornene copolymer (a) $\times 1500$ (b) $\times 5000$ (Copolymerization condition : $[\text{Zr}] = 6.7 \times 10^{-5} \text{M}$, $[\text{Al}]_{\text{MAO}}/[\text{Zr}] = 1000$, 50°C , 0.018 mole of ethylene consumption, 0.133 M of norbornene)

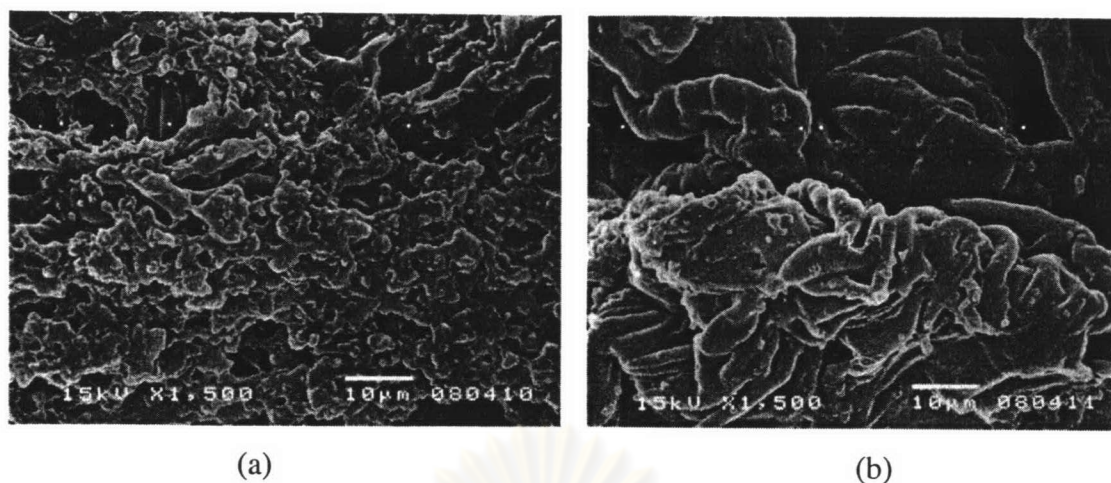


Figure 4.21. Scanning electron microscope image of ethylene and norbornene copolymer (a) $\times 1500$ (b) $\times 1500$ (Copolymerization condition : $[\text{Zr}] = 6.7 \times 10^{-5} \text{M}$, $[\text{Al}]_{\text{MAO}}/[\text{Zr}] = 1000$, 50°C , 0.018 mole of ethylene consumption, 0.2 M of norbornene)

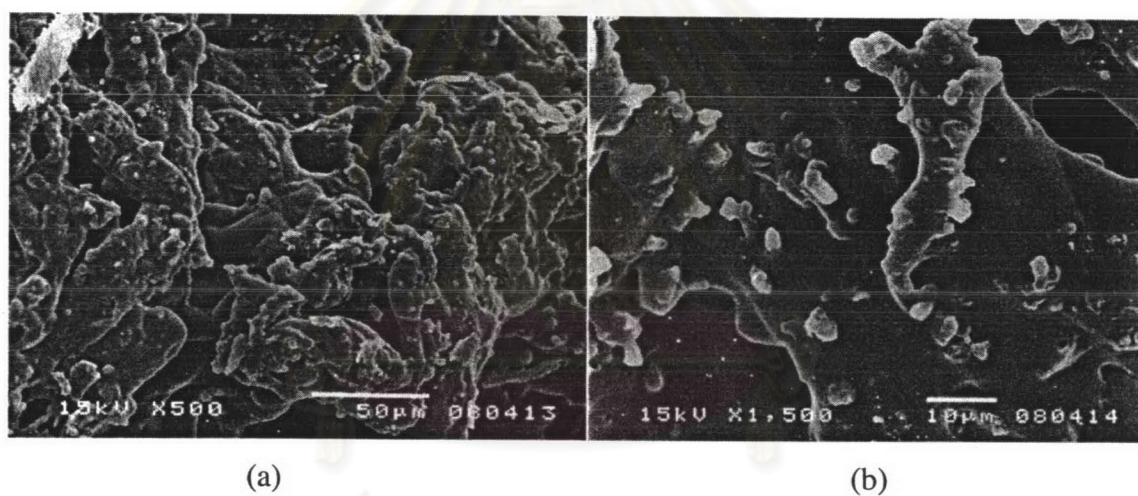


Figure 4.22. Scanning electron microscope image of ethylene and norbornene copolymer (a) $\times 500$ (b) $\times 1500$ (Copolymerization condition : $[\text{Zr}] = 6.7 \times 10^{-5} \text{M}$, $[\text{Al}]_{\text{MAO}}/[\text{Zr}] = 1000$, 50°C , 0.018 mole of ethylene consumption, 0.247 M of norbornene)

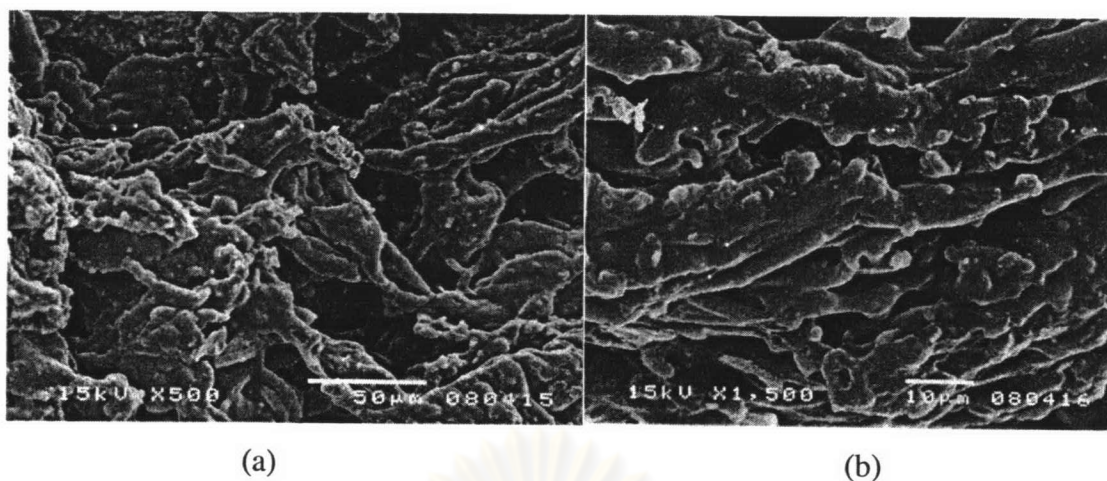


Figure 4.23. Scanning electron microscope image of ethylene and norbornene copolymer (a) $\times 500$ (b) $\times 1500$ (Copolymerization condition : $[Zr]=6.7 \times 10^{-5}M$, $[Al]_{MAO}/[Zr]=1000$, $50^{\circ}C$, 0.018 mole of ethylene consumption, 0.3 M of norbornene)

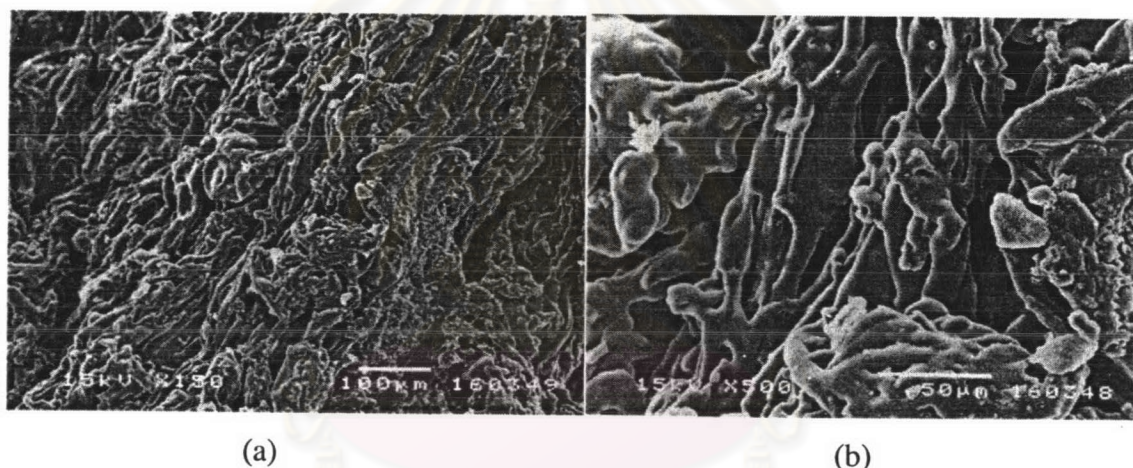


Figure 4.24. Scanning electron microscope image of ethylene and norbornene copolymer (a) $\times 150$ (b) $\times 500$ (Copolymerization condition : $[Zr]=6.7 \times 10^{-5}M$, $[Al]_{MAO}/[Zr]=1000$, $50^{\circ}C$, 0.018 mole of ethylene consumption, 0.4 M of norbornene)

The morphologies of homopolymer of ethylene, which is untidy wrinkle, were shown in Figures 4.15(a) and 14.15(b). The relationship between norbornene incorporation in the copolymers from Table 4.8 and morphologies found that at low norbornene contents, the copolymer exhibited morphologies with laminar shape due to spherical particles agglomerate from ethylene and norbornene coordination (Figures 4.16-4.18). In addition, the agglomeration is higher with high norbornene contents in the copolymer, thus the laminar shape was not occurred (Figures 4.19-4.24).