

CHAPTER V

RESULTS & DISCUSSIONS

5.1. Catalyst characterization

5.1.1. Characterization of $[\eta^5\text{-(indenyl)}]\text{titaniumtrichloride}$ by NMR technique

The nuclear magnetic resonance spectroscopy is a method for elucidating the structure of organic and inorganic species. The prepared IndTiCl_3 catalyst is characterized by ^1H NMR and ^{13}C NMR spectroscopy.

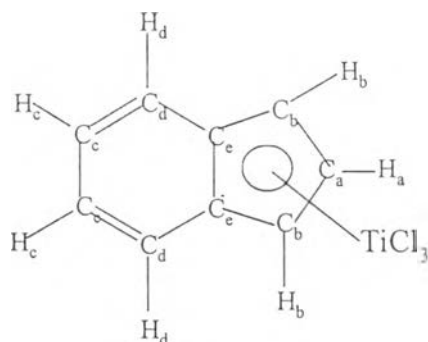


Figure 5.1. The chemical structure of $[\eta^5\text{-(indenyl)}]\text{titaniumtrichloride}$

Table 5.1 ^1H NMR data of $[\eta^5\text{-(indenyl)}]\text{titaniumtrichloride}$

chemical shift (δ , ppm)	multiplicity	position of protons	number of protons	coupling constant (J, Hz)
7.11	triplet	a	1	3.36, 3.36
7.21	doublet	b	2	3.05
7.53	multiplet	c	2	-
7.83	multiplet	d	2	-

^1H NMR spectroscopy of the synthesized IndTiCl_3 catalyst was shown in Figure 5.2-5.4. The identification of ^1H NMR spectrum of the prepared catalyst is assigned to the set of protons, referred to Figure 5.1, as summarized in Table 1.1. The chemical shift (δ) 7.11 ppm is the position of protons a, H_a . The signal of H_a is split into a triplet by coupling with two equivalents nearby protons, H_b . The intensities pattern of this triplet is 1:2:1. The coupling constants, J_{ab} and J_{bc} , are the same at 3.36 Hz as shown in Figure 5.2. The 1:1 doublet of H_b is due to successive splitting by H_a at the chemical shift 7.21 ppm and the coupling constant, J_{ab} is 3.05 Hz. Signal of H_c and H_d appears as a multiplet due to coupling between H_c and H_d . The chemical shift of H_c and H_d are 7.53 and 7.83 ppm, respectively. The number of H_a , H_b , H_c and H_d are 1, 2, 2 and 2, respectively, as indicated by the sizes of absorption peaks.

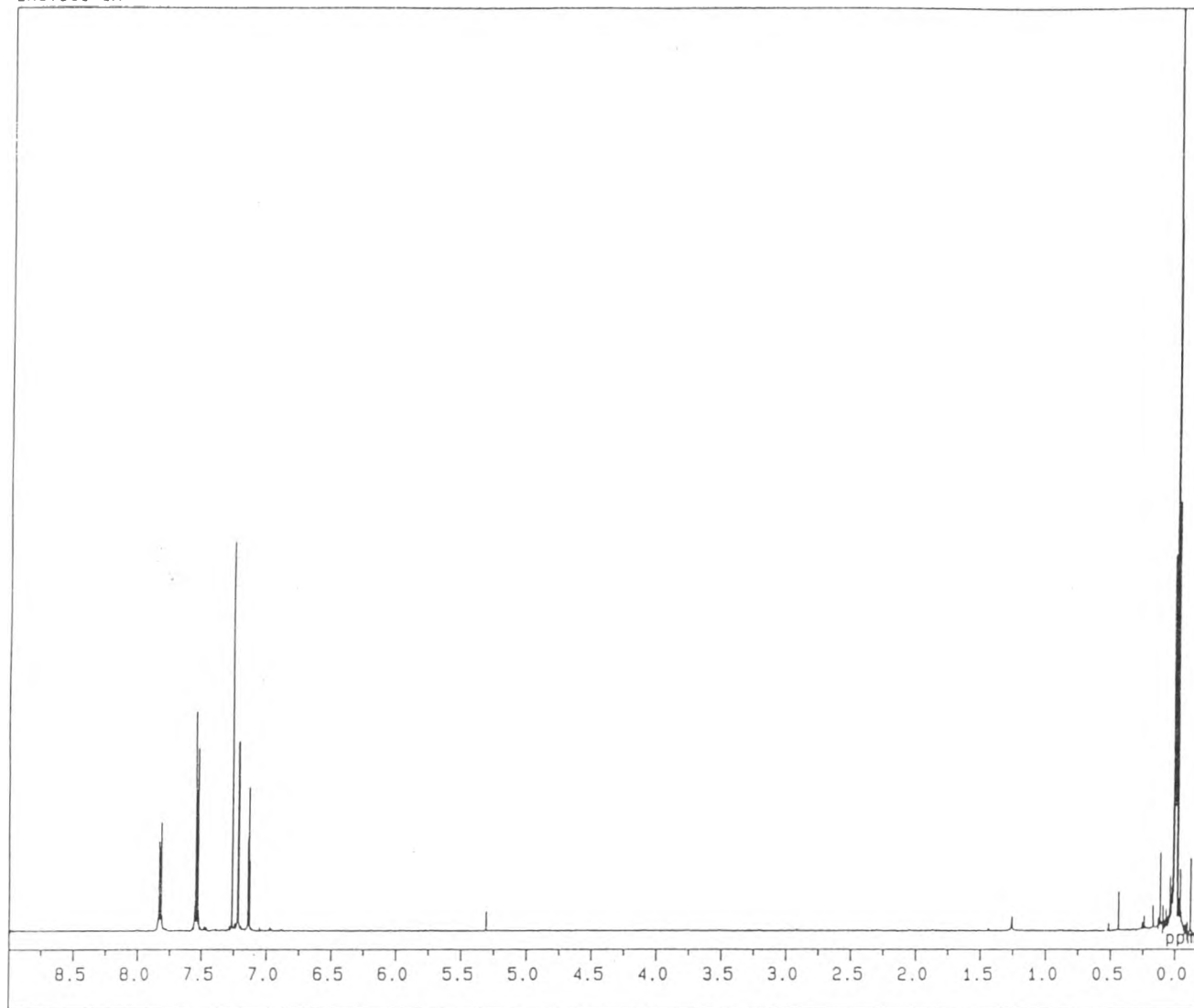
Table 5.2 ^{13}C NMR data of $[\eta^5\text{-(indenyl)}]\text{titaniumtrichloride}$

chemical shift (δ , ppm)	position of carbons	number of carbons
117.034	b	2
123.367	a	1
127.168	d	2
129.964	c	2
130.951	e	2

In the ^{13}C NMR spectrum as shown in Figure 5.5, the chemical shift values of each carbon for the prepared catalyst are following: C_b , 117.034 ppm; C_a , 123.367 ppm; C_d , 127.168 ppm; C_c , 129.964 ppm; C_e , 130.951. The sizes of absorption peaks are related to the number of carbons in the catalyst molecule as shown in Table 5.2.

The ^1H NMR and ^{13}C NMR data of the synthesized IndTiCl_3 catalyst in Table 5.1 and 5.2, respectively, shows nearly the same values in the literature[44].

IndTiCl₃-1H



15-SEP-1998 09:05:49.68

* CHULALONGKORN UNIVERSITY *
* JNM-A500 *

SFILE : [.WM0]IndTiCl₃-1H
COMNT : IndTiCl₃-1H

EXMOD : SINGL
IRMOD : NON
POINT : 32768
FREQU : 10000.00 Hz
SCANS : 16
DUMMY : 4
ACQTM : 3.2768 sec
PD : 3.0000 sec
RGAIN : 18
PW1 : 5.85 usec
OBNUC : 1H
OBFREQ : 500.00 MHz
OBSET : 162410.00 Hz

IRNUC : 1H
IRFREQ : 500.00 MHz
IRSET : 162410.00 Hz
IRATN : 120
IRRPW : 55.0 usec
IRBP1 : 30
IRBP2 : 6
IRRNS : 0

ADBIT : 16
CTEMP : 25.9 c
CSPED : 10 Hz
SLVNT : CDCL₃
RESOL : 0.31 Hz
BF : 0.00 Hz
REFVL : 0.00 ppm
XE : 4601.14 Hz
XS : 289.15 Hz

OPERATOR :

Figure 5.2. ¹H NMR spectrum of [η⁵-(indenyl)]titaniumtrichloride

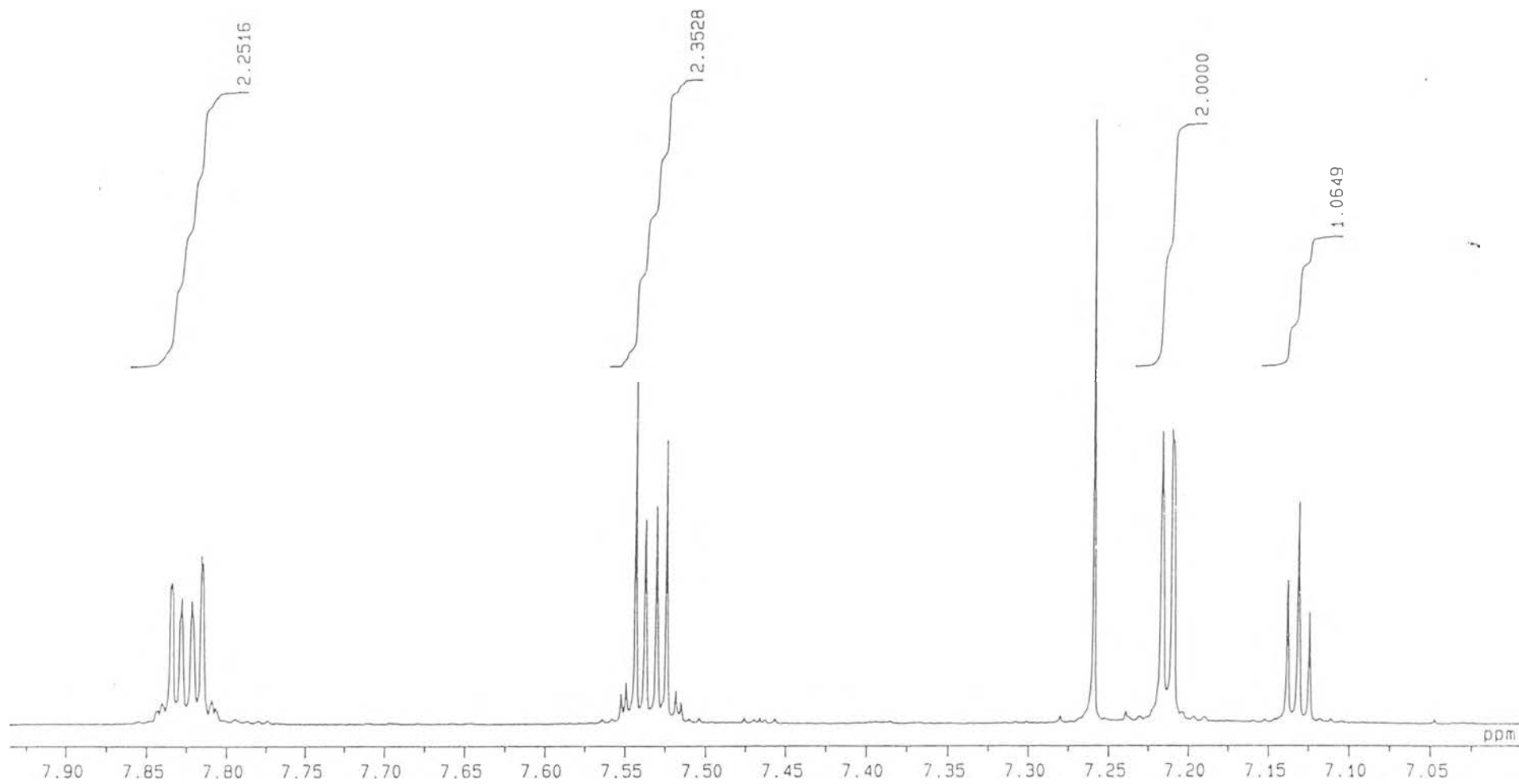


Figure 5.3. ^1H NMR spectrum of $[\eta^5\text{-(indenyl)}]\text{titaniumtrichloride}$

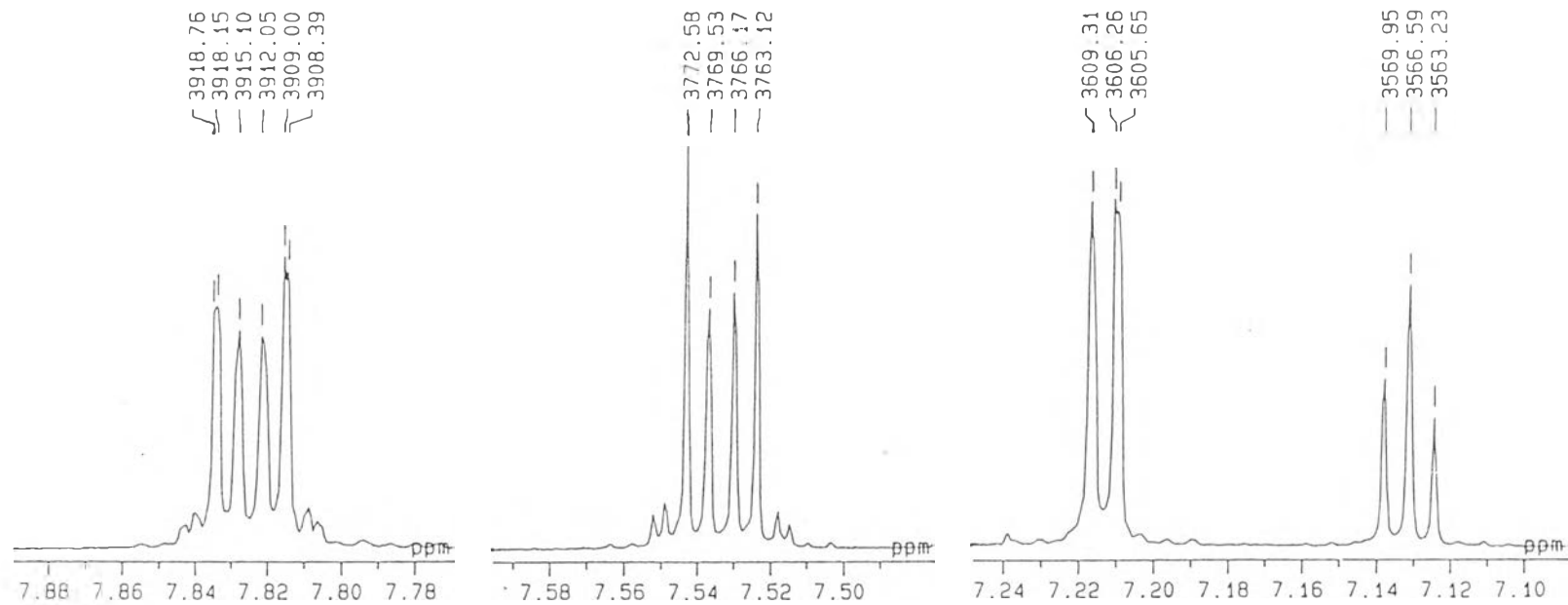
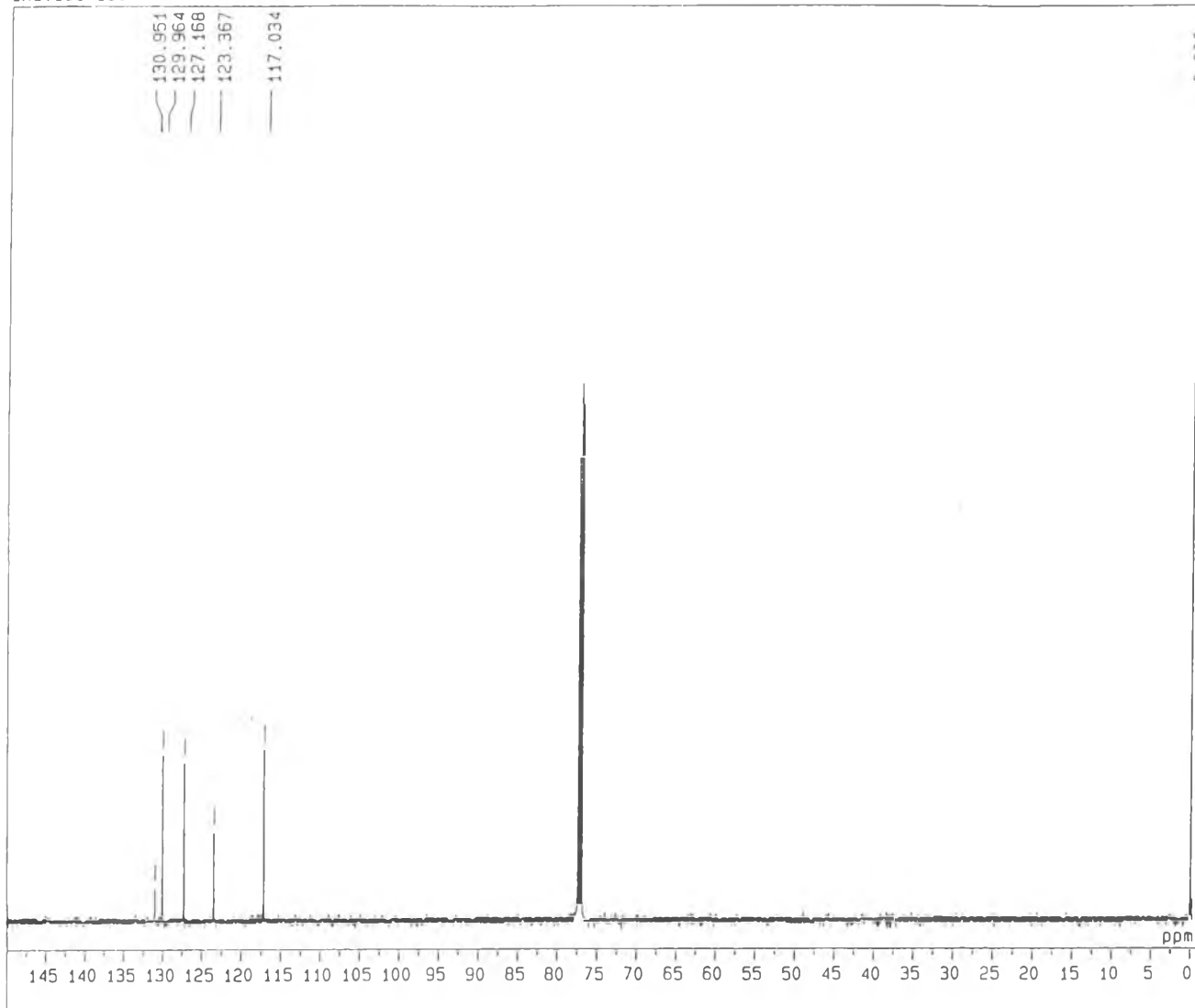


Figure 5.4. ^1H NMR spectrum of $[\eta^5\text{-(indenyl)}]\text{titaniumtrichloride}$

IndTiCl-13C



15-SEP-1998 10:18:28.42

* CHULALONGKORN UNIVERSITY *
* JNM-A500 *

SFILE : [.WMO]IndTiCl-BCM
COMNT : IndTiCl-13C

EXMOD : SINGL
IRMOD : BCM
POINT : 16384
FREQU : 33898.31 Hz
SCANS : 1487
DUMMY : 4
ACQTM : 0.4833 sec
PD : 2.0000 sec
RGAIN : 23
PW1 : 4.90 usec
OBNUC : 13C
OBFRQ : 125.65 MHz
OBSET : 127958.00 Hz

IRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 162410.00 Hz
IRATN : 120
IRRPW : 55.0 usec
IRBP1 : 30
IRBP2 : 6
IRANS : 0

ADBIT : 16
CTEMP : 26.2 c
CSPED : 10 Hz
SLVNT : CDCL3
RESOL : 2.07 Hz
BF : 2.07 Hz
REFVL : 0.00 ppm
XE : 18987.11 Hz
XS : 3282.45 Hz

OPERATOR :

Figure 5.5. ^{13}C MNR spectrum of $[\eta^5\text{-(indenyl)}]\text{titaniumtrichloride}$

5.2. Polymerization of styrene with prepared and commercial methylaluminoxane (MAO) as cocatalyst without catalyst

From the study of styrene polymerization by using prepared MAO without the catalyst (blank test), polystyrene was produced at any condition as shown in Table 5.3. Whereas replacing prepared MAO by commercial MAO, it were the opposite results, polystyrene was not produced. It was expected that trimethylaluminum (TMA) which is a reactant for the synthesis of prepared MAO was presented in the prepared MAO solution and styrene polymerization may be caused by the residual TMA. From this result, the role of TMA on styrene polymerization was studied in the following section.

Table 5.3 Blank test with prepared MAO^a

Polymerization temperature (°C)	PS yield (g)
50	1.2058
70	1.1596
90	1.1593

^aPolymerization conditions : [MAO] 0.28 mol/l, [styrene] 0.87 mol/l, toluene 38 ml, polymerization time 60 min.

5.3. Polymerization of styrene with trimethylaluminum (TMA)

5.3.1. The effect of polymerization time

The effect of various polymerization times on styrene polymerization using TMA initiator was investigated. The polymerization conditions were conducted in toluene 21.75 ml., [styrene] 1.2889 mol/l., [TMA] 0.4148 mol/l and polymerization temperature at 50°C with five different polymerization times viz., 10, 30, 60, 90, and 120 min. The experimental results and the relationship between % yield of polystyrene and polymerization time are shown in Table 5.4 and Figure 5.6, respectively.

Table 5.4 Yield of polystyrene produced at different polymerization times^b

polymerization time, min.	yield, g	PS yield, wt.%
10	1.3635	30.0993
30	1.4128	31.1876
60	1.4185	31.3135
90	1.4200	31.3466
120	1.4223	31.3974

^b Polymerization conditions: 50°C, [styrene] = 1.2889 mol/l., [TMA] = 0.4148 mol/l., toluene = 21.75 ml.

As shown in Figure 5.6, % yield of polystyrene rapidly increases at the early polymerization time and then % yield of polystyrene begins to get constant after 60 min. until terminal time at 120 min. According to a slight increase of % PS yield after 60 min, It was expected that the carbocation active species formed by the reaction of TMA and styrene monomer were shielded with the produced polystyrene. Hence, the polymerization time about 60 min. is the sufficient suitable time for the styrene polymerization, and a standard condition with using in further experiment.

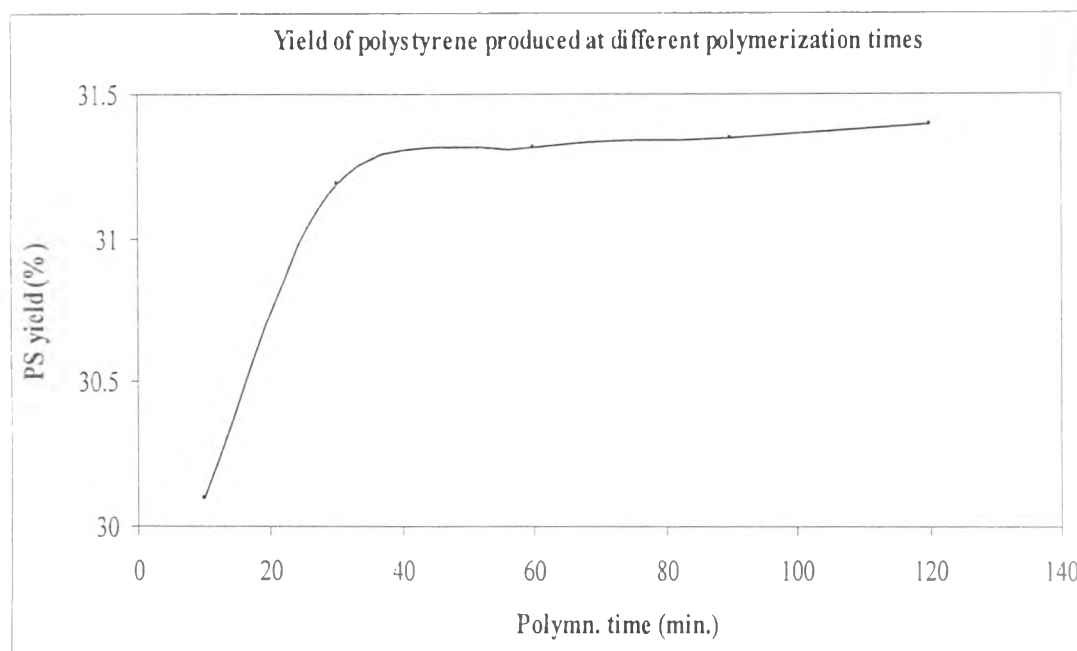
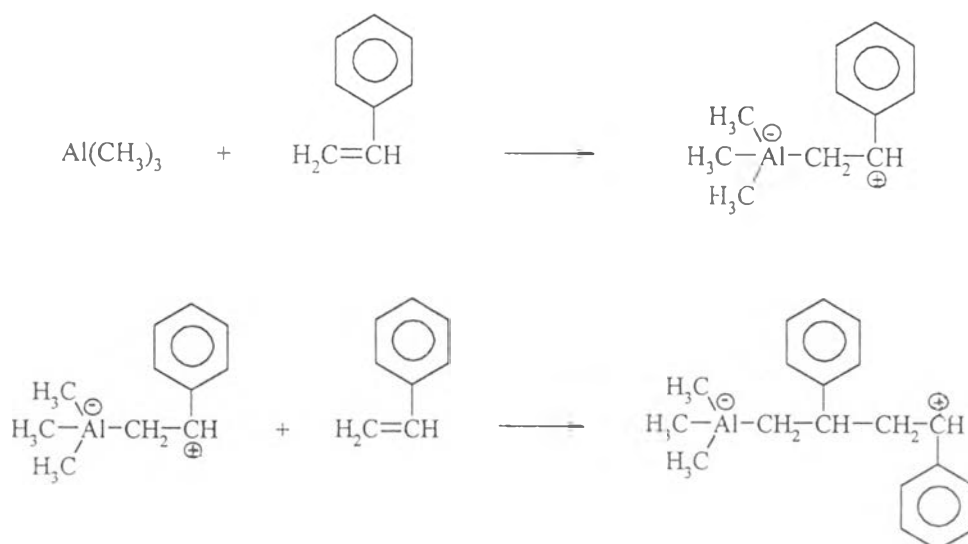
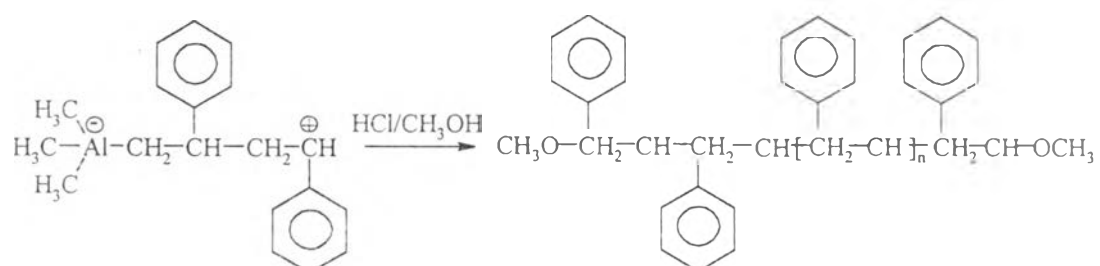


Figure 5.6. Yield of polystyrene produced at different polymerization times

5.3.2. The effect of polymerization temperature

Styrene polymerization using TMA initiator was performed at various polymerization temperatures in toluene. Polymerization was carried out in toluene 21.75 ml, [styrene] 1.2889 mol/l, [TMA] 0.4148 mol/l and polymerization time was 60 min. with four different polymerization temperatures viz., 30, 50, 70 and 90°C. The results are summarized in Table 5.5. The relation of % yield of polystyrene and the polymerization temperature is shown in Figure 5.7.

From Figure 5.7, % yield of polystyrene decreased with an increase in polymerization temperature (T_p) in the range between 30 and 90°C. The highest of catalytic activity, within the range of temperature varied, appeared at 30°C. It was known that TMA is lewis acid and a good electron withdrawing [284, 285]. Therefore, it could be effectively used as initiator for the cationic polymerization of styrene. The mechanism of the polymerization is probably proposed as the following (Scheme 5.1).

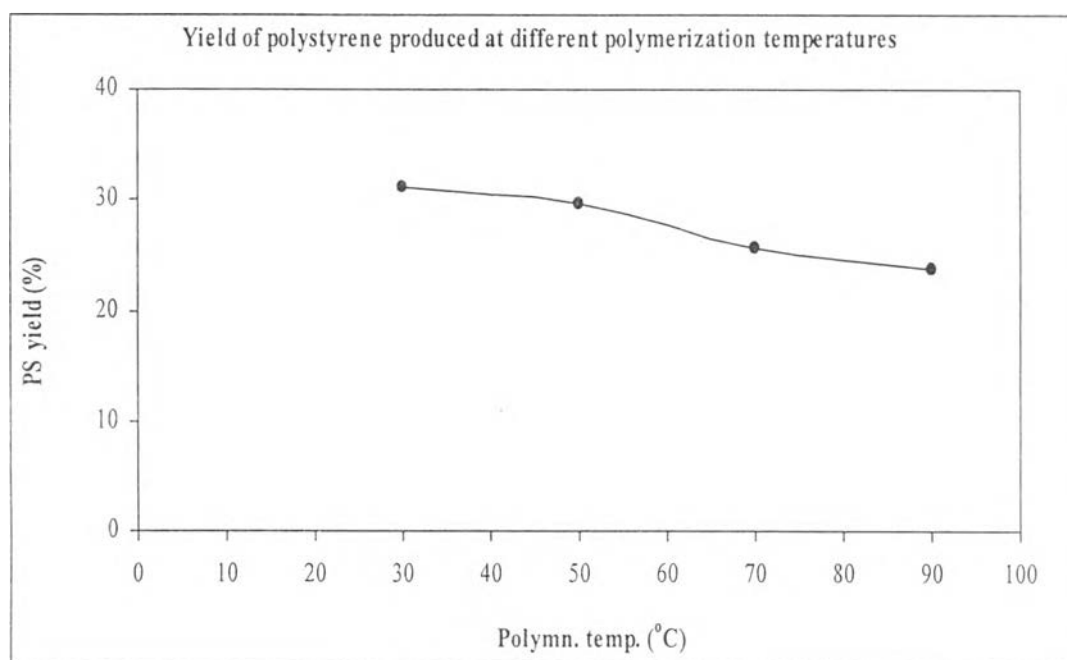
InitiationPropagationTermination

Scheme 5.1. The cationic styrene polymerization

Table 5.5 Yield of polystyrene produced at different polymerization temperatures^c

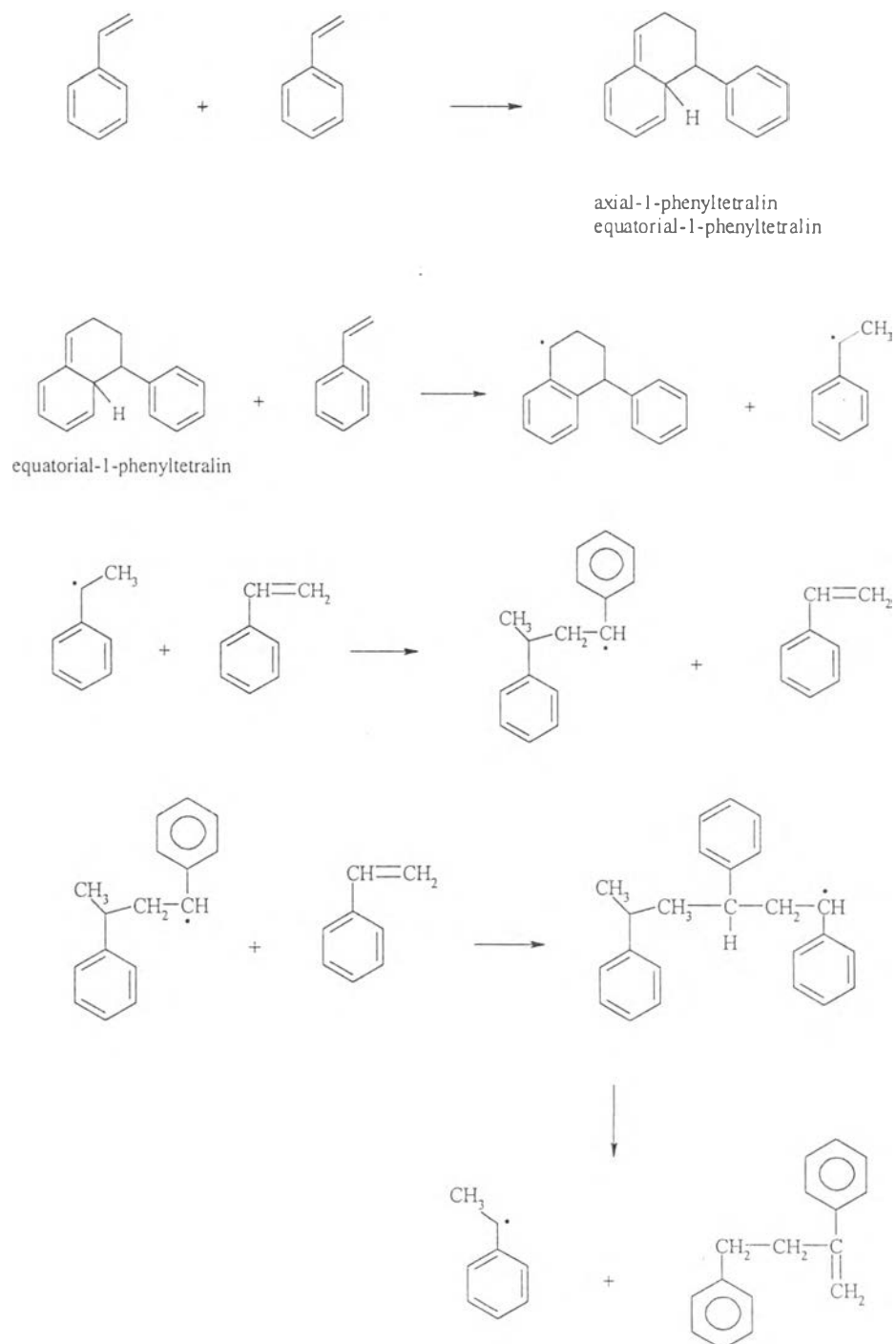
polymerization temperature, °C.	yield, g	PS yield, wt. %
30	1.4134	31.2009
50	1.3464	29.7219
70	1.1557	25.5121
90	1.0730	23.6865

^c Polymerization conditions: time 60 mins., [styrene] = 1.2889 mol/l., [TMA] = 0.4148 mol/l., toluene = 21.75 ml.

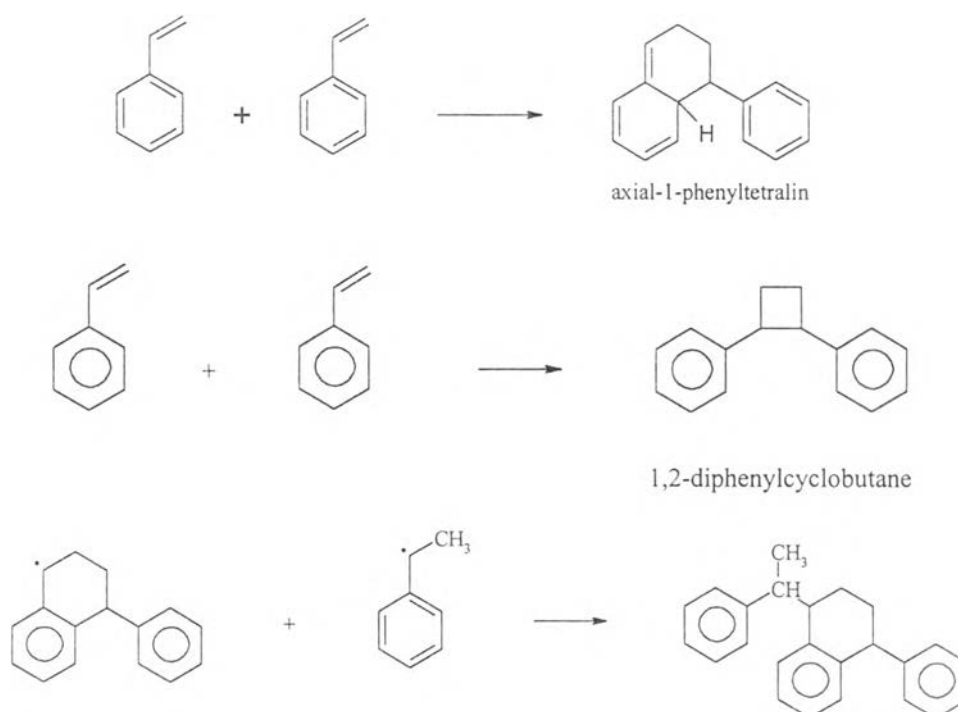
**Figure 5.7.** Yield of polystyrene produced at different polymerization temperatures

From the above experimental results, it was found that the catalytic activity gradually decreased at higher temperature. Hence, it is expected that the radical polymerization coincide with cationic polymerization. At higher temperature, styrene can be dissociated without a chemical initiator to radical species by heating and these radical species can polymerize styrene as shown in Scheme 5.2. The radical

styrene polymerization significantly leads to several side reactions, which are shown in the below Scheme 5.3.



Scheme 5.2. The radical styrene polymerization [277]



Scheme 5.3. The side reactions in radical styrene polymerization [277]

The produced side reactions may decrease the amount of styrene monomer by converting them to the other by-products such as 1,2-diphenylcyclobutane. From the previous reason, % yield of polystyrene reduced with the increasing temperature. At low temperature, the radical polymerization might be hard to occur whereas at high temperature showed the contradictory result.

5.3.3. The effect of trimethylaluminium concentration

The styrene polymerization using various TMA concentrations was studied. The polymerization was performed in toluene 21.75 ml, styrene 0.0435 mol, polymerization time 120 min. and polymerization temperature at 50°C with five different TMA concentrations viz., 0.1391 mol/l, 0.4148 mol/l, 0.5442 mol/l, 0.7186 mol/l, and 0.9662 mol/l. The experimental results are summarized in Table 5.6 and % yield of polystyrene versus the concentration of TMA is shown in Figure 5.8.

Table 5.6 Yield of polystyrene produced with different concentrations of TMA^d

TMA volume, ml.	TMA concentration, mol/l.	yield, g	PS yield, wt.%
2	0.1391	0.0000	0.0000
7	0.4148	1.1614	25.6380
10	0.5442	1.7832	39.3642
15	0.7186	2.6282	58.0177
25	0.9662	3.9000	86.0927

^d Polymerization conditions: time 120 mins., 50 °C, styrene = 0.0435 mol.,
toluene = 21.75 ml.

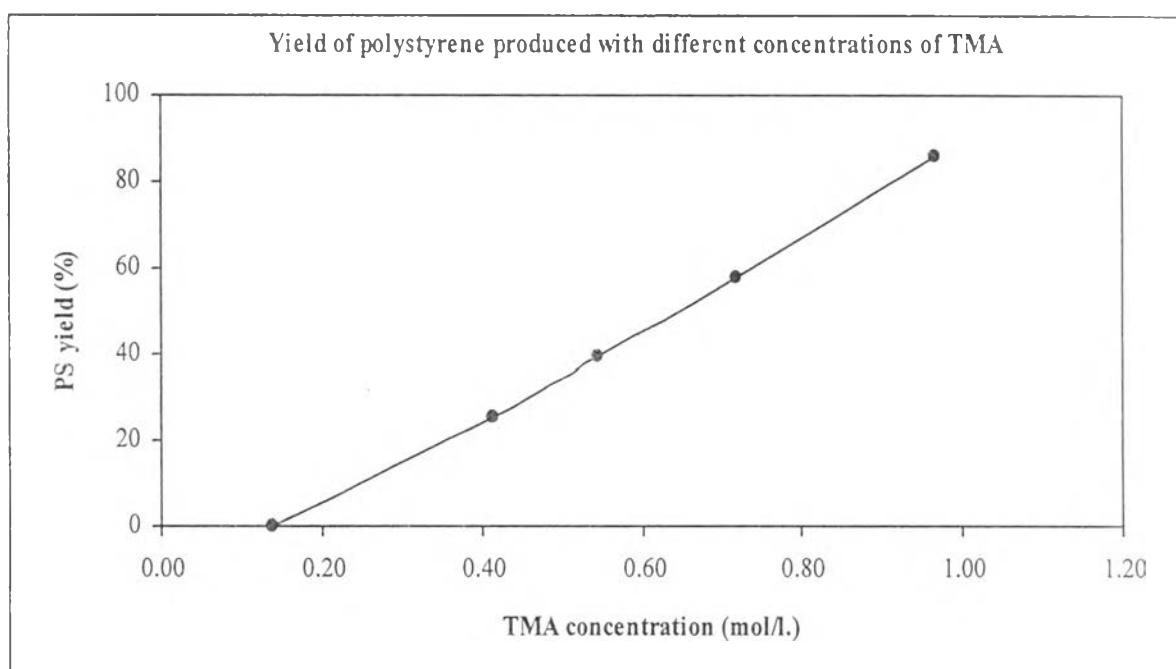


Figure 5.8. Yield of polystyrene produced with different concentrations of TMA

As shown in Figure 5.8, it was not found polystyrene at TMA concentration below 0.1391 mol/l. % Yield of polystyrene increased linearly with the increment of TMA concentration exceeding 0.1391 mol/l. At higher trimethylaluminum concentration, it is reasonable to suggest that the active carbocations for the styrene polymerization can be more introduced. These carbocations at high trimethylaluminum concentration had the higher chance to react with styrene monomer than that at low trimethylaluminum concentration. Hence, % yield of polystyrene with the higher trimethylaluminum concentration was on the increase.

In the section 5.2, it was observed that there was polystyrene formation in the blank test with prepared MAO. Consequently, it is assumed that the residual amount of TMA in prepared MAO more than 0.1391 mol/l.

5.4. Polymerization of styrene with IndTiCl_3 catalyst

5.4.1. The effect of concentration of titanium on catalytic activity

The effect of IndTiCl_3 catalyst concentration on activity was tested at the polymerization conditions of toluene 21.75 ml., Al/Ti mole ratio of 900, styrene/Ti mole ratio of 4000, temperature 50°C and polymerization time 2 hrs. The results are listed in Table 5.7 and the catalytic activity of different IndTiCl_3 catalyst concentrations is shown in Figure 5.9.

Table 5.7 Catalytic activity of different catalyst concentrations^e

catalyst concentration mole Ti/l.	catalytic activity, gPS/mmol Ti.hr
4.96×10^{-5}	24831
1.01×10^{-4}	24940
1.99×10^{-4}	49220
2.65×10^{-4}	57270
3.09×10^{-4}	38715

^epolymerization conditions: catalyst = IndTiCl_3 , cocatalyst = MAO, $[\text{Al}]/[\text{Ti}] = 900$, $[\text{styrene}]/[\text{Ti}] = 400$, time 120 mins., 50°C , Toluene 21.75 ml.

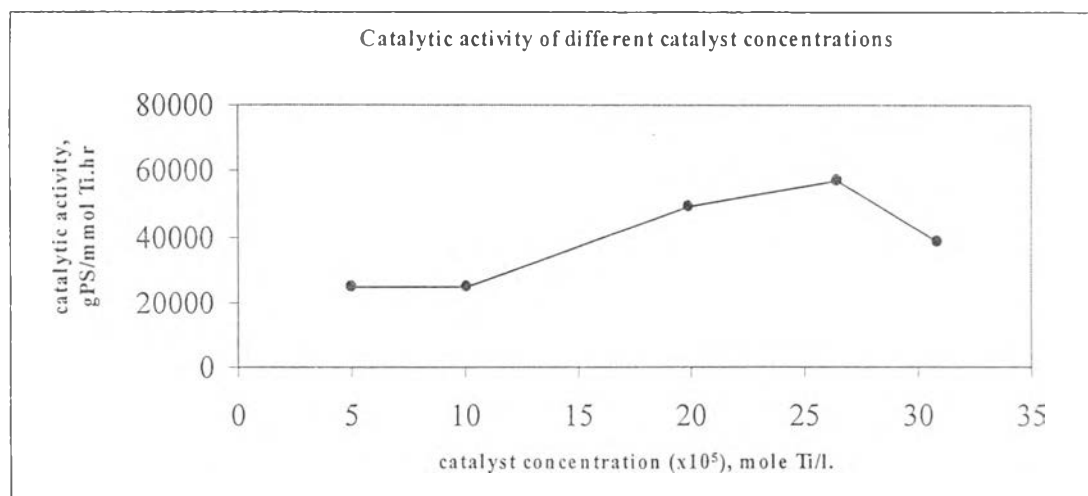


Figure 5.9. Catalytic activity of different catalyst concentrations

Figure 5.9 shows the catalytic activity strongly affected from the concentration of catalyst. It is found that at the concentration of Ti less than 2.65×10^{-4} mol/l, the catalytic activity increased with increasing Ti concentration. The maximum activity appears at Ti concentration of 2.65×10^{-4} mol/l and then the catalytic activity obviously decreases with the increment of Ti concentration. The rise of activity at low concentration of Ti could be attributed to the increase of active species $[C^*]$ [282, 286]. The decrease of activity with higher Ti concentration might be caused by the decline of $[C^*]$ due to the dimerization of C^* forming inactive species and/or due to the excessive MAO- C^* complexation [Scheme 5.6; deactivation]. For the MAO- C^* complexation at high Ti concentration, the absolute concentration of MAO in the reaction system was increased to keep the constant Al/Ti mole ratio [282].

5.4.2. The effect of polymerization temperature on catalytic activity

Styrene polymerization was conducted in 21.75 ml. of toluene using IndTiCl_3 and MAO as catalyst and cocatalyst, respectively, at different polymerization temperatures. Polymerization was carried out at Al/Ti mole ratio of 900, styrene concentration as 1.06 mol/l, polymerization time as 2 hrs. with three different polymerization temperatures viz., 30, 50 and 70 °C. The results for the influence of temperature on catalytic activity using the $\text{IndTiCl}_3/\text{MAO}$ catalyst system are presented in Table 5.8 and Figure 5.10.

Table 5.8 Catalytic activity of different polymerization temperatures (T_p)^f

polymerization temperature, T_p , °C	catalytic activity, gPS/mmol Ti.hr
30	32430
50	57270
70	54855

^f polymerization conditions: catalyst = IndTiCl_3 , cocatalyst = MAO, $[\text{Ti}] = 2.65 \times 10^{-4}$ mol/l, $[\text{Al}] = 0.2386$ mol/l, $[\text{styrene}] = 1.06$ mol/l, time = 120 mins., toluene 21.75 ml.

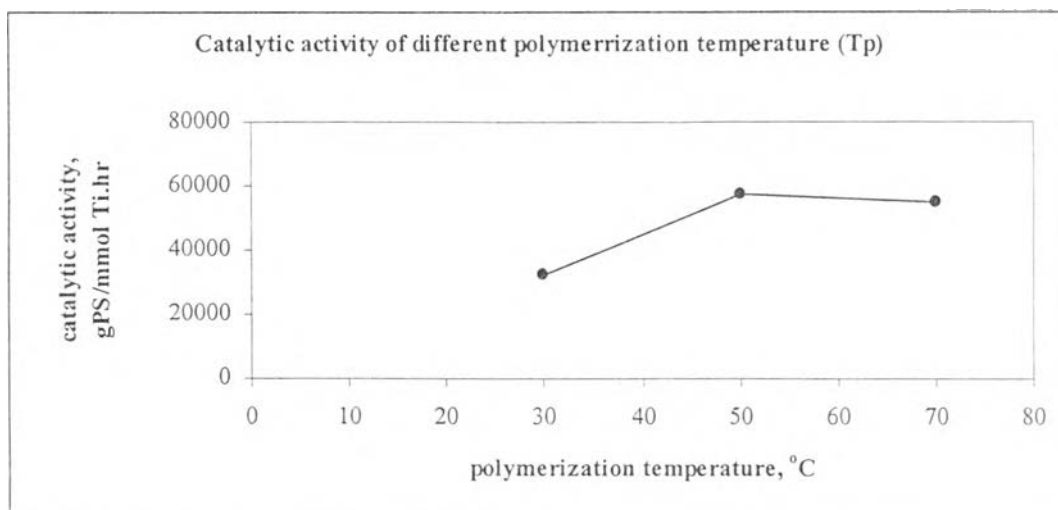
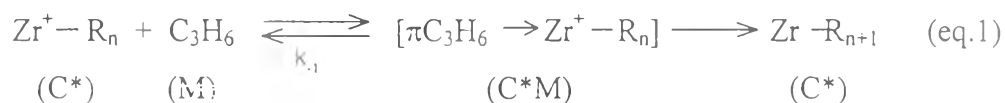


Figure 5.10. Catalytic activity of different polymerization temperature (T_p)

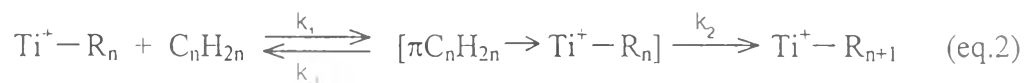
Figure 5.10 shows the catalytic activity of various polymerization temperatures for styrene polymerization catalyzed with $\text{IndTiCl}_3/\text{MAO}$ catalyst system. The catalytic activity increases with the increasing polymerization temperature (T_p) until maximum catalytic activity is reached at 50°C and slowly decreases later.

The variation of catalytic activity versus T_p catalyzed by the $\text{IndTiCl}_3/\text{MAO}$ catalyst system for styrene polymerization is a convex curve (Figure 5.10) as same as that catalyzed by the $\text{C}_4\text{H}_8\text{Si}(\eta^5\text{-Ind})_2\text{ZrCl}_2/\text{MAO}$ catalyst system for propylene polymerization reported by Tsai&Chien (Figure 5.11). According to Tsai&Chien [283] in the low temperature range, the activity increases with the rise of T_p . This might be reasonably attributed to the process of activated insertion. The subsequent decrease of activity with increasing T_p in the high temperature range indicated some kind of deactivation of the propagation species due to a shift of an equilibrium in the process.

It is postulated in the Cossee mechanism for Ziegler-Natta catalyst [289] that the formation of a π -complex of an olefin with a transition metal site was the prerequisite for the olefin insertion. The propagation process could be written as



From the above mention, it was explained in the case of IndTiCl₃/MAO catalyst system that the activity increased with the rise of T_p because of the activated insertion process. Subsequently, in the decrease of the activity with the increase of T_p in the high temperature range indicated some type of the propagation species deactivation because of the dissociation of the π-olefin complex. Therefore, the decline of activity with the increase of T_p might be due to a backward shift of equilibrium (see in eq.2).



Likewise, the Cossee mechanism for Ziegler-Natta catalysis could be also applied to metallocene catalyst systems for olefin polymerization. Therefore, the mechanism of IndTiCl₃/MAO catalyst system for styrene coordination polymerization could be written as shown in Scheme 5.4.

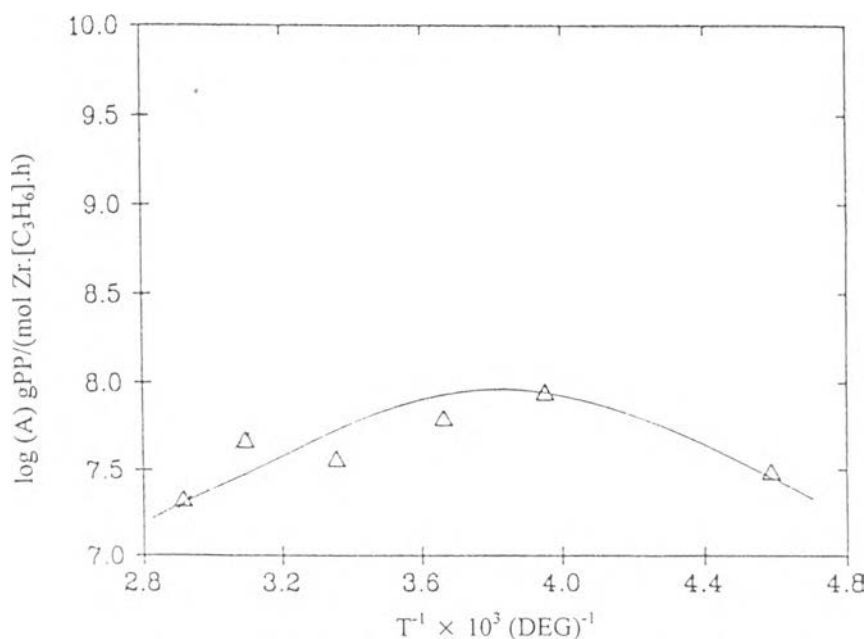
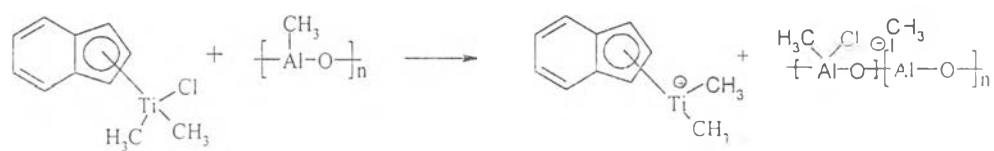
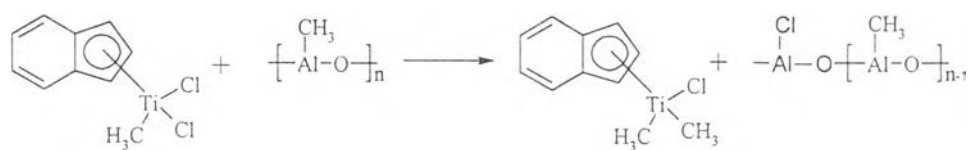
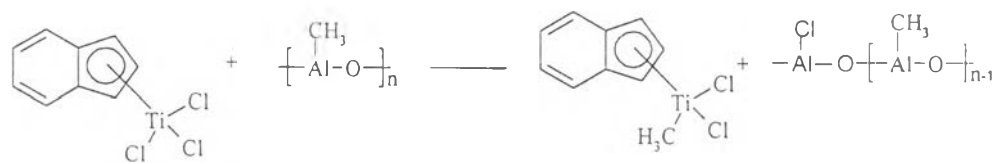
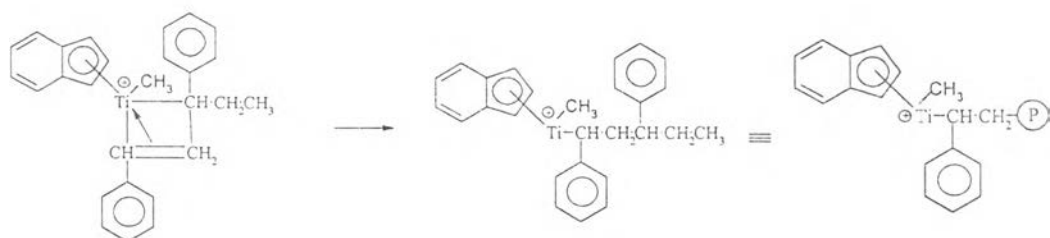
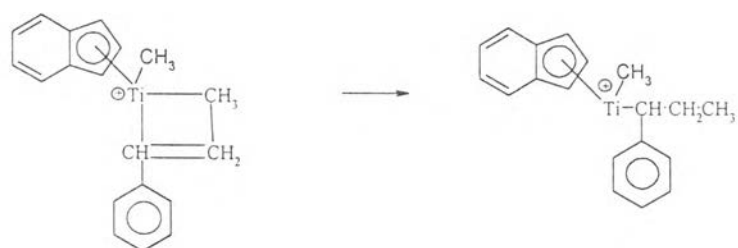


Figure 5.11. Variation of $\log(A)$ versus T_p^{-1} for propylene polymerizations catalyzed by $\text{C}_4\text{H}_8\text{Si}(\eta^5\text{-Ind})_2\text{ZrCl}_2/\text{MAO}$ catalyst system[283]

Initiation

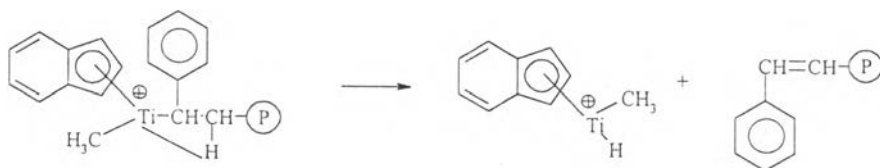


Propagation

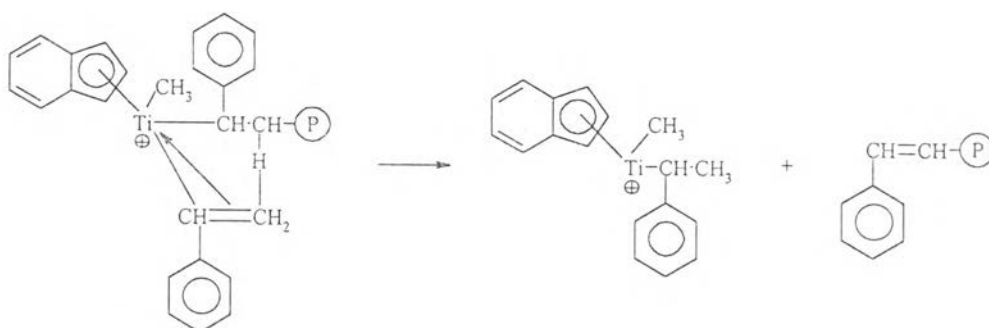


Termination

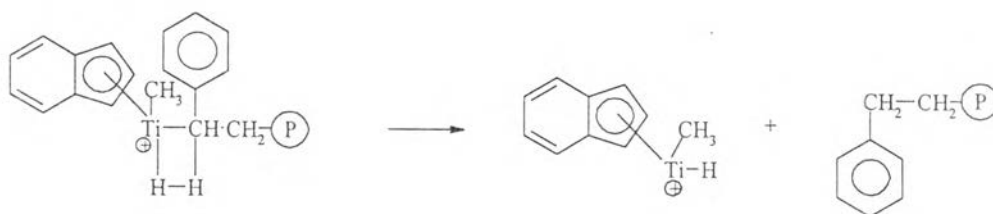
a) By β -H elimination



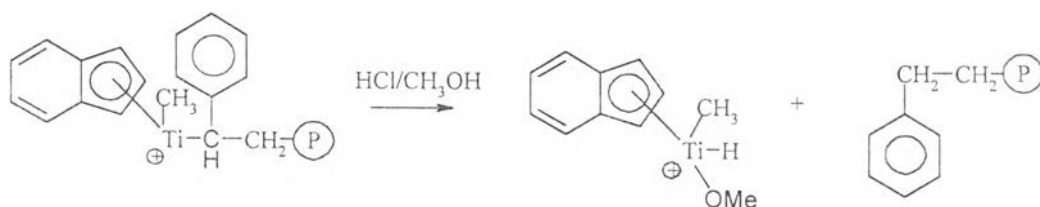
b) By β elimination with H transfer to monomer



c) By hydrogenation



d) quenching by $\text{HCl}/\text{CH}_3\text{OH}$



Scheme 5.4. The Cossee mechanism for $(\eta^5\text{-Indenyl})\text{titaniumtrichloride}$ catalyst

5.4.3. The effect of Al/Ti mole ratio on catalytic activity

Styrene polymerization conducted in toluene using IndTiCl_3 as catalyst and MAO as cocatalyst at different Al/Ti mole ratios was studied. In a typical polymerization experiment, the appropriate amount of cocatalyst was injected into a known constant volume of styrene monomer in 21.75 ml of toluene and the reaction was started by catalyst injection. Polymerization was carried out at 50°C , styrene monomer 0.0345 mole, Ti 8.615×10^{-6} mol, and polymerization time as 2 hrs. with four different mole ratios of Al/Ti viz., 900, 2000, 4000, and 6000. The results were summarized in Table 5.9. The relation between the catalytic activity and Al/Ti mole ratio is shown in Figure 5.12. The catalytic activity was referred to gram of produced polystyrene per millimole of titanium per unit hour of polymerization time, [gPS/mmol Ti. \times hr].

Table 5.9 Catalytic activity of different Al/Ti mole ratios^b

Al/Ti mole ratio	catalytic activity, (gPS/mmol Ti \times hr)
900	57270
2000	116265
4000	208035
6000	198950

^b polymerization conditions: catalyst = IndTiCl_3 , cocatalyst = MAO, Ti = 8.615×10^{-6} mol, styrene = 0.0345 mol, polymerization temperature = 50°C , 120 mins., Toluene 21.75 ml.

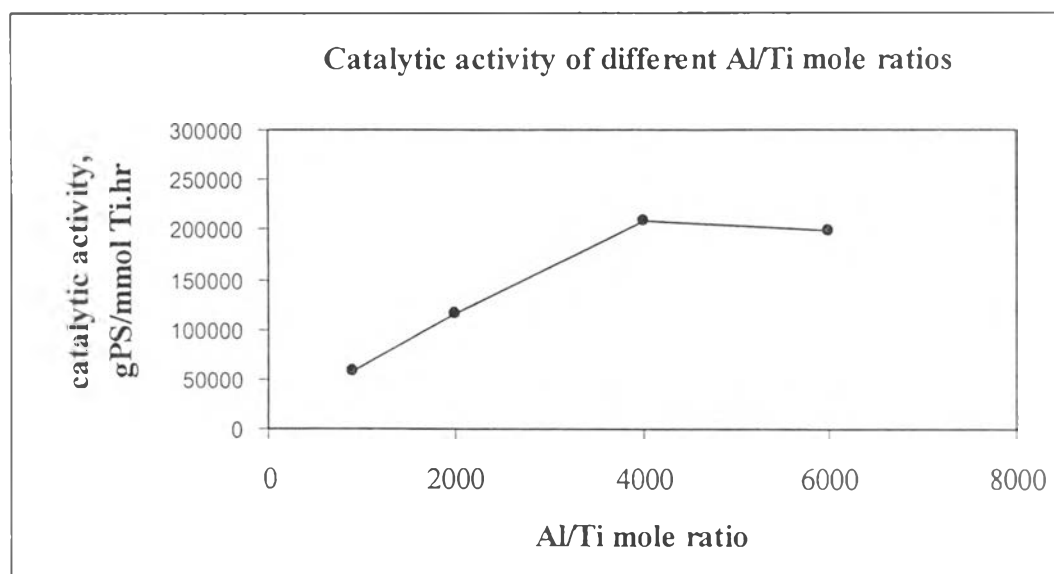


Figure 5.12. Catalytic activity of different Al/Ti mole ratios

Figure 5.12 clearly shows that maximum activity appears at Al/Ti mole ratio of 4000. At mole ratio less than 4000, activity increases nearly linear with an increase of [MAO] in the reaction system. However, at mole ratio more than 4000, the catalytic activity gradually decreases with a further increase of [MAO].

For $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ catalyst system in propylene polymerization, a bell-shaped A-log ($[\text{Al}]/[\text{Zr}]$) curve with a maximum activity between $[\text{Al}]/[\text{Zr}] = 3000$ and 4000 was reported by Chein and Sugimoto as shown in Figure 5.13 [234, 282]. It was explained that the linear increase of A with [MAO] at low $[\text{Al}]/[\text{Zr}]$ is a reflection of the formation of active species (C^*) and the decrease of A with very large amounts of MAO might be attributed to excessive complexation of MAO to active sites.

It is known that the reactions of metallocene with MAO besides complexation, methylation and activation, alpha-hydrogen transfer between MAO and metallocene are side reactions such as the side reaction in $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalyst system for ethylene polymerization as shown in Scheme 5.5.[286]. Similarly, it is reasonable to note that these reactions also occur in $\text{IndTiCl}_3/\text{MAO}$ catalyst system for styrene polymerization as shown in Scheme 5.6.

This side reaction is responsible for the production of methane. The condensation of metallocene and MAO causes the formation of Ti-CH₂-Al which has been known to be inactive [281] and to be a significant cause to the metallocene catalyst deactivation.

So, it could be explained that the increasing activity of IndTiCl₃/MAO catalyst system at low Al/Ti mole ratio was a reflection of the active species Ti-CH₃ formation and the decreasing activity with varying the large amount of MAO (high [Al]/[Ti]) might be attributed to the formation of inactive species by the deactivation of active Ti species.

According to the experimental result of this research and Huang et al. [282], it could be concluded that MAO might exert two types of conflicting effects on activity: 1) positive effects, which include creating and stabilizing catalytically active species as well as scavenging impurities, and 2) negative effects, which include an excessive complexation of MAO to active sites and probably some extent of activity reduction caused by chain transfer to MAO.

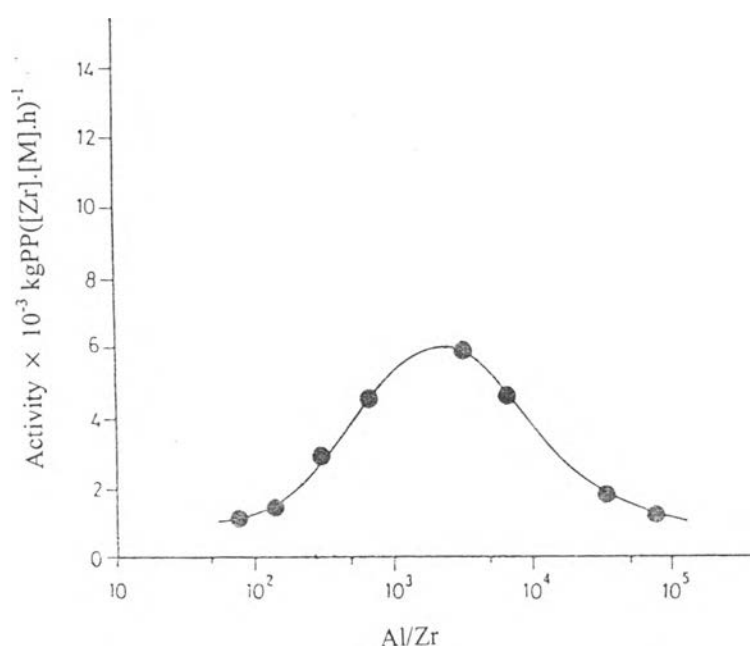
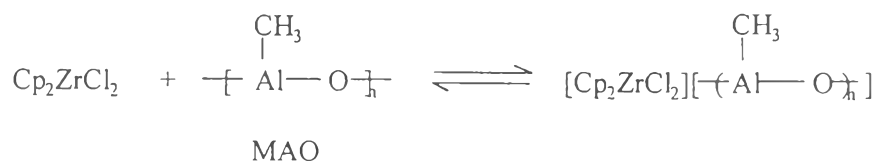
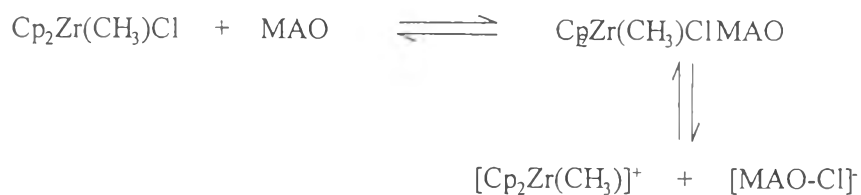
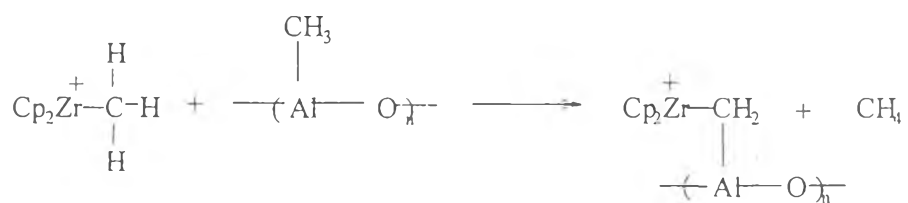


Figure 5.13. Variation of propylene polymerization activity with [Al]/[Zr] ratio using Et(H₄Ind)₂ZrCl₂/MAO catalyst system[234]

ComplexationMethylationActivationDeactivationReactivation**Scheme 5.5.** Reaction of zirconocene with MAO[286]

5.5. Characterization of active species of the catalyst in polymerization

In the ESR study, all operations were performed in the nitrogen atmosphere because cocatalyst and catalyst used in the styrene polymerization were sensitive to moisture and oxygen and then cocatalyst and catalyst were converted into new inactive forms, especially to oxidation state of transition metal in catalyst. In this research, ESR spectroscopy was used to examine the oxidation state of active species in the styrene polymerization.

Initially, for IndTiCl_3 /styrene/toluene system, active species of the catalyst were investigated and this experiment was called the blank test by using Ti concentration of 1.95×10^{-4} mol/l., styrene concentration of 2.66×10^{-4} mol/l. The obtained ESR result can not be detected signals. Hence, it is explained that there is no oxidation state changing of catalyst.

In case of sample test which consist of toluene, styrene, MAO, and IndTiCl_3 catalyst, it was measured signal at various Al/Ti mole ratios, $[\text{Al}]/[\text{Ti}] = 2,000; 4,000$, and various IndTiCl_3 catalyst concentration viz., 1.86×10^{-4} mol/L, 2.29×10^{-4} mol/L. It was observed that the obtained ESR signal was shown in Figure 5.14-5.16. The g value of ESR pattern of experiment were 2.0181, 2.0046 at $[\text{Al}]/[\text{Ti}]$ 900 and $[\text{IndTiCl}_3]$ 2.29×10^{-4} mol/l; 2.0163, 2.0050 at $[\text{Al}]/[\text{Ti}]$ 2000; 2.0185, 2.0046 at $[\text{IndTiCl}_3]$ 1.86×10^{-4} mol/l slightly different.

From reference [278], the system was composed of toluene, styrene, MAO and CpTiCl_3 catalyst. And then it was measured at 50°C with a catalyst concentration 10^{-4} mol/L. and $[\text{Al}]/[\text{Ti}]$ ratio of 500. The polymerization condition was conducted at microwave frequency 9.4 GHz, magnetic modulation frequency 100 kHz, intensity 10-30 dB, central magnetic field: 3390, swift range: 100 G, Gain: 2×10^3 and modulation amplitude: 4. ESR signal was appeared at g value 1.996 and 1.981. The ESR signal could be ascribed to the oxidation state changing of the catalyst and it was claimed that this signal was the Ti^{3+} , active species in the styrene polymerization.

Compared with the signal shape and g value of ESR pattern to the reference [278], these of ESR pattern of experiment were slightly different because of the differences of catalyst systems, polymerization conditions and ESR measurement conditions. Consequently, the signal obtained from the experiment seemed to be Ti^{3+} which was the active species.

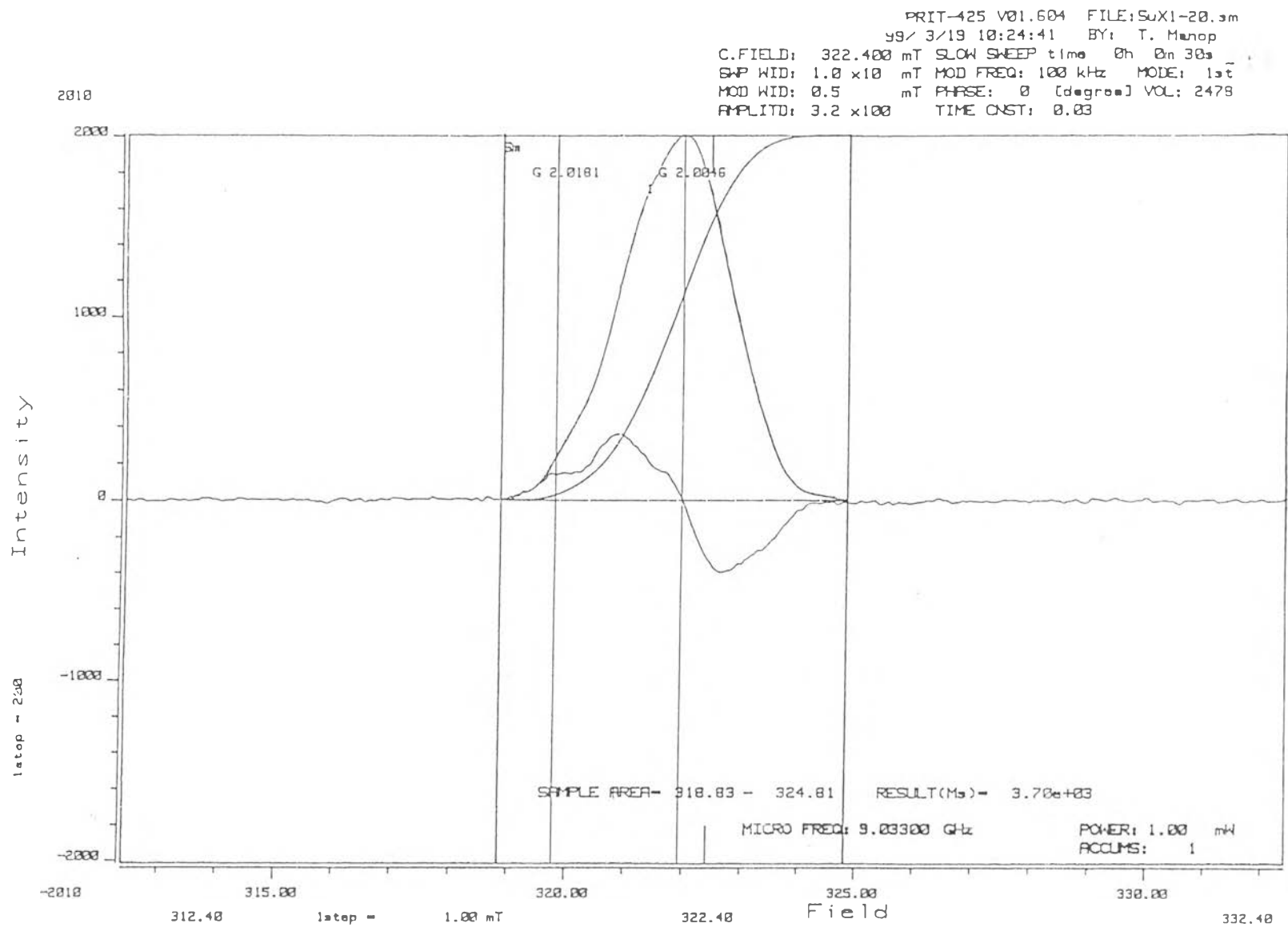


Figure 5.14. ESR spectrum at mole ratio of Al/Ti = 900, $[\text{IndTiCl}_3] = 2.2856 \times 10^{-4}$ mol/l

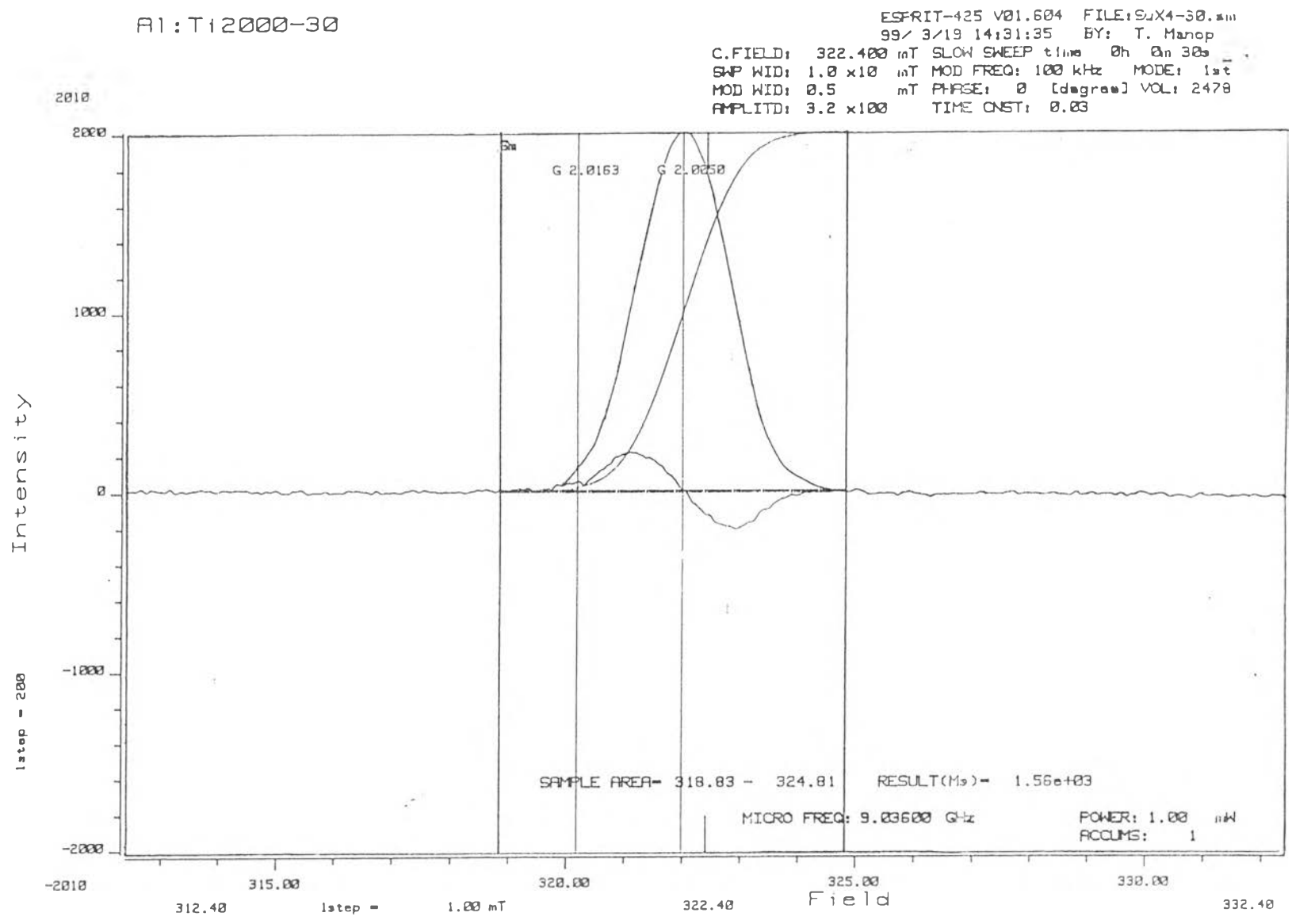


Figure 5.15. ESR spectrum at mole ratio of Al/Ti = 2000

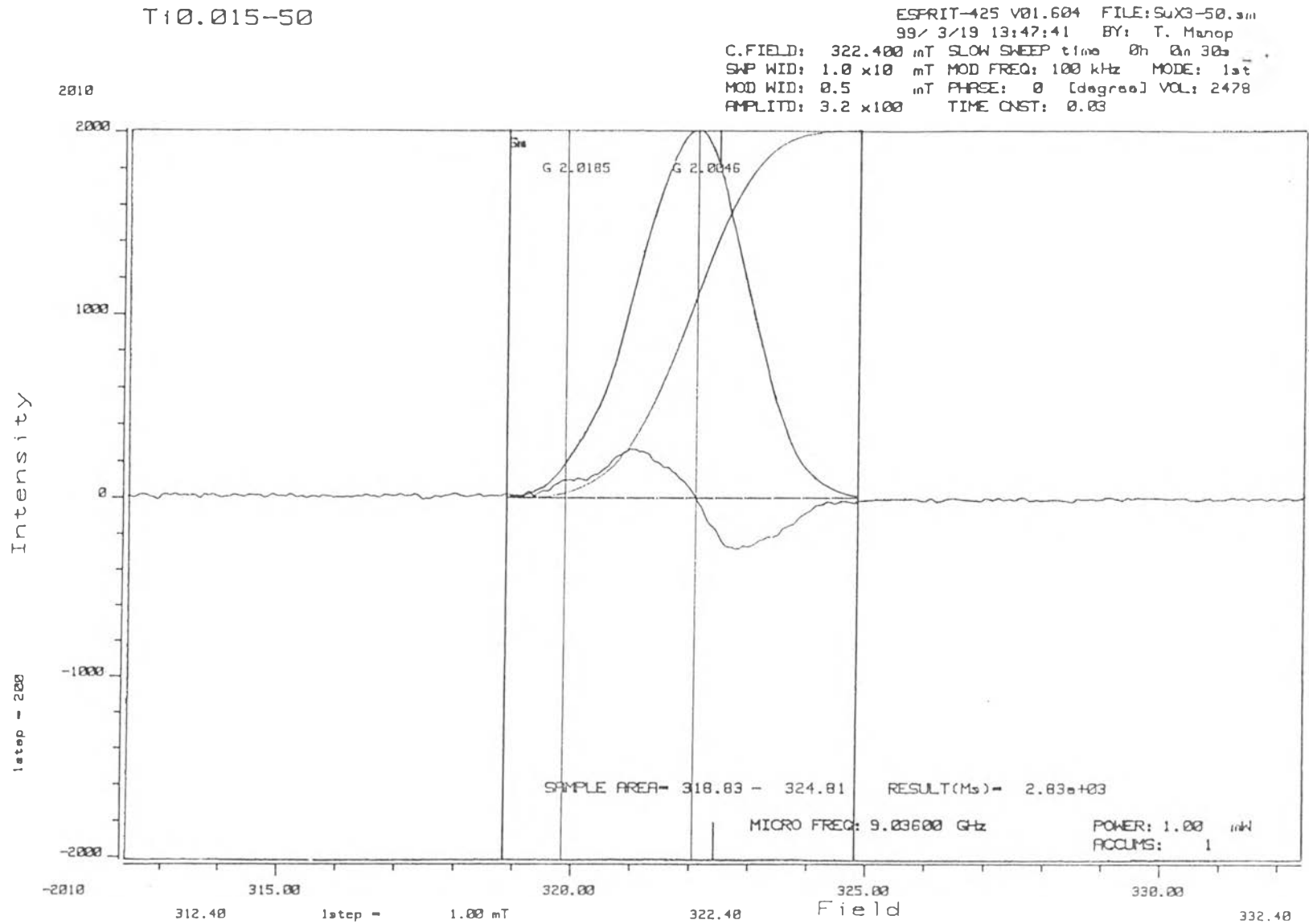


Figure 5.16. ESR spectrum at $[\text{IndTiCl}_3] = 1.6330 \times 10^{-4} \text{ mol/l}$

5.6. Characterization of polystyrene

5.6.1. Syndiotacticity

Analysis of syndiotacticity of polystyrene products in this work was divided into two cases: (1) the polystyrenes synthesized with using trimethylaluminum(TMA) as initiator, (2) the polystyrenes polymerized by using IndTiCl₃/MAO system catalyst. The results of the analysis were discussed below.

5.6.1.1. Trimethylaluminum/styrene system.

1. The effect of trimethylaluminum(TMA) concentration

Syndiotacticity of produced polystyrenes with various trimethylaluminum concentrations are shown in Table 5.10 and Figure 5.17.

Table 5.10 Syndiotacticity of polystyrene products at various trimethylaluminum concentrations^h

TMA concentration, mol/l.	syndiotacticity, %sPS
0.1391	-
0.4148	79.03
0.5442	78.78
0.7186	80.88
0.9662	79.53

^h polymerization conditions: styrene = 0.0435 mol, time = 120 mins., 50°C, toluene 21.75 ml.

All polystyrene products with various the concentration of TMA have nearly the same syndiotacticity as shown in Figure 5.17.

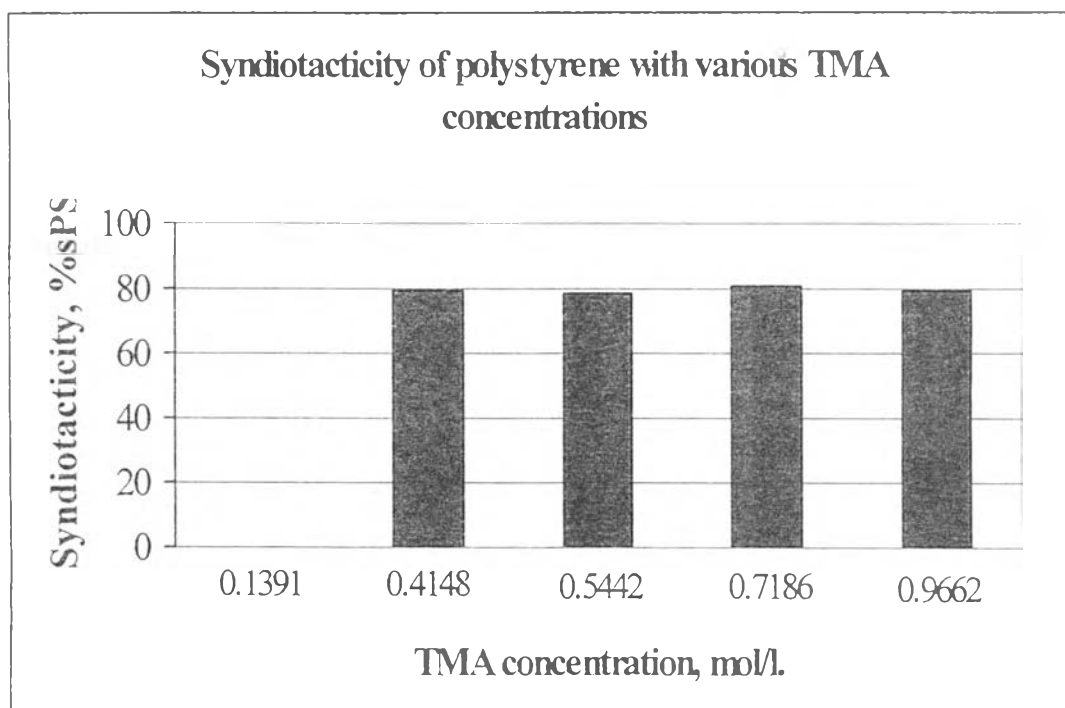


Figure 5.17. Syndiotacticity of polystyrene products at various trimethylaluminum concentration

2. The effect of polymerization time

Syndiotacticity of polystyrene products with variation of polymerization time by using TMA as initiator are presented in Table 5.11 and Figure 5.18.

Table 5.11 Syndiotacticity of polystyrene products at various polymerization times¹

polymerization time, min.	syndiotacticity, %sPS
10	78.63
30	78.04
60	80.14
90	79.51
120	79.37

¹ polymerization conditions: [styrene] = 1.2885 mol/l., [TMA] = 0.4148, 50°C, toluene 21.75 ml.

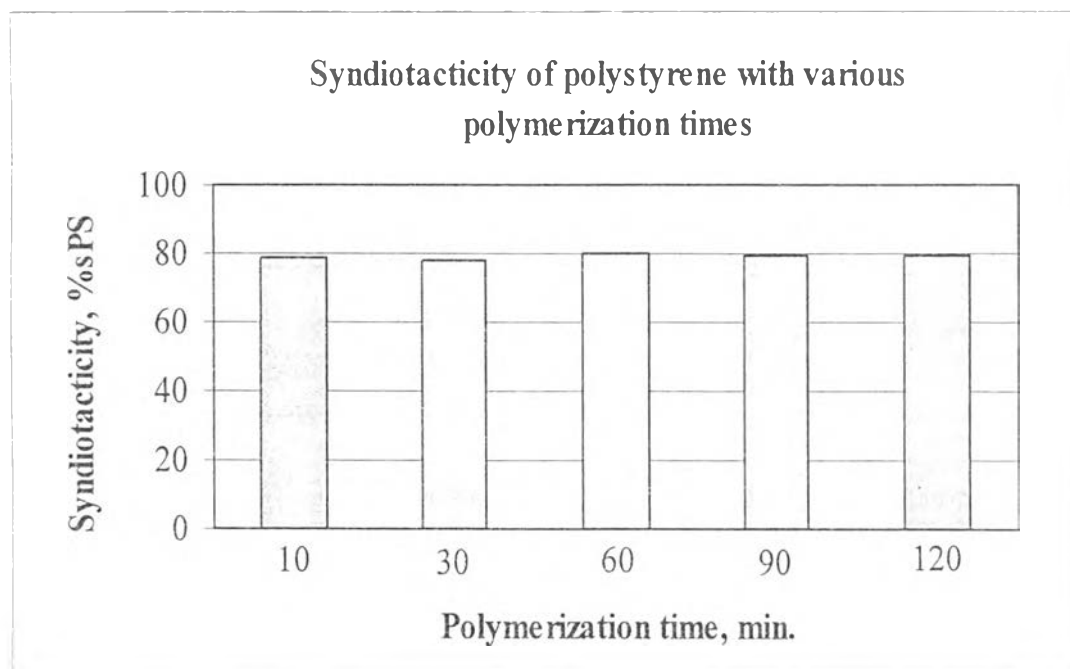


Figure 5.18. Syndiotacticity of polystyrene products at various polymerization times

The Figure 5.18 showed that syndiotacticity of polystyrenes has not the great difference in every polymerization time.

3. The effect of Polymerization temperature

Determination of syndiotacticity of prepared polystyrene with various polymerization temperature by using TMA as initiator are shown in Table 5.12 and Figure 5.19.

Table 5.12 Syndiotacticity of polystyrene products at various polymerization temperatures¹

polymerization temperature, °C	syndiotacticity, %sPS
30	81.05
50	79.93
70	80.57
90	79.82

¹ polymerization conditions: [styrene]=1.2885 mol/l., [TMA]=0.4148, time 60 mins., toluene 21.75 ml.

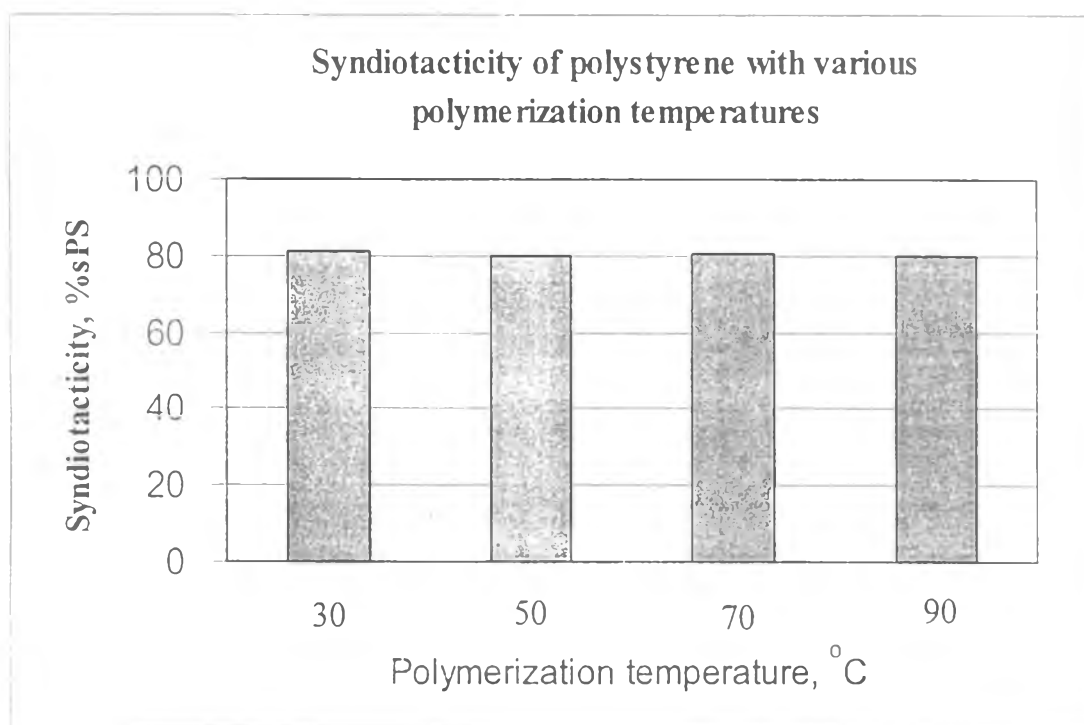


Figure 5.19. Syndiotacticity of polystyrene products with various polymerization temperatures

From Figure 5.19, all polystyrene products with the different polymerization temperature have closely the same syndiotacticity.

According to the syndiotacticity results of prepared polystyrenes as shown in Figure 5.17-5.19, all polystyrene products with various the TMA concentration, polymerization time, and polymerization temperature have not the great difference in syndiotacticity. The results indicated that TMA has not an effect on the syndiotacticity of polystyrene products.

5.6.1.2. IndTiCl₃/MAO/styrene system1. The effect of IndTiCl₃ concentration

Syndiotacticity of polystyrene products with various IndTiCl₃ concentrations are shown in Table 5.13 and Figure 5.20.

The results from the Figure 5.20 showed that the syndiotacticity of polystyrene slightly increased with the increase of IndTiCl₃ catalyst concentration from the range of 4.96×10^{-5} to 2.65×10^{-4} mol/l. The maximum syndiotacticity of polystyrene stood at IndTiCl₃ catalyst concentration of 2.65×10^{-4} mol/l and then syndiotacticity decreased with the increment of IndTiCl₃ concentration.

Table 5.13 Syndiotacticity of polystyrene products with different IndTiCl₃ concentrations^k

catalyst concentration, mol/l.	syndiotacticity, %sPS
4.96×10^{-5}	89.36
1.01×10^{-4}	89.55
1.99×10^{-4}	91.24
2.65×10^{-4}	93.75
3.09×10^{-4}	92.07

^k polymerization conditions: catalyst = IndTiCl₃, cocatalyst = MAO, [Al]/[Ti] = 500, [styrene]/[Ti] = 400, time 120 mins., 50 °C, toluene 21.75 ml.

A. Kucht et al.[31] studied styrene polymerization catalyzed by (η^5 -tetramethylcyclopentadienyl)triisopropoxytitanium; (η^5 -C₅HMe₄)Ti(o-i-Pr)₃/MAO. It was observed that the catalyst concentration influenced on the syndiotacticity of produced polystyrene at constant [Al]/[Ti] ratio. The highest syndiotacticity of polystyrene is reached at [Ti] = 0.3 mM; polymerization condition: [Al]/[Ti] ratio = 500; T_p = 25 °C. This result corresponded to the case of styrene polymerization with IndTiCl₃ catalyst. Therefore, the catalyst concentration had an effect on the syndiotacticity of polystyrene.

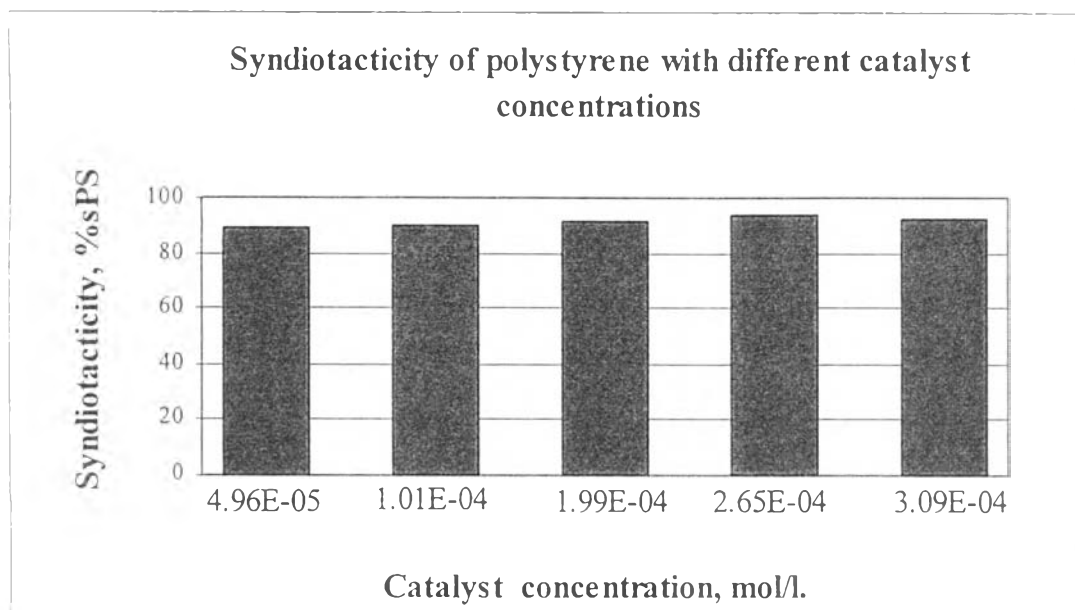


Figure 5.20. Syndiotacticity of polystyrene products with different IndTiCl_3 concentrations

2. The effect of Al/Ti mole ratio

Table 5.14 and Figure 5.21 presented the syndiotacticity results of polystyrene with the different Al/Ti mole ratios.

Table 5.14 Syndiotacticity of polystyrene products with the different Al/Ti mole ratios¹

[Al]/[Ti] mole ratio	syndiotacticity, %sPS
900	93.75
2000	93.86
4000	94.03
6000	93.50

¹ polymerization conditions: catalyst = IndTiCl_3 , cocatalyst = MAO, $[\text{Ti}] = 8.615 \times 10^{-6}$ mol/l., styrene = 0.0345 mol, time 120 mins., 50 °C, toluene 21.75 ml.

From the Figure 5.21, the syndiotacticity of polystyrenes has marginal difference in every testing Al/Ti mole ratios.

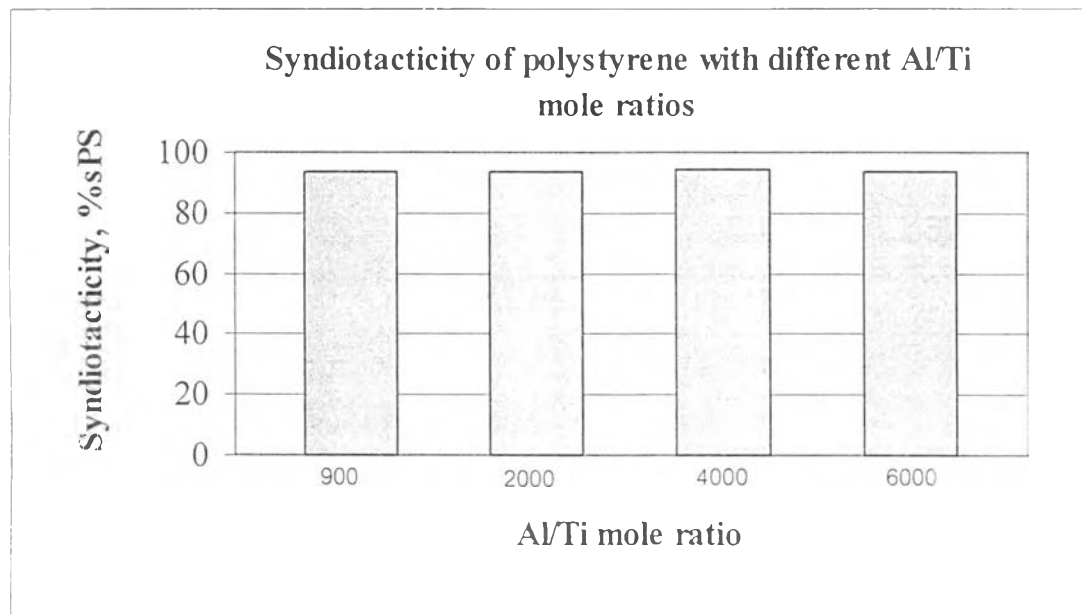


Figure 5.21. Syndiotacticity of polystyrene products with the different Al/Ti mole ratios

According to the work of A. Kutch et al.[31], the $(\eta^5\text{-cyclopentadienyl})\text{triisopropoxytitanium}$; $(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\text{o-i-Pr})_3/\text{MAO}$ catalyst system could polymerized styrene monomer. It was discovered that the mole ratio of Al/Ti had an effect on the polystyrene syndiotacticity at constant Ti concentration. The obtained result with $(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\text{o-i-Pr})_3$ catalyst was similar to that with IndTiCl_3 catalyst for styrene polymerization. Consequently, the Al/Ti mole ratio influenced on the polystyrene syndiotacticity.

3. The effect of polymerization temperature

The testing of syndiotacticity of polystyrene products with various polymerization temperatures was presented in Table 5.14 and Figure 5.20.

The Figure 5.22 clearly showed that the syndiotacticity of polystyrene obtained with various temperatures had the slight difference. The

maximum syndiotacticity of polystyrene occurred at T_p 50 °C. This above result was similar to the case of styrene polymerization with cyclopentadienyltribenzyloxytitanium; $CpTi(OBz)_3/MAO$ catalyst system[42] in which the syndiotacticity of polystyrene depended on the polymerization temperature. The syndiospecificity of this catalyst remained high up to 70 °C and decreased with further increase of polymerization temperature. Hence, it was concluded that the polymerization temperature affected on polystyrene syndiotacticity.

Table 5.15 Syndiotacticity of polystyrene products with different polymerization temperatures^m

polymerization temperature, °C	syndiotacticity, %sPS
30	91.83
50	93.75
70	92.16

^m polymerization conditions: catalyst = $IndTiCl_3$, cocatalyst = MAO, $[Ti] = 2.65 \times 10^{-4}$ mol/l., $[Al] = 0.2386$ mol/l., $[styrene] = 1.06$ mol/l., time = 120 mins., toluene 21.75 ml.

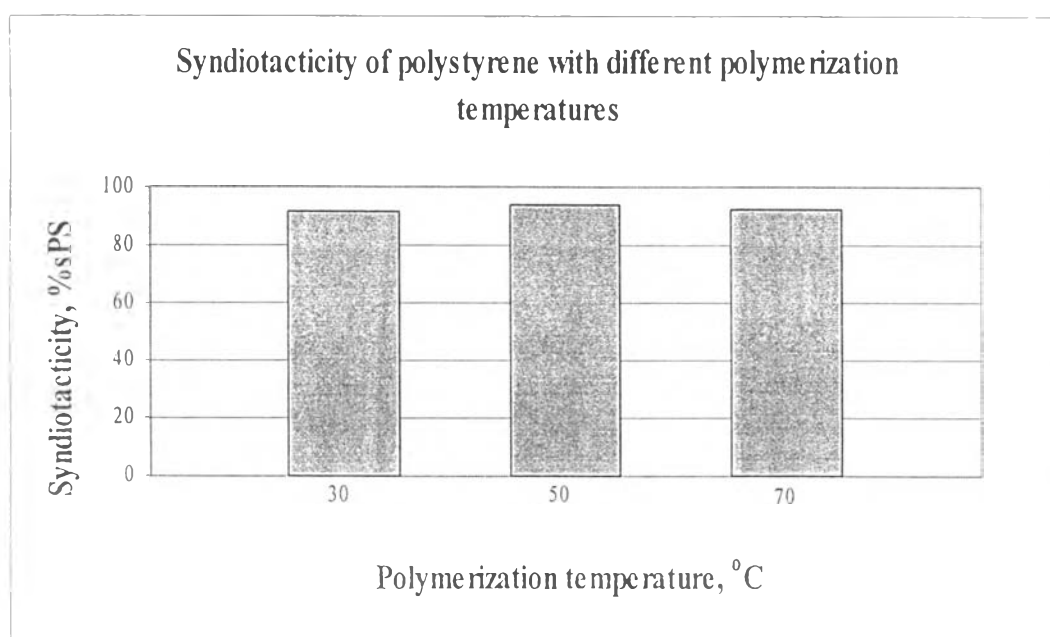


Figure 5.22. Syndiotacticity of polystyrene products with different polymerization temperatures

For the syndiotacticity results of produced polystyrenes as shown in Figure 5.20-5.22. It could be noted that the syndiotacticity of the produced polystyrenes by using $\text{IndTiCl}_3/\text{MAO}$ catalyst system with various Al/Ti mole ratios polymerization temperature and $[\text{IndTiCl}_3]$ catalyst is slightly different. Therefore, the syndiotacticity was slightly sensitive to polymerization conditions.

From the comparison between the syndiotacticity results in Figure 5.17-5.19 and in Figure 5.20-5.22, the polystyrene products with using $\text{IndTiCl}_3/\text{MAO}$ catalyst system showed higher the syndiotacticity than that with using TMA initiator. This might be attributed to the constrain geometry of IndTiCl_3 catalyst. The constrain geometry of IndTiCl_3 can control the stereoregularity of polystyrene by forcing styrene monomer to interact the active site identically, whereas the active species of TMA is carbocation that can react with styrene monomer unidentically.

5.6.2. Infrared Spectroscopy

The infrared spectroscopy is the effective method to determine the microstructure of polymer. It is sufficient to characterize the functional groups of polystyrene in the wave number of 4000-400 cm^{-1} .

Table 5.16 IR Spectrum data of polystyrene [287, 288]

wave number range, cm^{-1}	assignment
3100-3000	=C-H stretching aromatic rings
2960-2850	-C-H stretching aliphatic
1600	C=C aromatics
1500	C=C aromatics
1470-1350	-CH ₂ -, -CH ₃
1000-970	CH=CH ₂ vinylidene
860-670	=C-H bending aromatic rings

The infrared spectra of polystyrene produced from TMA initiator or IndTiCl₃/MAO catalyst system was the same pattern as shown in Figure 5.21 and 5.23, respectively. The identification of polystyrene infrared spectrum was assigned to the functional groups as summarized in Table 5.16.

An aromatic ring shows C-H stretching at 3000-3100 cm^{-1} and there are C=C stretching at 1500 and 1600 cm^{-1} and C-H out-of-plane bending in the 860-670 cm^{-1} region. The wave number range in 2960-2850 cm^{-1} indicates C-H stretching of an aliphatic hydrocarbon. There is -CH₂-, -CH₃ bending of aliphatic hydrocarbon between 1350 and 1470 cm^{-1} . The peaks in the wave number between 970 and 1000 cm^{-1} were the vinylidene chain end of polystyrene. When the produced polystyrene infrared spectrum was compared to the reference polystyrene spectrum (Figure 5.23), it was found that both spectrums were mostly similar pattern. Therefore, it was confirmed that polymers produced with TMA initiation or IndTiCl₃/MAO catalyst system were polystyrene.

670 cm^{-1} region. The wave number range in 2960-2850 cm^{-1} indicates C-H stretching of an aliphatic hydrocarbon. There is $-\text{CH}_2-$, $-\text{CH}_3$ bending of aliphatic hydrocarbon between 1350 and 1470 cm^{-1} . The peaks in the wave number between 970 and 1000 cm^{-1} were the vinylidene chain end of polystyrene. When the produced polystyrene infrared spectrum was compared to the reference polystyrene spectrum (Figure 5.23), it was found that both spectrums were mostly similar pattern. Therefore, it was confirmed that polymers produced with TMA initiation or $\text{IndTiCl}_3/\text{MAO}$ catalyst system were polystyrene.

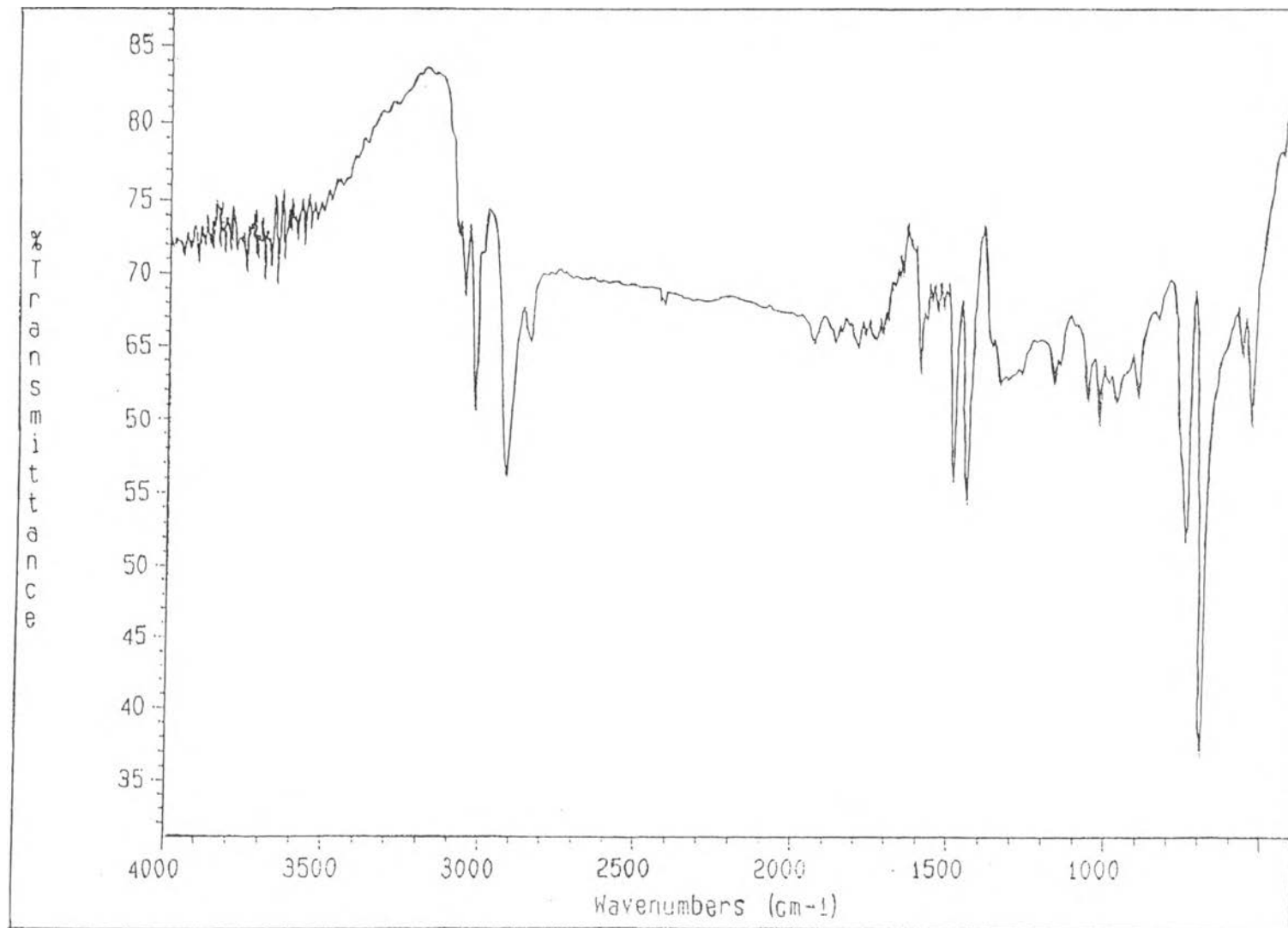


Figure 5.23. IR spectrum of the obtained polystyrene with TMA initiator

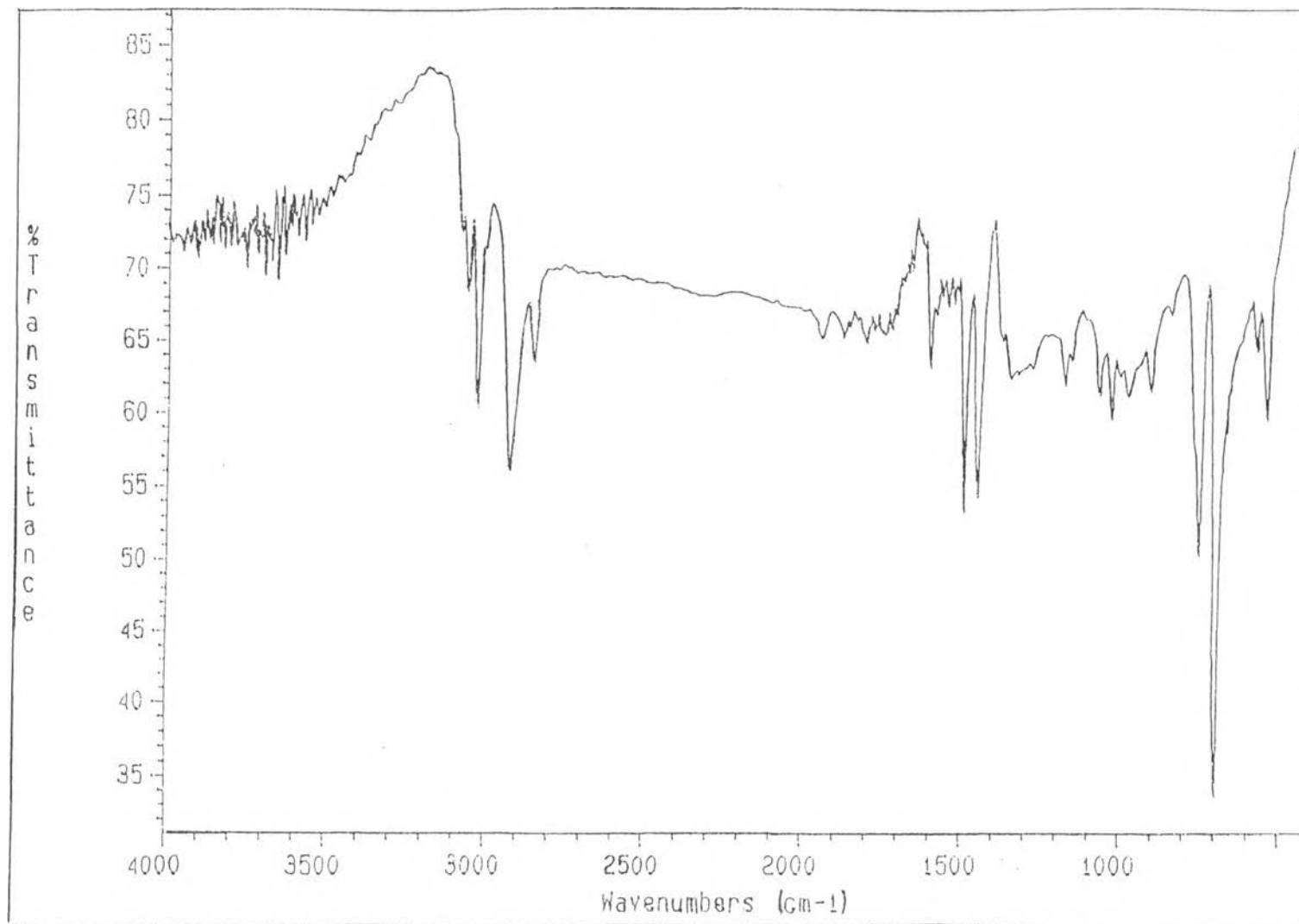


Figure 5.24. IR spectrum of the obtained polystyrene with IndTiCl₃/MAO catalyst system

10.2-13-5
Poly(styrene), secondary standard
Typical M.W. 321,000, typical M.N. 85,000

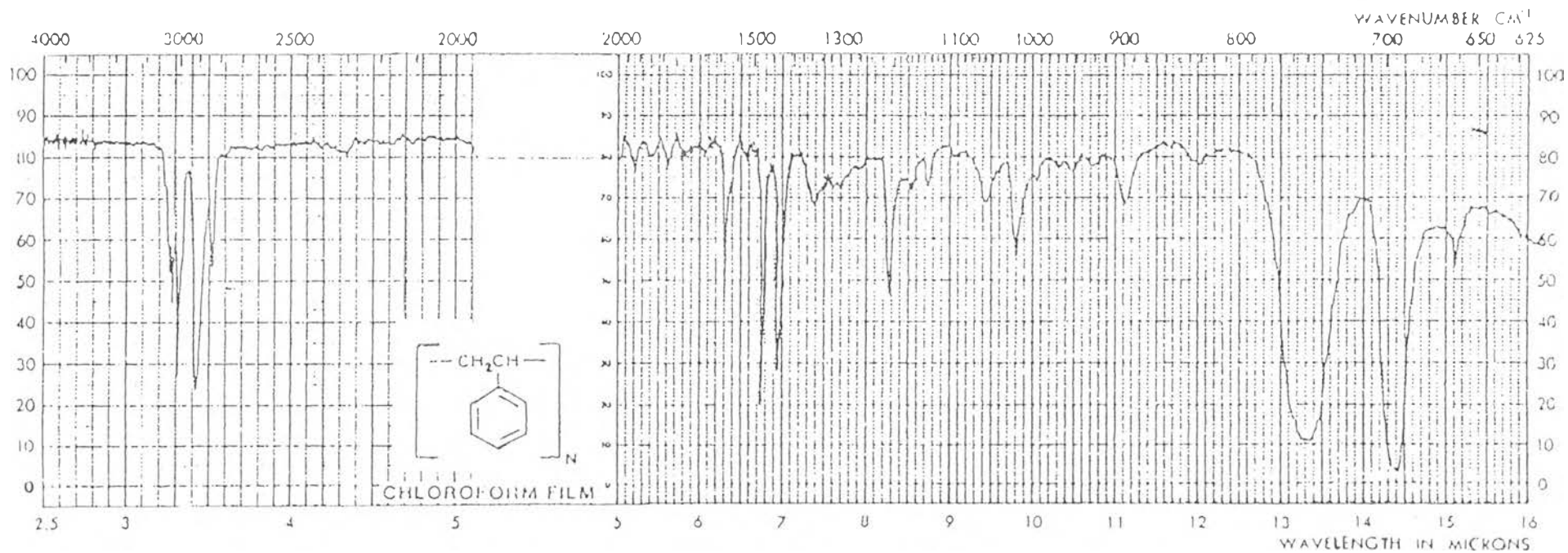


Figure 5.25. IR spectrum of the standard polystyrene (Reference)