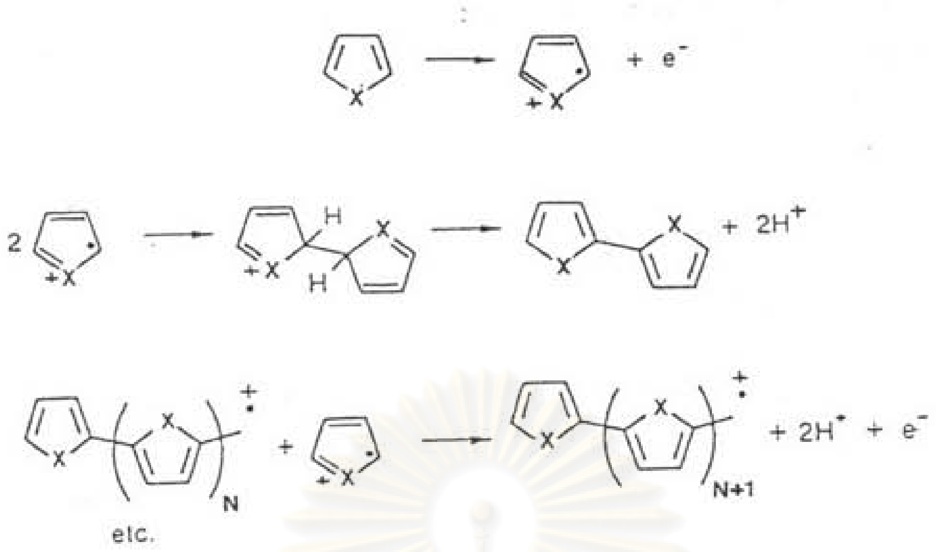
CHAPTER IV

RESULTS AND DISCUSSTION

4.1 The Synthesized Polymers

As mentioned earlier, conducting polymer could be prepared by employing several methods. In this study, chemical polymerization in solution was used. The chemical synthesis method involves the polymerization and oxidation with oxidative transition metal, i.e., $FeCl_3$. Polypyrrole, polythiophene and poly (3-methylthiophene) were synthesized under several different conditions. At each condition, the polymer obtained could be denoted by the sequential number subscribed besides the letters PP, PT and P3MT as shown in Table 3.1-3.11 .

The polymerization mechanism was a radical-cation coupling polymerization as shown in the following reaction:



polypyrrole ; X = NH and polythiophene; X = S

The products were a typical highly conjugated carbon backbone, which containing nitrogen (N) or sulphur (S) atoms. The dopant ion (Cl^-), called " counter ion " that resides between polymer chains, was stabilized the charge on the polymer chain. Several differently experimental techniques has identified chlorine to be present as at least two different species in the polymer powder. Thus, the Cl^- anion have been identified by using of XPS (X-ray Photoelectron Spectroscopy) [39]. In addition to these Cl^- active dopant species, molecular chlorine,Cl_2, is presented in the powder. This large excess of Cl_2 residing preferentially on the surface of the powder is easily removed by vacuum pumping at room temperature. The experiment was achieved by pumping the synthesized polymer powder in vacuum at room temperature over night, thus, obtaining a sample composition with more stable dopant concentration.

4.2 Synthesis of Polypyrrole

In this research, reaction conditions for synthesized high electrical conductivity polyrrole were studied in order to select the optimum condition. The major conditions that influence the quality of the conductive polymer which 1.00 ml of pyrrole monomer using are as follow:

- Reaction temperature
- Concentration of the $FeCl_3$ solution
- Amount of $FeCl_3$ solution
- Reaction time
- Solvent for preparing $FeCl_3$ solution

It has been found that polypyrrole can be simply prepared by oxidation of pyrrole with $FeCl_3$ in methanol solution. A black powder was formed almost instantaneously after the injection of vaccum-distilled pyrrole in the solution.

4.2.1 Effect of Pressure Pressed on Polypyrrole Disc

In synthesis of these polypyrrole the concentrations of $FeCl_3$ oxidant solutions are 1.5 M (PP_1), 2.5 M (PP_6) and 3.5 M (PP_{11}) in methanol, volume of $FeCl_3$ solution 20.0 ml, volume of pyrrole 1.00 ml, reaction temperature 0 ^oC and reaction time 20 min.

After washing and dring polypyrrole powder, it was pressed into disc form by special evacuable die at 2-6 ton before measured its electrical conductivity. The effect of pressure is clearly shown in figure 4.1 .

Figure 4.1 shows a plotting between pressing force (ton) and electrical conductivity (Scm^{-1}) .

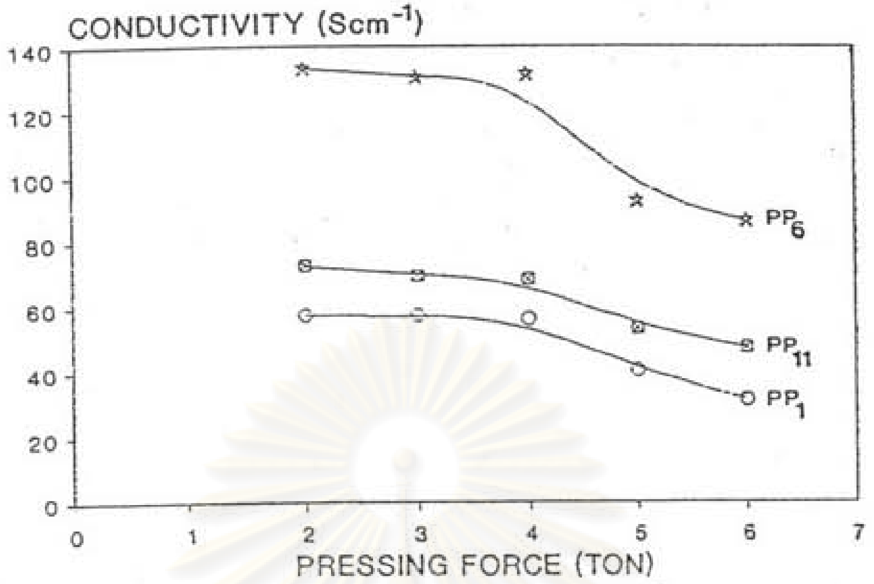


Figure 4.1 The electrical conductivities of disc polypyrroles at various pressing force.

From Figure 4.1 electrical conductivity of polypyrrole disc gradually decreased as the pressing force increased up to 4 tons. At higher force the conductivity sharply decreased, it was expected that high pressing force tilted the polymer chain. So that we could not used force higher than 4 tons . A pressure of 2 tons was chosen for preparation of polymer discs in this work . (in order to maximize the electrical conductivity).

4.2.2 The Study of Reaction Conditions

4.2.2.1 Effect of reaction temperature

Polypyrrole was prepared at various reaction temperatures from 0-50 ^{0}C . Table 4.1 shows the dependence of the electrical conductivity on the reaction temperature while the other paremeters were kept constant, i.e., the reaction time of 20 minute, 20 ml of 1.5 M, 2.5 M or 3.5 M $FeCl_3$ solution and 1.00 ml of pyrrole monomer.

Table 4.1 Effect of reaction temperature

Sample No.*	Reaction temp. (^{o}C)	Product yield (g)	Conductivity (Scm^{-1})
1.5 M			
PP_1	0	0.68	57.04
PP_2	10	0.40	30.14
PP_3	20	0.31	31.12
PP_4	35	0.29	17.45
PP_5	50	0.16	13.36

Sample No.*	Reaction temp. (^{o}C)	Product yield (g)	Conductivity (Scm^{-1})
2.5 M			
PP_6	0	0.80	133.02
PP_7	10	0.72	59.35
PP_8	20	0.49	47.29
PP_9	35	0.25	40.16
PP_{10}	50	0.10	39.18
3.5 M			
PP_{11}	0	0.88	72.44
PP_{12}	10	0.67	37.15
PP_{13}	20	0.56	34.36
PP_{14}	35	0.38	27.27
PP_{15}	50	0.11	26.52

* See experiment 3.2.1.2

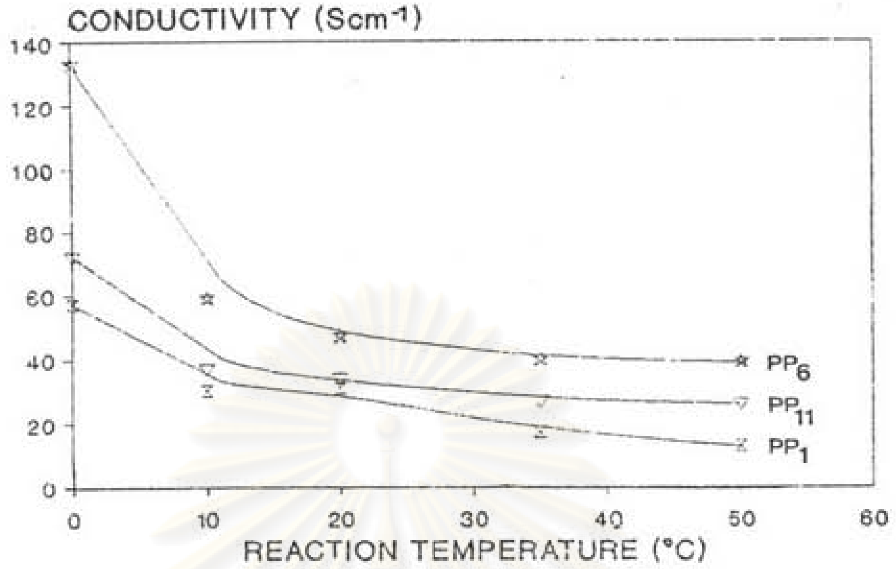


Figure 4.2 The electrical conductivity of polypyrrole at various reaction temperatures.

volume of $FeCl_3$ solution 20.0 ml
volume of pyrrole 1.00 ml
reaction time 20 min

The results from Table 4.1 suggest that at lower temperature higher yield of polypyrrole with higher conductivity was obtained. A maximum conductivity of 133.02 Scm^{-1} was recorded for PP_6 prepared in 2.5 M $FeCl_3$ at 0 °C.

At each concentration of $FeCl_3$ solution, polypyrrole obtained seemed to have lower conductivity at higher temperature. This may be explained that self-polymerization of pyrrole has occurred instead of the oxidation polymerization of pyrrole by $FeCl_3$. Therefore, less doped polypyrrole was formed which induced lower conductivity. The other explanation could probably be the short conjugated polymer chain during formation which will be mentioned later on.

Polypyrrole was also prepared at temperature below $0^{o}C$, i.e., -20 ± 5 ^{o}C in 2.5 M $FeCl_3$. It was led to the product with low electrical conductivity of 42 Scm^{-1} and very low yield (0.15 g)

4.2.2.2 Effect of the Concentration of $FeCl_3$ Solution

In this experimental, the concentration of $FeCl_3$ solutions were varied. Since the oxidation potential of $FeCl_3$ in methanol solution is different at each concentration which will affect the polymerization, it should thus be recorded. This was performed by construction the calibration curve as shown in Figure 4.3 . It is apparent that the oxidation potential increases with increasing concentration of $FeCl_3$.

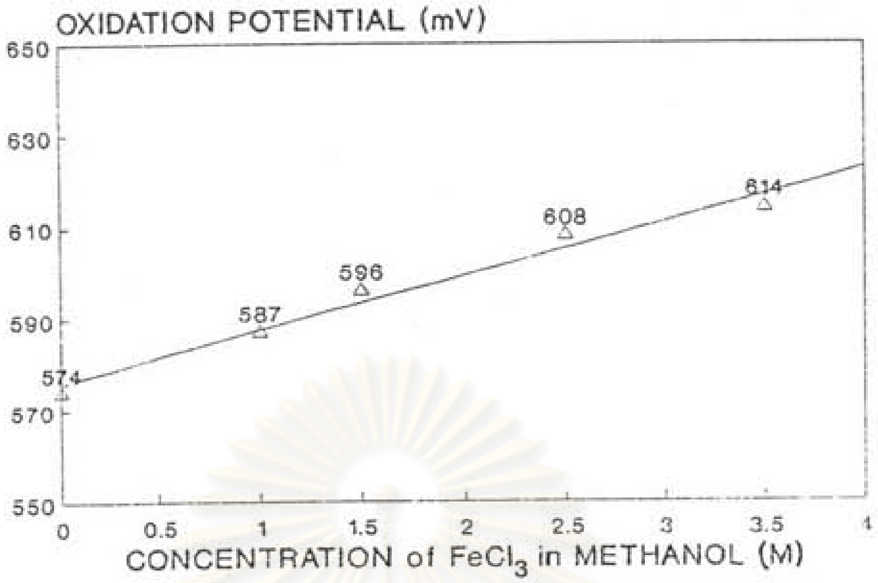


Figure 4.3 The change in oxidation potential of $FeCl_3$ in methanol at various concentrations.

In this part of research, polypyrrole was synthesized by various concentrations of $FeCl_3$, from 0.3 M to 3.5 M. The upper limit was 3.5 M because when the concentration greater than 3.5 M $FeCl_3$ was not completely dissolved in methanol. The initial oxidation potential of each solutions are obtained from Figure 4.3 (shows in Table 4.2).

Table 4.2 Effect of concentration of $FeCl_3$ solution

Sample No.*	Conc. of $FeCl_3$ solution (M)	Initial oxidation potential (mV) (versus SCE)	Product yield (g)	Conductivity (Scm^{-1})
PP_{16}	0.3	578	0	-
PP_{17}	0.6	582	0	-
PP_{18}	1.0	587	0.28	22.45
PP_1	1.5	596	0.32	57.04
PP_{19}	2.0	600	0.80	79.98
PP_6	2.5	608	0.83	133.02
PP_{20}	3.0	610	0.81	85.87
PP_{11}	3.5	614	0.88	72.44

* See experiment 3.2.1.3

By plotting conductivity and $FeCl_3$ concentration (Figure 4.4), it clearly exhibited that higher conductivity was obtained as the concentration was increasing. However, when the concentration was higher than 2.5 M, the conductivity suddenly decreased. This must be associated with the oxidation potential of $FeCl_3$ solution.

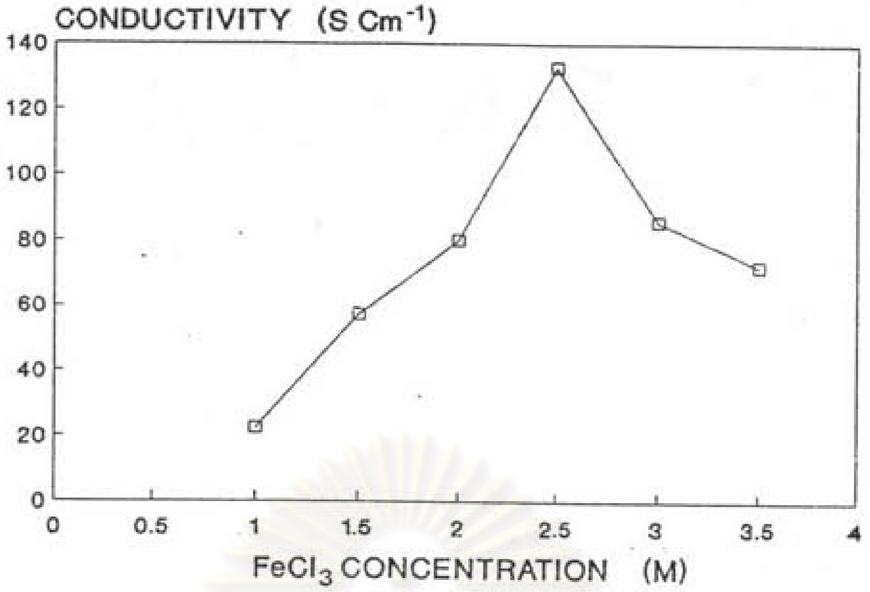
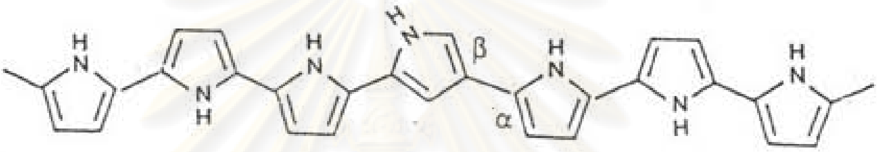


Figure 4.4 The electrical conductivity of polypyrrole at various concentration of $FeCl_3$ solution

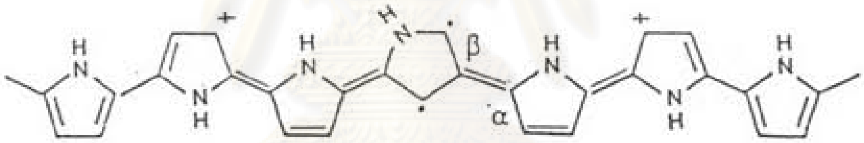
volume of $FeCl_3$ solution	20.0	ml
volume of pyrrole	1.00	ml
reaction time	20	min
reaction temperature	0	^oC

From the fact that , bonding in the five-membered heterocyclic rings can occur through the α- or β-position. In the pyrrole ring the reactivity of the α-position is much higher than that of the β-position so that coupling of the pyrrole unit to form polymer is expected to happen essentially through the α,α'-position. In this case polypyrrole was synthesized with 2.5 M $FeCl_3$ (oxidation potential 608 mV) to obtain with a fully conjugate backbone. Which capable of supporting bipolarons, the main form of charge carrier in polypyrrole.

At high concentration, the oxidation potential of the solution was too high. Normally the polymer should occur at α-position, but at high oxidation potential the β-linkage polymerization can be induced, as studied and determined by elemental analysis (see section 4.4.1). This phenomenon defect the polymer backbone that can destroy the conjugating pattern shows as follows:



non-oxidized β-linkage polymer



oxidized β-linkage polymer

Consequently, the oxidized β-linkage polymer could not form the bipolaron in the polymer chain. This type of structure makes the conductivity of whole polymer lower.

In summary, the optimum concentration for synthesis of high conductivity polypyrrole was 2.5 M $FeCl_3$ (initial oxidation potential 608 mV versus SCE).

4.2.2.3 . Effect of Volume of $FeCl_3$ Solution

The polymerization reaction was carried out by various volume of 2.5 M $FeCl_3$ solution from 15-50 ml. Table 4.3 shows the dependence of the electrical conductivity on amount of 2.5 M $FeCl_3$ solution while the other parameters were kept constant, i.e., the reaction temperature 0 °C, the reaction time 20 min and 1.00 ml of pyrrole monomer.

Table 4.3 Effect of volume of $FeCl_3$ solution

Sample No*	Reaction volume (ml)	Product yield (g)	Conductivity (Scm^{-1})
PP_{21}	15	0.84	95.24
PP_6	20	0.83	133.02
PP_{22}	30	0.87	87.10
PP_{23}	40	0.85	50.27
PP_{24}	50	0.77	9.95

* See experiment 3.2.1.4

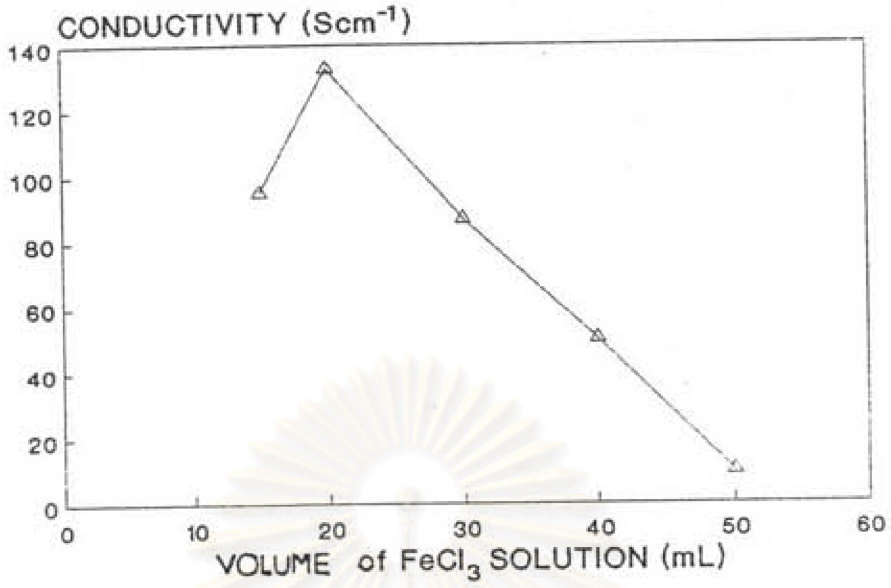


Figure 4.5 The electrical conductivity of polypyrrole at various volume of 2.5 M $FeCl_3$ solution

volume of pyrrole	1.00	ml
reaction time	20	min
reaction temperature	0	^oC

Under these conditions it could be compared the conductivity of the products obtained from using various volume of $FeCl_3$ solution could be compared. By plotting conductivity and volume of $FeCl_3$ solution (Figure 4.5), it clealy exhibited that the optimum volume of $FeCl_3$ solution was about 20 ml. At smaller volume than 20 ml, it was observed that the solution became very viscous once pyrrole was added into the solution which made it difficult to stir. At large volume of $FeCl_3$ solution, the pyrrole radical cations could also react more difficultly as the volume was increasing. Although the product yields at each condition was nearly the same but their conductivities were quite different. This could be due to the formation of the shorter conjugating chain of the product comparing to the one when $FeCl_3$ solution was 20 ml the reaction.

In summary, the optimum volume of 2.5 M $FeCl_3$ solution for the synthesis of high conductivity polypyrrole was 20.0 ml.

4.2.2.4 Effect of Reaction Time

The polymeization reaction was carried out by various reaction times from 5 min to 60 min.Table 4.4 showed the dependence of the electrical conductivity on the reaction time while the other parameters were kept constant, i.e., the reaction temperature 0 °C, 20 ml of 2.5 M $FeCl_3$ solution and 1.00 ml pyrrole monomer.

Table 4.4 Effect of reaction time

Sample No*	Reaction time (min)	Product yield (g)	Conductivity (Scm^{-1})
PP$_{25}$	5	0.69	66.36
PP$_{26}$	10	0.77	72.49
PP$_{6}$	20	0.83	133.02
PP$_{27}$	30	0.89	97.47
PP$_{28}$	40	0.93	60.98
PP$_{29}$	60	0.95	49.23

* See experiment 3.2.1.5

By plotting conductivity and reaction time (Figure 4.6), it clearly exhibited that maximum electrical conductivity at 20 min. As mentioned previously (Figure 2.2), while the polymerization reaction occurred, the oxidation potential of the solution slowly decreased.

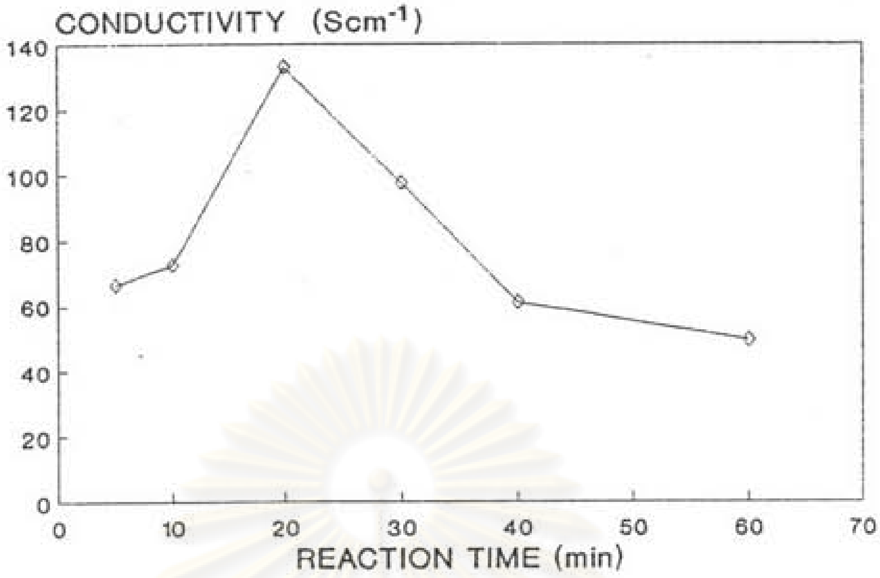


Figure 4.6 The electrical conductivity of polypyrrole at various reaction time

volume of 2.5 M $FeCl_3$ solution	20.0 ml
volume of pyrrole	1.00 ml
reaction temperature	0 °C

Thus, at longer reaction time, shorter conjugated chain polymer may be obtained and lead to low electrical conductivity. But high product yield is due to the fact that solution has still had sufficiently high oxidation potential during the reaction. At short time the polymerization was not complete thus resulted in the shorter conjugate chain length and lower product yield.

4.2.2.5 Effect of Solvent

The polymerization reactions were carried out by various ratios of mix-solvents (MeOH:CH_3Cl). Table 4.5 showed the dependence of the electrical conductivity on the ratios of MeOH:$CHCl_3$ mixture while the other parameters were kept constant, i.e., 20 ml of 2.5 M $FeCl_3$ solution, the reaction temperature 0^{o} C, the reaction time 20 min and 1.00 ml of pyrrole monomer. Since the oxidation potential of $FeCl_3$ solution was different at each ratio of MeOH:$CHCl_3$ which would affect the polymerization, it should thus be recorded.

Figure 4.7 showed relationship between the oxidation potential of $FeCl_3$ solution (versus SCE) and ratio of methanol to chloroform in the solution. It was apparent that the oxidation potential increases with decreasing ratio of mixture solvent. Additionally each ratio of solution must read the initial oxidation potential. (shows in Table 4.5)

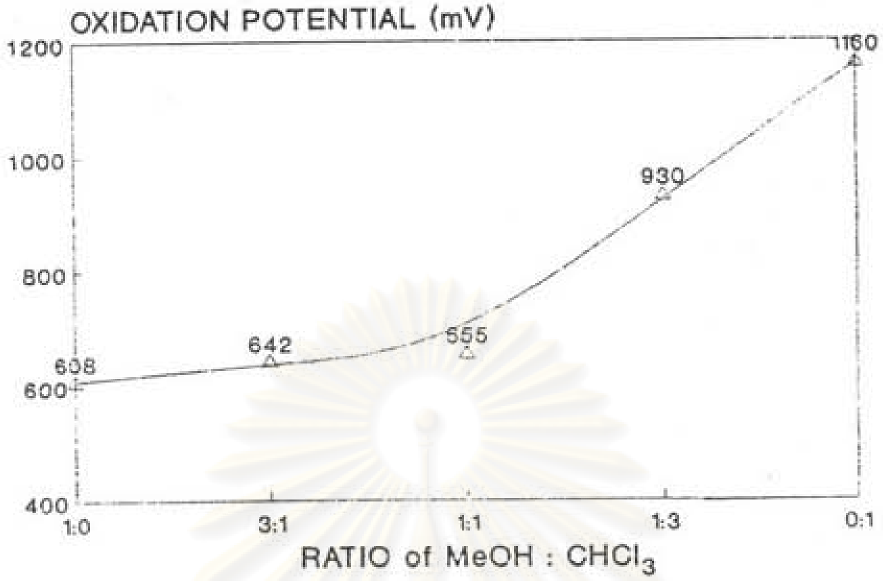


Figure 4.7 The change in oxidation potential of $FeCl_3$ in $MeOH-CHCl_3$ at various ratio of $MeOH:CHCl_3$

Table 4.5 Effect of solvent

Sample No.*	Ratio MeOH:$CHCl_3$	Initial oxidation potential (mV) (versus SCE)	Product yield (g)	Conductivity (Scm^{-1})
PP_6	MeOH	608	0.83	133.02
PP_{30}	9:1	619	0.33	37.70
PP_{31}	4:1	638	0.10	5.69
PP_{32}	3:1	642	0.05	2.57
PP_{33}	1:1	655	0	-
PP_{34}	1:3	930	0	-
PP_{35}	$CHCl_3$	1160	0	-

* See experiment 3.2.1.6

Figure 4.8 shows the electrical conductivity of polypyrrole at various ratio of MeOH:$CHCl_3$ in solution. It was found that with blank mixture solvent, oxidation potential of the solution was higher than the oxidation potential of solution which synthesizing polypyrrole, 608 mV, as can be seen in section 4.1.2.2. It seemed that this reaction required the $FeCl_3$ solution which had the oxidation potential of 608 mV no matter what type of solvent was.

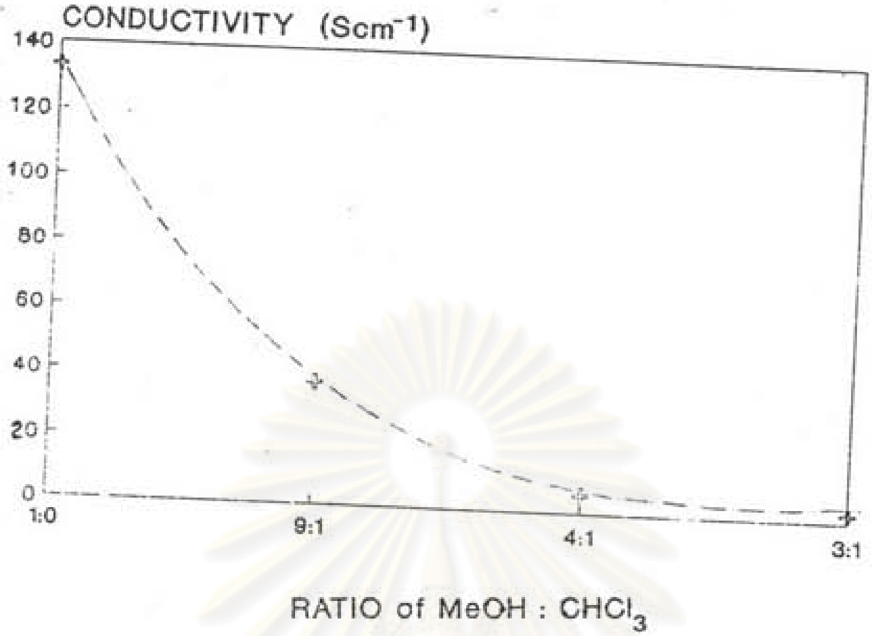


Figure 4.8 The electrical conductivity of polypyrrole at various ratio of MeOH:CHCl$_3$ in solution

volume of 2.5 M FeCl$_3$ solution	20.0	ml
volume of pyrrole	1.00	ml
reaction temperature	0	°C

4.2.3 Time-Decay Conductivity of Polymer Disc

After stored polypyrrole disc in open air at room temperature for a period of time and repeatedly measured its conductivity, it was found that conductivity decreased as the time went by. The decreasing rate of conductivity also decreased with time. As expected, the experiment showed that eventually reached some constant value.

From Table 4.6 and Figure 4.9, it was quite possible that anions near the surface of the polymer disc were more readily removed from the polymer matrix than those held deeper in the polymer. This phenomenon could be explained that the conductivity diminishes rapidly within the first period of measurement and rather slowly thereafter. This suggested that there was a minimum conductivity to which thicker disc could be driven down because of the presence of trapped ions. The employment of amount of dopant ions was also held deeper in polymer disc which resulted in lower conductivity.

Table 4.6 Time-decay conductivity of disc polypyrrole

Days	Conductivity (Scm^{-1})	
	Sample No.	
	PP_6	PP_{20}
1	133.02	85.87
30	-	66.01
33	100.05	-
45	-	59.60
55	-	42.90
90	69.18	-
115	-	42.85
119	-	38.10
146	-	31.95
158	38.50	-
176	-	30.80
183	38.00	-
206	-	30.05
210	36.05	-
240	35.96	-

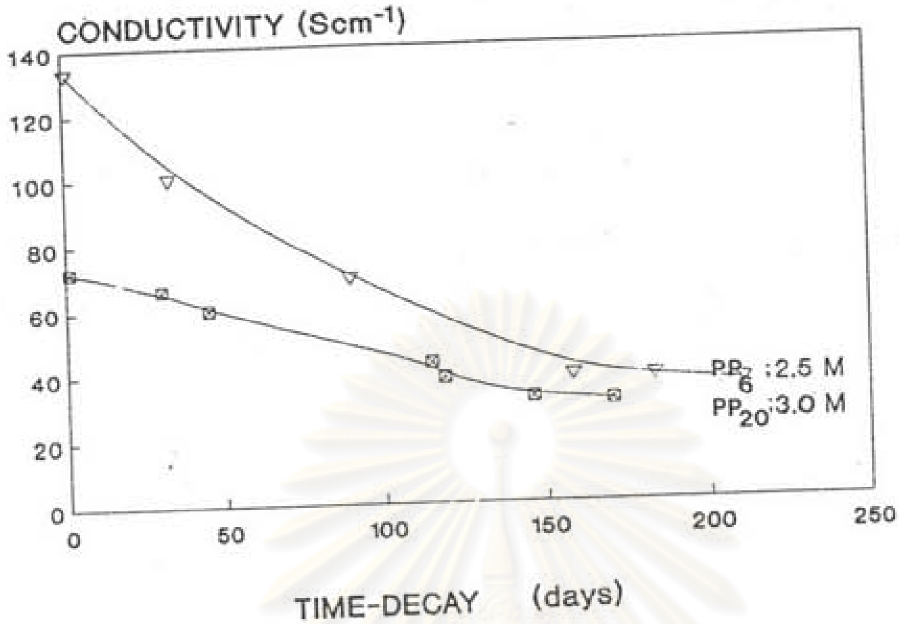


Figure 4.9 Time-decay conductivity of polypyrrole disc

4.2.4 The Stability of Conducting Polypyrrole

The stability of conductivity of synthesised conducting polymer powder was studied in various conditions, as discussed as follows;

4.2.4.1 Temperature

As can be seen in Table 4.7 and Figure 4.10, the thermal stability of polypyrrole powder was studied by means of electrical conductivity measurment. The results showed the conductivity as a function of time at difference temperature for polypyrrole (PP_6) of initial conductivity 133.02 Scm^{-1}. During heating period, it was found that conductivity of polypyrrole decreased with time. Polypyrrole stored at higher temperatures had higher decreasing rate than the one stored at lower temperatures, as shown in Figure 4.10. In this Figure, it was suggested that high temperature may accelerate the removal of anions from the polymer matrix or enhance the thermal decomposition of the active dopant species, Cl^- into Cl_2, Thus it resulted in the lower conductivity.

Table 4.7 Effect of temperature to stability conductivity of polypyrrole

Temp. (^oC)	Conductivity (Scm^{-1})				
	Days				
	1	2	3	4	7
4^oC	-	132.89	-	132.47	132.04
room	-	-	131.15	-	130.10
50^oC	111.74	-	-	100.01	90.67
75^oC	97.13	-	-	72.87	69.75
100^oC	-	72.02	-	57.71	35.46

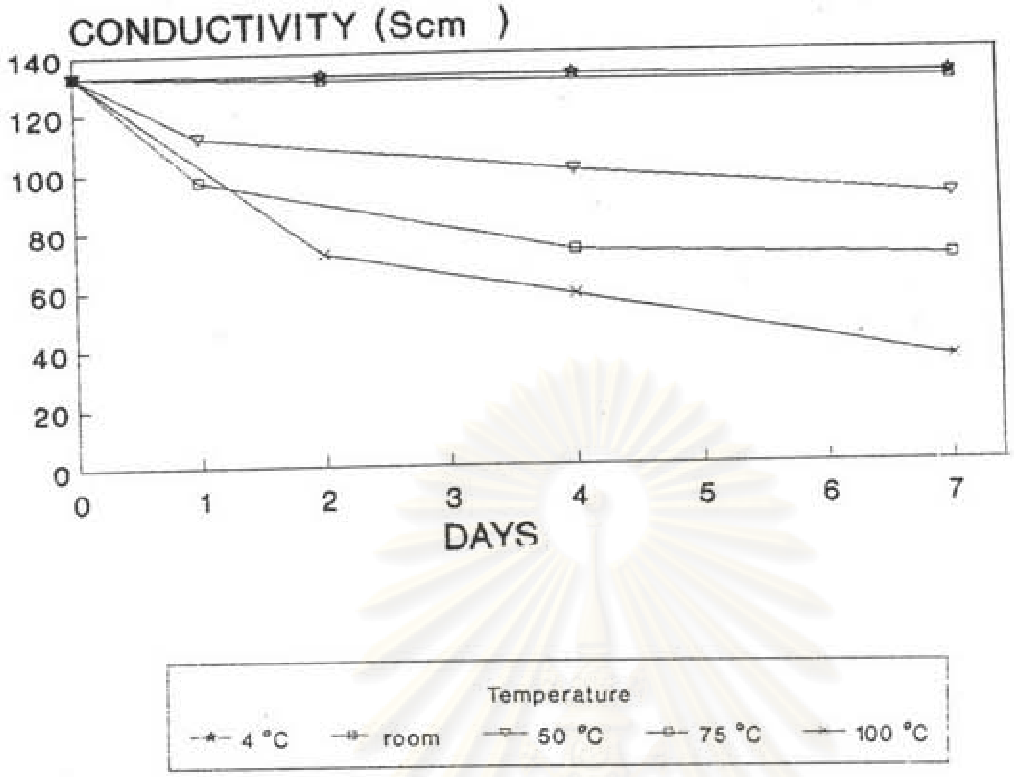


Figure 4.10 Conductivity change of the polypyrrole after thermal treatment

The FTIR spectra for thermal treatment were exhibited in the Figure 4.11. After the exposure at high temperature, The polymer exhibited weak absorption band of the doping-induced mode at 1000-1300 cm^{-1} (indicated with broken line), accompanied by decrease in conductivity.

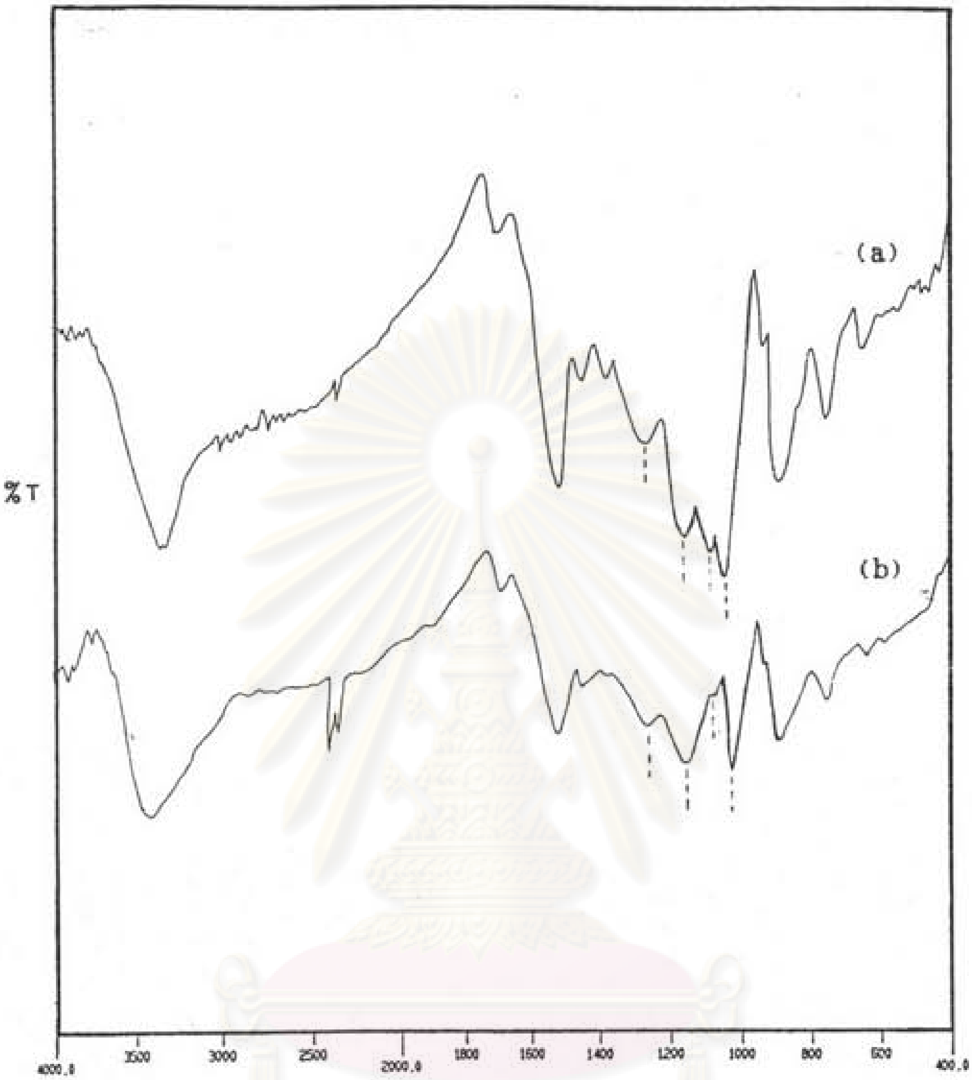


Figure 4.11 FTIR (KBr) of polypyrrole after temperature treatment

(a) PP_6 at 4 ^{o}C : 132.04 Scm^{-1}

(b) PP_6 at 100^{o}C : 35.46 Scm^{-1}

4.2.4.2 Acid/Base solution

Experimental results on the treatment of the polymer powder which has initial conductivity of 85.87 Scm^{-1} (PP_{20}) with various concentration of H_2SO_4 and NaOH from 0.25 M to 1.00 M at room temperature for 7 days, was reported in table 4.8 and Figure 4.12.

Table 4.8 Effect of acid/base solution to stability conductivity of polypyrrole

Concentration (M)	Conductivity (Scm^{-1})	
	H_2SO_4	NaOH
0	64.47	64.47
0.25	33.87	21.75
0.50	37.18	19.07
0.75	36.48	19.92
1.00	34.28	20.69

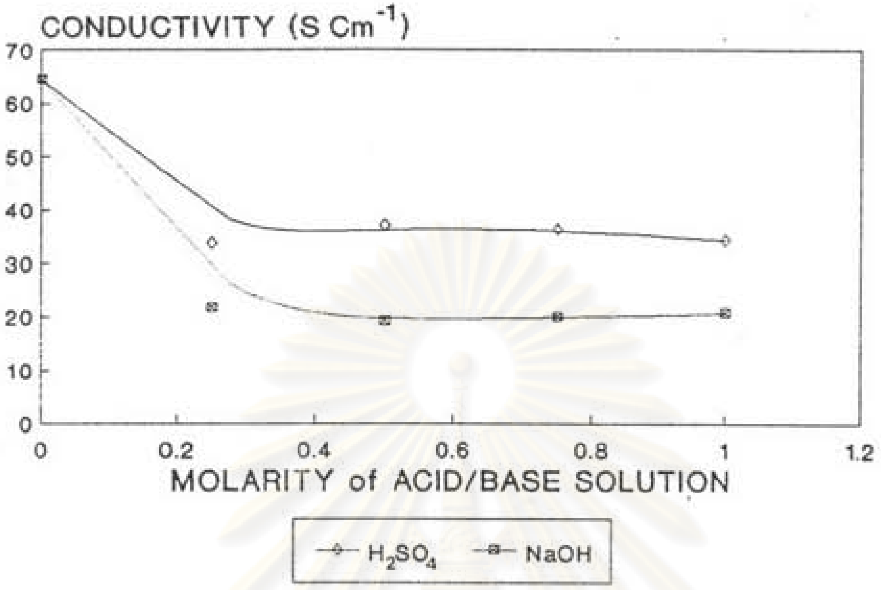
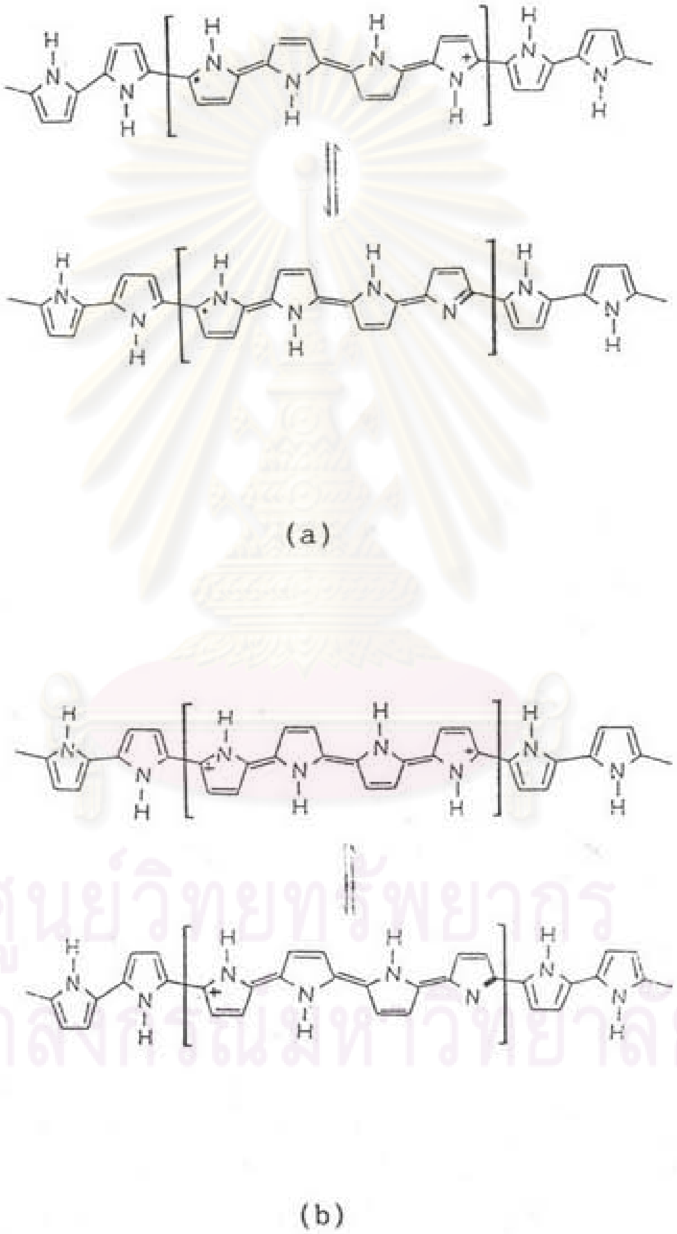


Figure 4.12 Conductivity change of the polypyrrole after acid/base treatment

As could be seen in Table 4.8 and Figure 4.12, NaOH treatment gave less conductivity of polypyrrole than H_2SO_4 treatment, and this decrease, by any mean, was not a function of the concentration in the range studied . From the result, it was found that the treatment of polypyrrole with acid and base solution led to a decrease of conductivity. When it was treated with NaOH, it was expected that there was also reversible deprotonation at the nitrogen atoms in the polymer. This will affect the electronic structure of the polymer, by leaving a single electron on the polymer backbone during deprotonation[. The deprotonation may also lead to a decrease of polaron or bipolaron of the conjugated chain length of the polymer. as proposed in Figure below.



Deprotonation at nitrogen atom in the polymer

(a) polaron (b) bipolaron

Treatment of polypyrrole with H_2SO_4, the conductivity of this sample was slightly reduced, as compared to the NaOH treatment. It probably resulted in the exchange of sulfateion for chlorideions, as studied and determined by spectra in Figure 4.13. Consequuently, its mechanism may then partially account for a slight decrease in conductivity for the acid-treated sample.

The FTIR spectra for acid/base treated polypyrrole powder (PP_{20}) were shown in Figure 4.13 (a), (b) and (c). The FTIR spectra in all three cases showed a long absorption from 4000 to about 2000 cm^{-1}. These long absorption tails have been assigned to be the tail of OH covalent bond formation with polypyrrole. The FTIR spectra of H_2SO_4/NaOH treated still showed bands characteristic of pyrrole rings in the polymer.

The FTIR spectra of polypyrrole when treated wtih H_2SO_4 show absorption bands at 1110- 610 cm^{-1} which were characteristic of the sulphate anion.

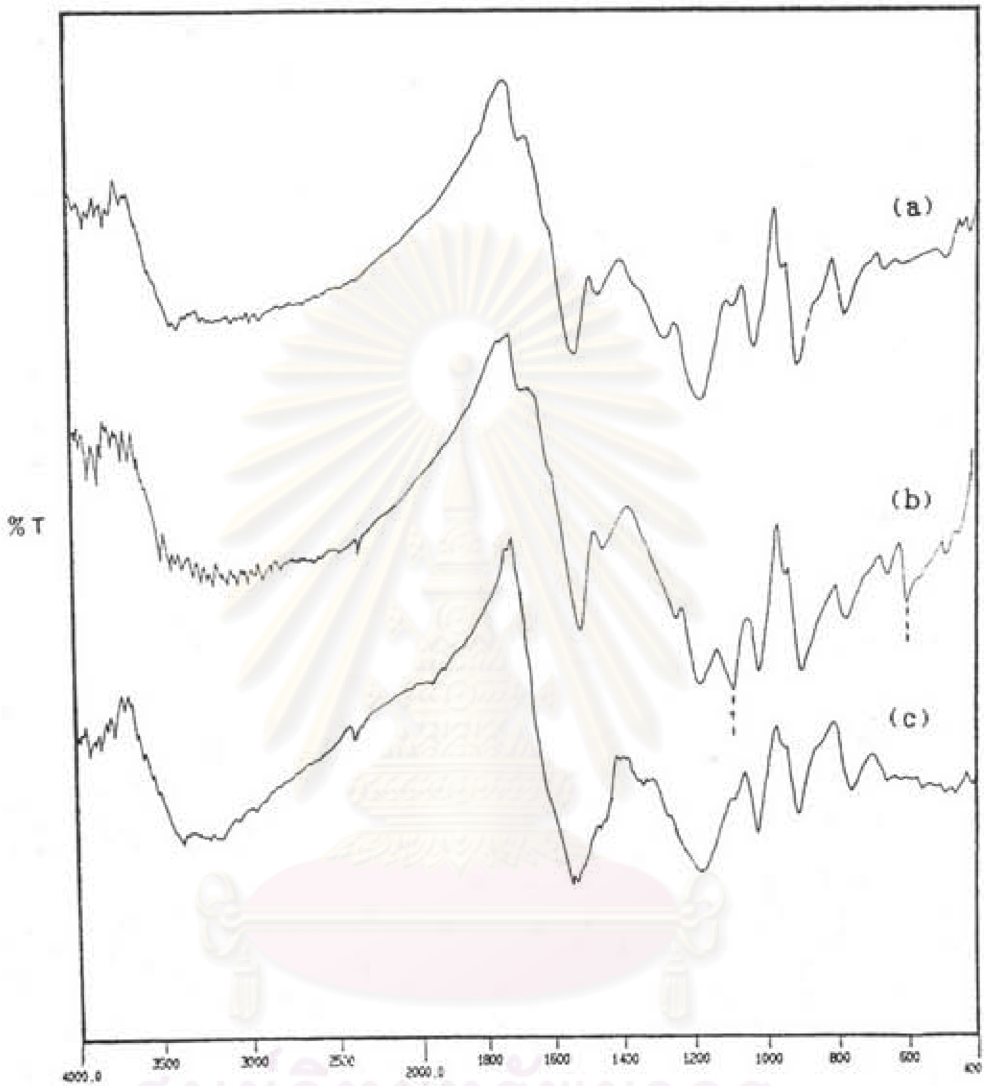


Figure 4.13 FTIR (KBr) spectrum of polypyrrole after acid/base treatment

(a) PP_{20} treatment with H_2O : 64.47 Scm^{-1}

(b) PP_{20} treatment with 1.0 M H_2SO_4 : 32.28 Scm^{-1}

(c) PP_{20} treatment with 1.0 M NaOH : 20.29 Scm^{-1}

4.2.4.3 The Effect of Atmosphere on Conductivity

The decreasing of conductivity of polypyrrole has been tested by storing the polymer powder in different atmospheres , namely , O_2 , N_2 gas and dry air (in desiccator) for one month. After one month the conductivities of the polypyrrole were measured and reported in Table 4.9.

Table 4.9 Conductivity of polypyrrole after stored in various atmospheres for one month

Sample No.	conductivity (Scm^{-1})				
	Initial*	O_2	N_2	Dry air	Open air
PP_{11}	72.44	69.94	64.49	64.27	54.32
PP_{20}	85.87	81.20	75.62	78.58	66.01
PP_{27}	97.47	96.53	95.23	93.62	76.90

* Result from section 4.2.2

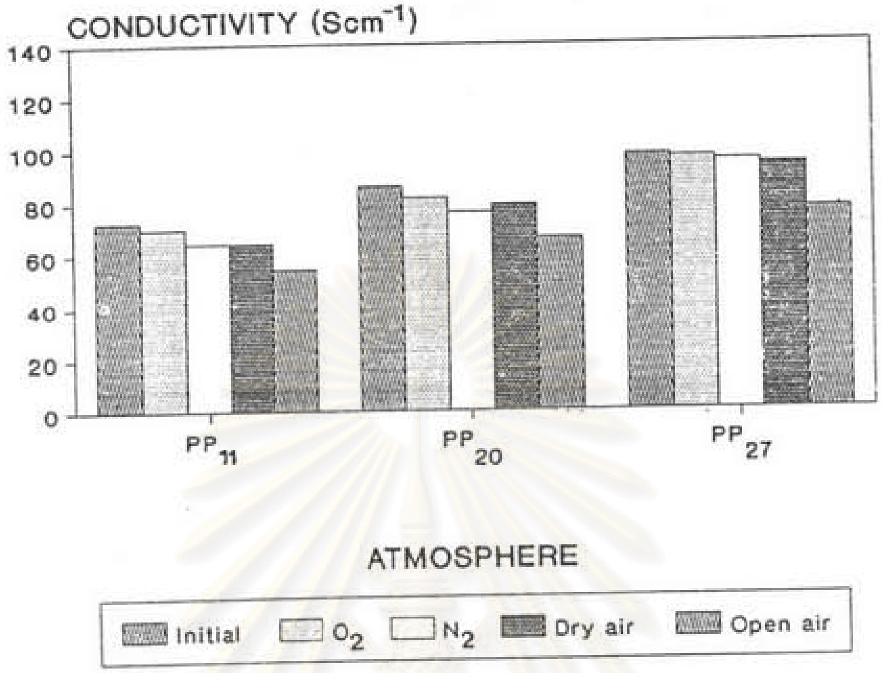


Figure 4.14 Conductivity change of polypyrrole after storage in various atmospheres

As can be seen from Table 4.9, a one month, the conductivities of polymer powder which stroed in the seal package under O_2, N_2 gas or dry air (in desiccator) were higher than that stored in open air. It is quite possible that for the polymer which stored under open air circulation, the charge decay was accelelated. This can be expected that the moisture in open air might interfere with the interaction force between polymer chain with doping anion, as studied and determined by spectra in Figure 4.15. Thus the conductivity was reduced.

FTIR spectrum of the polypyrrole stroaged in O_2, N_2 gas and dry air in desiccator at room temperature for one month did not bring significant change in the FTIR spectra and conductivity (see Figure 4.15). But in open air (Figure 4.15 (a)) there are absorption band at 2500-3500 cm^{-1} which indicated OH covalent bond in the polymer chains.

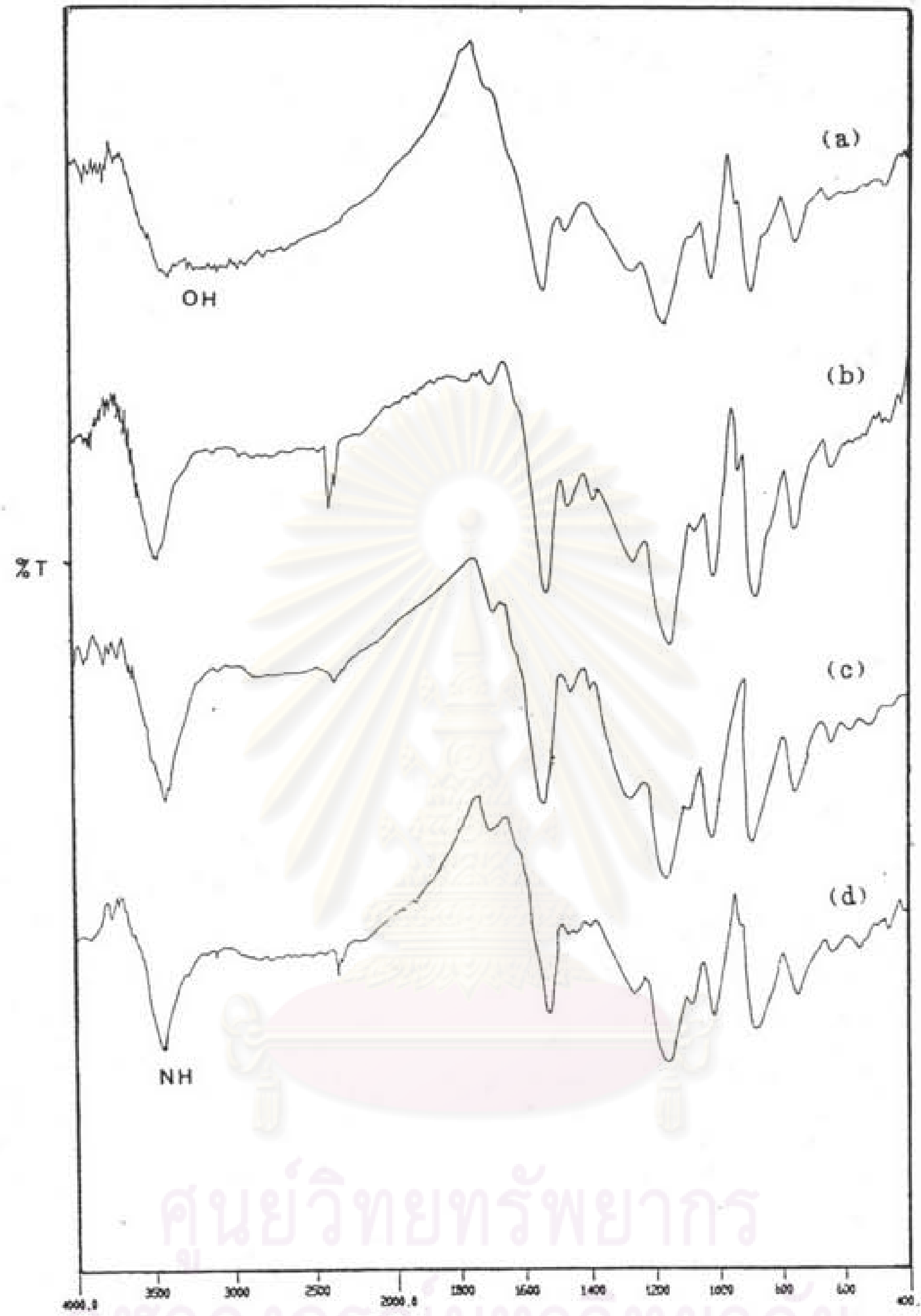


Figure 4.15 FTIR (KBr) spectrum of polypyrrole storaged in various atmosphere

(a) PP_{20} in open air : 66.01 Scm^{-1}
(b) PP_{20} in dry air : 78.58 Scm^{-1}
(c) PP_{20} in O_2 gas : 81.20 Scm^{-1}
(d) PP_{20} In N_2 gas : 75.62 Scm^{-1}

4.3 Synthesis of Polythiophene

4.3.1 Synthesis of Polythiophene in Methanol

From experimental result, polythiophene can not be prepared by chemical polymerization with $FeCl_3$ in methanol solution. It was expected that the solution had too low oxidation potential to proceed the reaction,because , as mentioned in section 4.2.2.2 , the highest oxidation potential of solutions prepared was 614 mV in the concentration range of 0.5 M-3.5 M $FeCl_3$ in methanol. Thus, it was obvious that $FeCl_3$ in methanol solution was not suitable for the synthesis of polythiophene.

4.3.2 Synthesis of polythiophene in chloroform

The synthesis was done by using chloroform, as a solvent and employing various concentrations of $FeCl_3$. The concentrations were ranged from 0.5 M - 4.0 M, which had oxidation potential in the range of 950-1270 mV. Since the oxidation potential of $FeCl_3$ in chloroform solution various which the concentration of $FeCl_3$ this will affect the polymerization and thus should be investigated. This was performed by construction the calibration curve as shown in Figure 4.12. It is apparent that the oxidation potential increases with increasing concentration of $FeCl_3$.

Additionally for each reaction the initial oxidation potential of solution must be recorded (shows in Table 4.10).

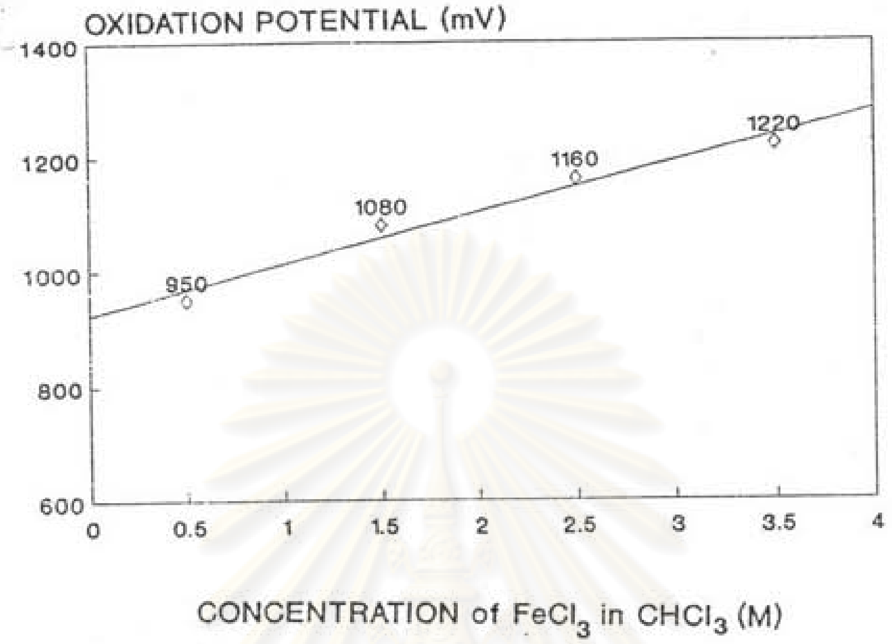


Figure 4.16 The oxidation potential of $FeCl_3$ in chloroform at various concentrations.

From experimental resulting, polythiophene was prepared by using $FeCl_3$ in chloroform solution. The prepared polythiophene showed insulating behaviour (conductivity below 10^{-5} Scm^{-1}). However, high yield product (0.6- 0.7 g) was obtained. It was expected that $FeCl_3$ in chloroform solution had enough oxidation potential for polymerizing polythiophene but this is not optimum oxidation potential for synthesised conducting polythiophene. It was posible that oxidation potential in the range of 950-1220 mV produced mostly shorten conjugated chain of polythiophene.

Table 4.10 Synthesis of polythiophene in chloroform solution

Sample No. *	Initial Oxidation potential (mV) (versus SCE)	Product yield (g)	Conductivity (Scm^{-1})
PT_{19}	950	0.62	$<10^{-5}$
PT_{20}	950	0.60	$<10^{-5}$
PT_{21}	1000	0.64	$<10^{-5}$
PT_{22}	1000	0.71	$<10^{-5}$
PT_{23}	1010	0.78	$<10^{-5}$
PT_{24}	1010	0.73	$<10^{-5}$
PT_{25}	1010	0.71	$<10^{-5}$
PT_{26}	1010	0.77	$<10^{-5}$
PT_{27}	1080	0.67	$<10^{-5}$
PT_{28}	1080	0.79	$<10^{-5}$
PT_{29}	1160	0.72	$<10^{-5}$
PT_{30}	1160	0.75	$<10^{-5}$
PT_{31}	1220	0.69	$<10^{-5}$
PT_{32}	1220	0.76	$<10^{-5}$
PT_{33}	1270	0.67	$<10^{-5}$
PT_{34}	1270	0.65	$<10^{-5}$

* See experiment 3.2.3.2

4.3.3 Synthesis of Polythiophene in Acetonitrile

Synthesis of polythiophene with $FeCl_3$ in acetonitrile solution was done in various concentrations of $FeCl_3$ range from 0.3 M - 4.0 M. The oxidation potential of these solutions vs SCE increases with increasing concentration of $FeCl_3$ as shown in Figure 4.17. Additionally for each reaction the initial oxidation potential of solution must be read (shows in Table 4.11), the oxidation potential in the range of 1100-1430.

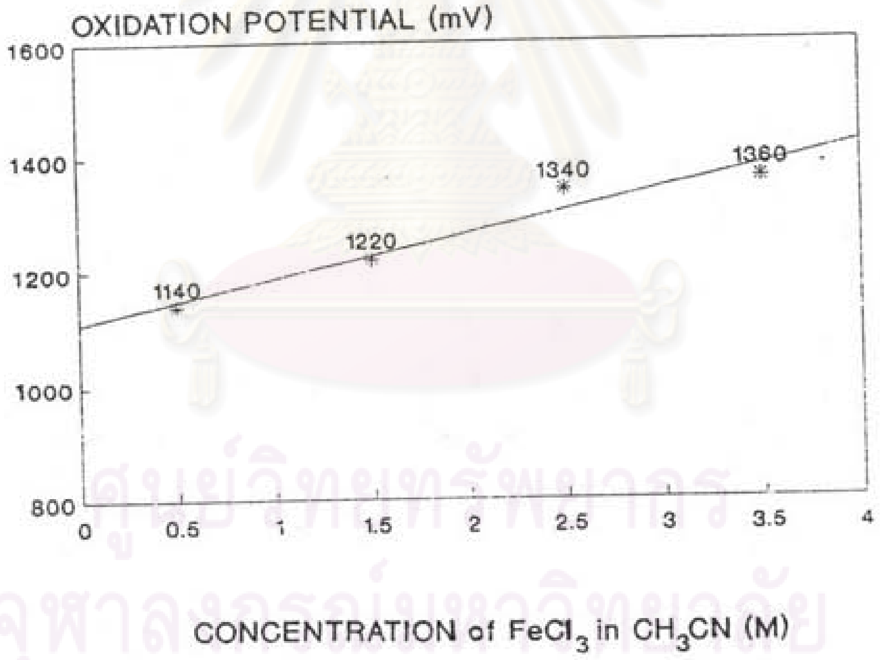


Figure 4.17 The oxidation potential of $FeCl_3$ in acetonitrile at various concentrations

Table 4.11 Conductivity of polythiophene synthesis in acetonitrile solution

Sample No.*	Initial Oxidation potential (mV) (versus SCE)	Product yield (g)	Conductivity (Scm^{-1})
PT$_{35}$	1100	0.49	$< 10^{-5}$
PT$_{36}$	1100	0.53	$< 10^{-5}$
PT$_{37}$	1140	0.55	$< 10^{-5}$
PT$_{38}$	1140	0.47	$< 10^{-5}$
PT$_{39}$	1190	0.51	$< 10^{-5}$
PT$_{40}$	1190	0.48	$< 10^{-5}$
PT$_{41}$	1340	0.46	$< 10^{-5}$
PT$_{42}$	1340	0.43	$< 10^{-5}$
PT$_{43}$	1350	0.63	$1.17*10^{-5}$
PT$_{44}$	1350	0.65	$5.20*10^{-5}$
PT$_{45}$	1350	0.59	$2.83*10^{-5}$
PT$_{46}$	1350	0.55	$1.22*10^{-5}$
PT$_{47}$	1350	0.59	$1.62*10^{-5}$
PT$_{48}$	1350	0.57	$1.41*10^{-5}$
PT$_{49}$	1360	0.77	$< 10^{-5}$
PT$_{50}$	1360	0.64	$< 10^{-5}$
PT$_{51}$	1430	0.72	$< 10^{-5}$
PT$_{52}$	1430	0.68	$< 10^{-5}$

* See experiment 3.2.3.3

Table 4.11 shows that 2.8 M $FeCl_3$ in acetonitrile which oxidation potential vs SCE is 1350 mV is the most suitable solution for preparing conducting polythiophene . With other solution concentration , polythiophene could be produced but would have only very low conductivity (insulating, conductivity< 10^{-5} Scm^{-1}). It is expected that this solution could be used to prepare conducting polythiophene. However, conductivities obtained were much lower than that of polypyrrole, as compared with the result in section 4.2. Thus, synthesis of polythiophene with various conductivities range, from insulator to semiconductor, could be easily controlled by changing the the concentration of $FeCl_3$.

4.4 Synthesis of Poly (3-methylthiophene)

Poly (3-methythiophene), a derivative of polythiophene has been synthesized with the objective of obtaining a conducting polymer of lower energy band gap and high conductivity.

4.4.1 Synthesis of Poly (3-methylthiophene) in Methanol

Similar to the synthesis of polythiophene mentioned in section 4.3.1, poly(3-methylthiophene) can not be prepared by chemical polymerization with $FeCl_3$ in methanol solution . It was expected that the solution had too low oxidation potential (614 mV versus SCE) for the polymerization reaction of poly (3-methylthiophene).

4.4.2 Synthesis of Poly(3-methylthiophene) in Chloroform

This section shows the results of synthesis of polythiophene with $FeCl_3$ in chloroform solution by various concentration of $FeCl_3$; from 0.3 M - 1.2 M (oxidation potential 925-1010 mV vs SCE; see calibration curve in section 4.3.2). The result of this synthesis is shown in Table 4.12.

Table 4.12 Conductivity of poly (3-methylthiophene) synthesized in chloroform solution

Sample No.*	Initial Oxidation potential (mV) (versus SCE.)	Product yield (g)	Conductivity (Scm^{-1})
$P3MT_{19}$	925	0.59	$4.12*10^{-5}$
$P3MT_{20}$	925	0.47	$7.78*10^{-5}$
$P3MT_{21}$	950	0.78	$6.60*10^{-4}$
$P3MT_{22}$	950	0.67	$1.50*10^{-4}$
$P3MT_{23}$	950	0.79	$7.32*10^{-4}$
$P3MT_{24}$	1000	0.63	$6.72*10^{-4}$
$P3MT_{25}$	1000	0.68	$2.00*10^{-4}$
$P3MT_{26}$	1000	0.58	$8.93*10^{-4}$
$P3MT_{27}$	1010	0.73	$3.23*10^{-2}$
$P3MT_{28}$	1010	0.71	$3.20*10^{-2}$

* See experiment 3.2.4.2

Conducting poly(3-methylthiophene) can be prepared with $FeCl_3$ in chlorofrom solution . When The higher concentration of $FeCl_3$ was used,thehigher conductivity of polymer was obtained. From this result, it can be expected that conducting poly(3-methylthiophene) can be prepared in the solution, which oxidation potential is as high as 925 mV versus SCE.

4.4.3 Synthesis of Poly (3-methylthiophene) in Acetonitrile

The result of the synthesis of poly (3-methyl thiophene with $FeCl_3$ in acetonitrile solution at various concentrations of $FeCl_3$; from 0.3 M - 4.0 M (oxidation potential 1100-1360 mV versus SCE, was shown in Table 4.14.)

As can be seen in the Table 4.14, conducting poly(3-methylthiophene) was prepared with 0.3 M - 2.8 M $FeCl_3$ in acetonitrile solution (oxidation potential 1100-1350 mV versus SCE, see calibration curve in section 4.3.3). But at higher concentration (3.5 M - 4.0 M) there are more oxidation potential (> 1350 mV), synthesised polythiophene as an insulator. It was expect that conducting poly (3-methylthiophene) can be prepared in solution which has oxidation potential 1000-1350 mV versus SCE.

Table 4.13 Conductivity of poly(3-methylthiophene) synthesised in acetonitrile solution

Sample No.*	Initial Oxidation potential (mV) (versus SCE)	Product yield (g)	Conductivity (Scm^{-1})
P3MT$_{29}$	1100	0.73	$1.15*10^{-3}$
P3MT$_{30}$	1100	0.61	$1.37*10^{-3}$
P3MT$_{31}$	1140	0.63	$2.29*10^{-3}$
P3MT$_{32}$	1140	0.54	$2.78*10^{-3}$
P3MT$_{33}$	1180	0.72	$3.76*10^{-3}$
P3MT$_{34}$	1180	0.61	$2.24*10^{-3}$
P3MT$_{35}$	1340	0.75	$4.23*10^{-3}$
P3MT$_{36}$	1340	0.59	$5.19*10^{-3}$
P3MT$_{37}$	1350	0.78	$5.77*10^{-3}$
P3MT$_{38}$	1350	0.81	$2.40*10^{-2}$
P3MT$_{39}$	1350	0.86	$2.80*10^{-2}$
P3MT$_{40}$	1350	0.56	$3.71*10^{-3}$
P3MT$_{41}$	1350	0.62	$2.26*10^{-2}$
P3MT$_{42}$	1350	0.61	$5.19*10^{-2}$
P3MT$_{43}$	1360	0.72	$<10^{-5}$
P3MT$_{44}$	1360	0.68	$<10^{-5}$
P3MT$_{45}$	1430	0.63	<10-5
P3MT$_{46}$	1430	0.67	<10-5

* See experiment 3.2.4.3

4.4 Product Characterization

4.4.1 Elemental Analysis

The results of the elemental analysis of polypyrrole (PP), polythiophene (PT) and poly (3-methylthiophene) (P3MT) are summarized in Table 4.14.

Table 4.14 Elemental analysis for polymers

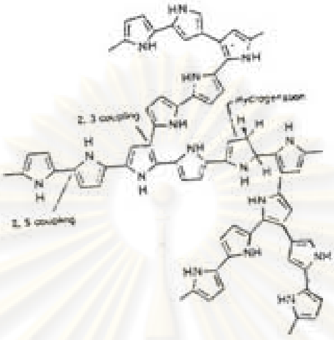
sample	% C	% H	% N	% S	% Cl	% O
PP$_{6}$	55.12	4.32	16.56	–	14.13	9.87
PP$_{22}$	57.15	3.06	16.37	–	13.10	10.32
PT$_{26}$	54.12	2.83	–	38.72	4.76	–
PT$_{27}$	55.08	2.59	–	38.41	3.92	–
P3MT$_{31}$	59.43	4.09	–	31.59	4.89	–
P3MT$_{32}$	58.67	4.34	–	31.41	5.58	–

Table 4.15 Empirical formular of polymer

sample No*	empirical formular	conductivity* (SCm^{-1})
PP$_6$	$C_{3.88}H_{3.65}N_1Cl_{0.34}O_{0.52}$	133.02
PP$_{22}$	$C_{4.07}H_{2.61}N_1Cl_{0.31}O_{0.55}$	72.44
PT$_{26}$	$C_{3.76}H_{2.35}S_1Cl_{0.11}$	5.20*10^{-5}
PT$_{27}$	$C_{3.85}H_{2.17}S_1Cl_{0.09}$	2.83*10^{-5}
P3MT$_{31}$	$C_{5.02}H_{4.15}S_1Cl_{0.14}$	2.62*10^{-2}
P3MT$_{32}$	$C_{4.99}H_{4.43}S_1Cl_{0.16}$	5.19*10^{-2}

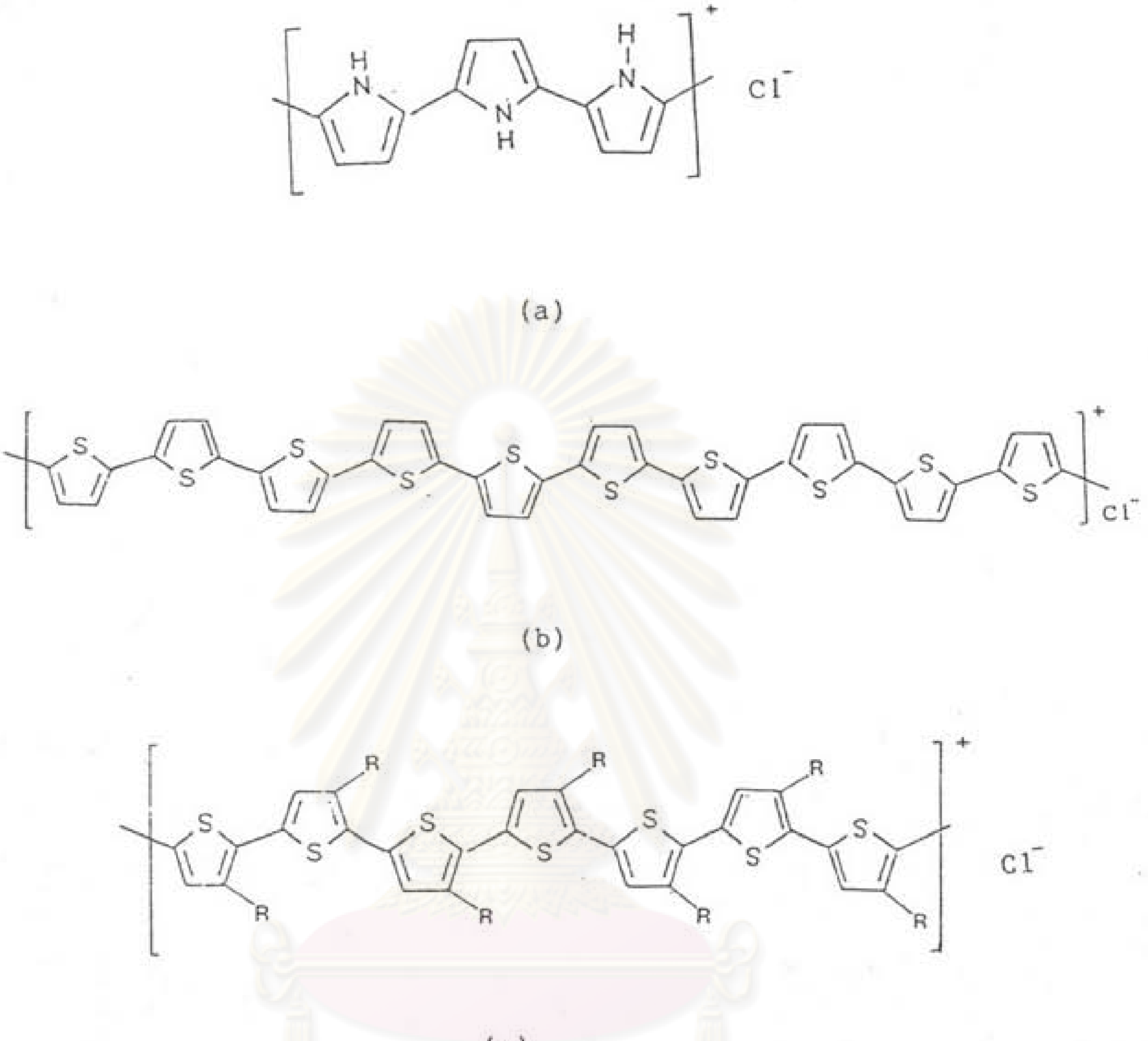
* Result from section 4.1-4.3

Fromthe elemental analysis, the empirical formular of the polymer could be identified (Table 4.15). For polypyrrole PP$_6$ and PP$_{11}$ they could be calculated for its repeating unit as shown in scheme 4.1 (a). That for approximatedly in every three pyrrole units there should be one counter anion , Cl$^-$ ion . However , the calculation cleary indicated that oxygen must be involved in the structure. Similar result was also reported by Machida et al. [14]. They proposed that the oxygen in polypyrrole was mainly present in the form a charge-transfer complex between the oxygen molecule and the pyrrole units. In case of PP$_{11}$, it was found that number of hydrogen incorporated in the empirical formular was less than it should be. This meant that there should be some substitution in the pyrrole ring, possibly, the 2,3-coupling shown below.



Crosslinking the chain in the polymer

Similarly, the elemental formular of the polythiophene and poly(3-methylthiophene) could be calculated for their repeating unit. For polytrhiophene, it was expected that in approximate, there is one Cl^- ion in every ten thiophene units. Its empirical formular isproposed to be $[C_4H_2S)_{10}^+ \ Cl^-]_n$ as presented in Scheme 4.1 (b) . For poly(3-methylthiophene), its empirical formular is proposed to be $[C_5H_4S)_7^+ \ Cl^-]_n$. That there are seven units of 3-methylthiophene per one Cl^- ion as presented in Scheme 4.18 (c), where only α,α'-linkage was assumed to be present in this ideal structure.



(a)

(b)

(c)

Scheme 4.1 polymer structure of polymers as expected from elemental analysis

It should be noted that these three types of conducting polymers had different conductivity values which were consistent with the length of the conjugated polymer chain in one repeating or with one counteranion. The longer the conjugation was, the higher the conductivity would be.

4.4.2 FTIR (Fourier Transform Infared) Measurements

Due to the insolubility of the solid products. FTIR is the significant method for characterize these products. The assignment of the principal absorption bands for three polymers (polypyrrole, PP; polythiophene, PT and poly(3-methylthiophene), P3MT) are given in Figure 4.18, 4.19 and 4.20 respectively.

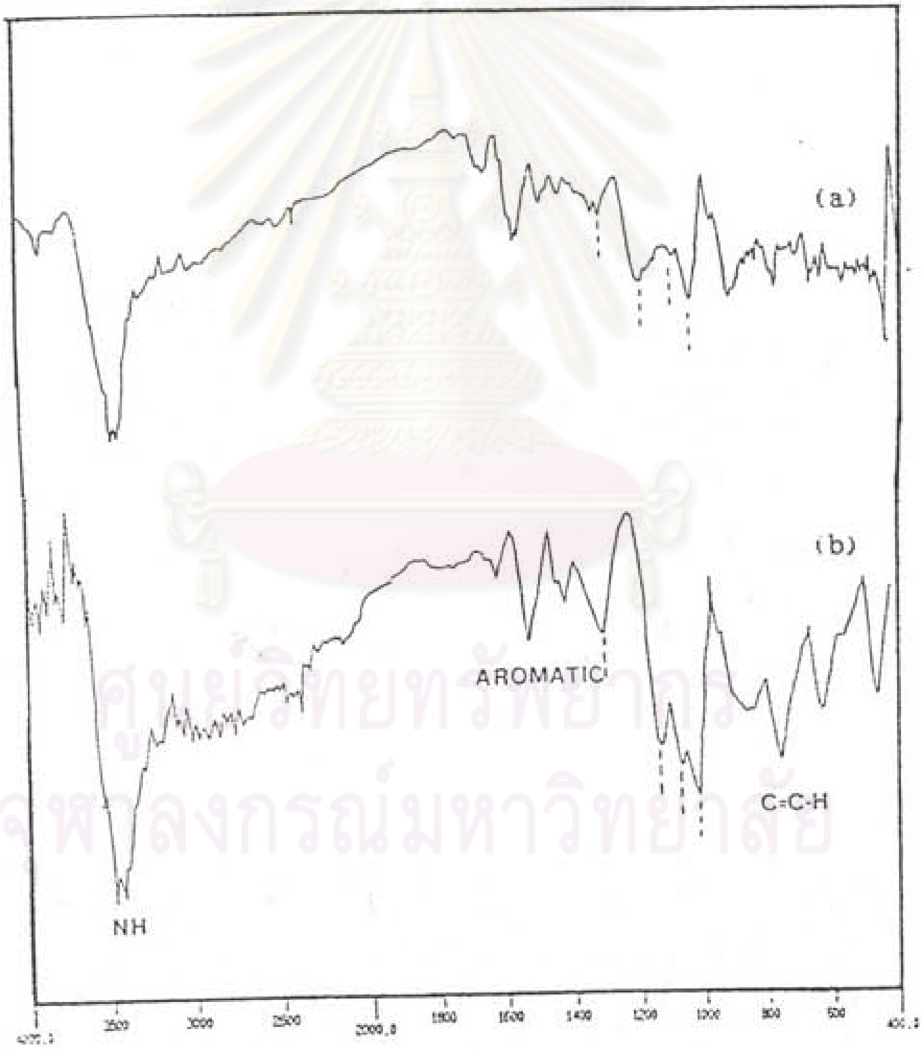


Figure 4.18 FTIR (KBr) spectra of polypyrrole

(a) PP_{24} : 9.95 Scm_{-1}

(b) PP_6 : 133.02 Scm^{-1}

Table 4.16 The assignment for the IR spectrum of polypyrrole

Wavenumber ν (cm^{-1})	Assignment
3450	NH stretching
1600	ring stretching
1510	
1450	
1420	
1300	doping-induced mode
1180	
1140	
1100	
760	aromatic CH out of plane
620	

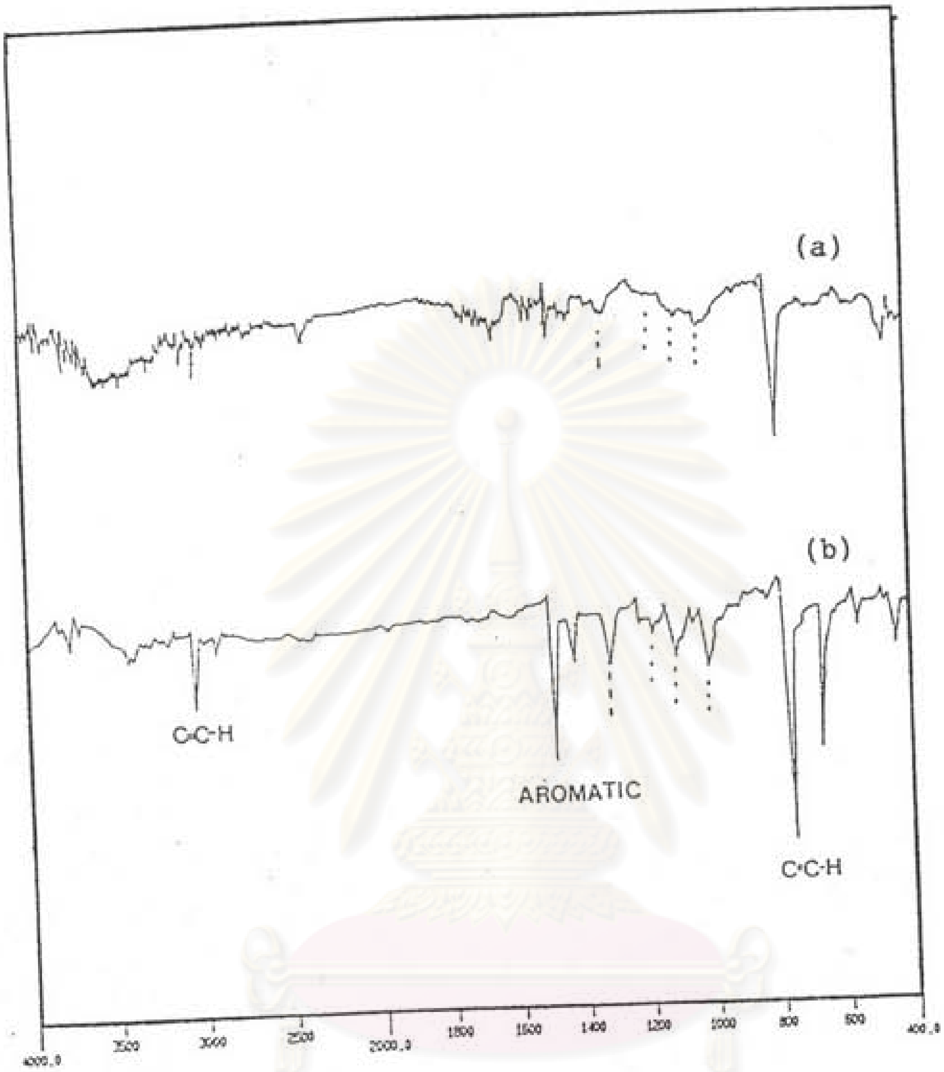


Figure 4.19 FTIR (KBr) spectra of polythiophene

(a) PP_{43} : $<10^{-5}$ Scm^{-1}

(b) PP_{44} : $5.2*10^{-5}$ Scm-1

Table 4.17 The assignment for the IR spectrum of polythiophene

Wavenumber ν (cm^{-1})	Assignment
3010	aromatic CH stretching
1480	ring stretching
1440	
1300	doping-induced mode
1200	
1160	
1000	
780	aromatic CH out of plane
650	

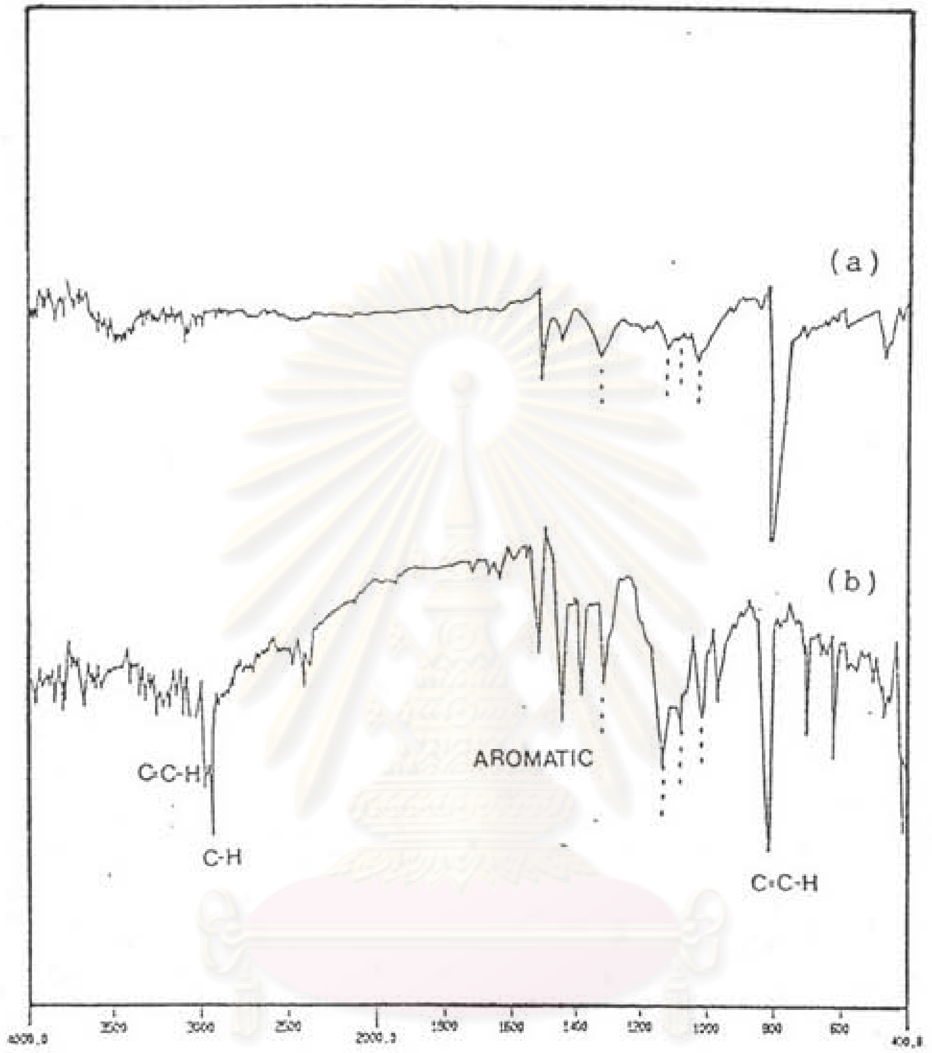


Figure 4.20 FTIR spectra of poly (3-methylthiophene)

(a) $P3MT_{43}$: $< 10^{-5}$ Scm^{-1}

(b) P3MT : $2.26*10^{-2}$ Scm^{-1}

Table 4.18 The assignment for the IR spectrum of poly (3-methylthiophene)

Wavenumber ν (cm^{-1})	Assignment
3060	aromatic CH stretching
2980	aliphatic CH stretching
2920	
1520	ring stretching
1450	
1400	
1330	doping-induced mode
1150	
1130	
810	aromatic CH out of plane
700	

In summary, base on FTIR spectra comparison, three polymers (polypyrrole, polythiophene and poly (3-methylthiophene) have nearly identical organic backbone structures and all of them consist of mostly unalternate monomer units. But they might differ in the polymer backbone and ratio of dopant content thus resulting in difference in conductivity.

4.4.3 Thermogravimetric Analysis

In a thermogravimetric analysis (TGA), the mass of sample is recorded continuously as its temperature is increased linearly from ambient to as high as 1000 °C. The most important applications of thermogravimetric method are found in the study of polymers[40]. Thermograms provide information about decomposition mechanisms for various polymers. In this section, the thermal stability of polymers were studied by means of weight loss.

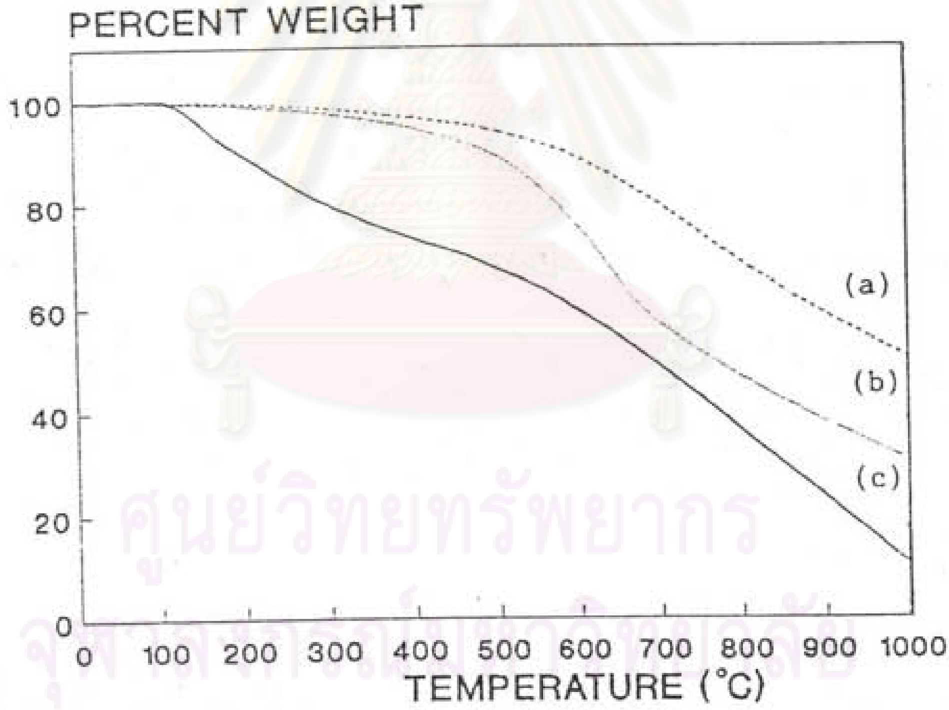


Figure 4.21 TGA of polymers

a) polythiophene

b) poly (3-methylthiophene)

c) polypyrrole

Table 4.19 Weight loss (%) of polymers by TGA

Sample No.	decomposition temp. (°C)	Temp. at 50% weight loss (°C)	weight at 1000 °C (%)
PP_6	125	690	10
PT_{26}	250	1000	50
$P3MT_{31}$	240	800	30

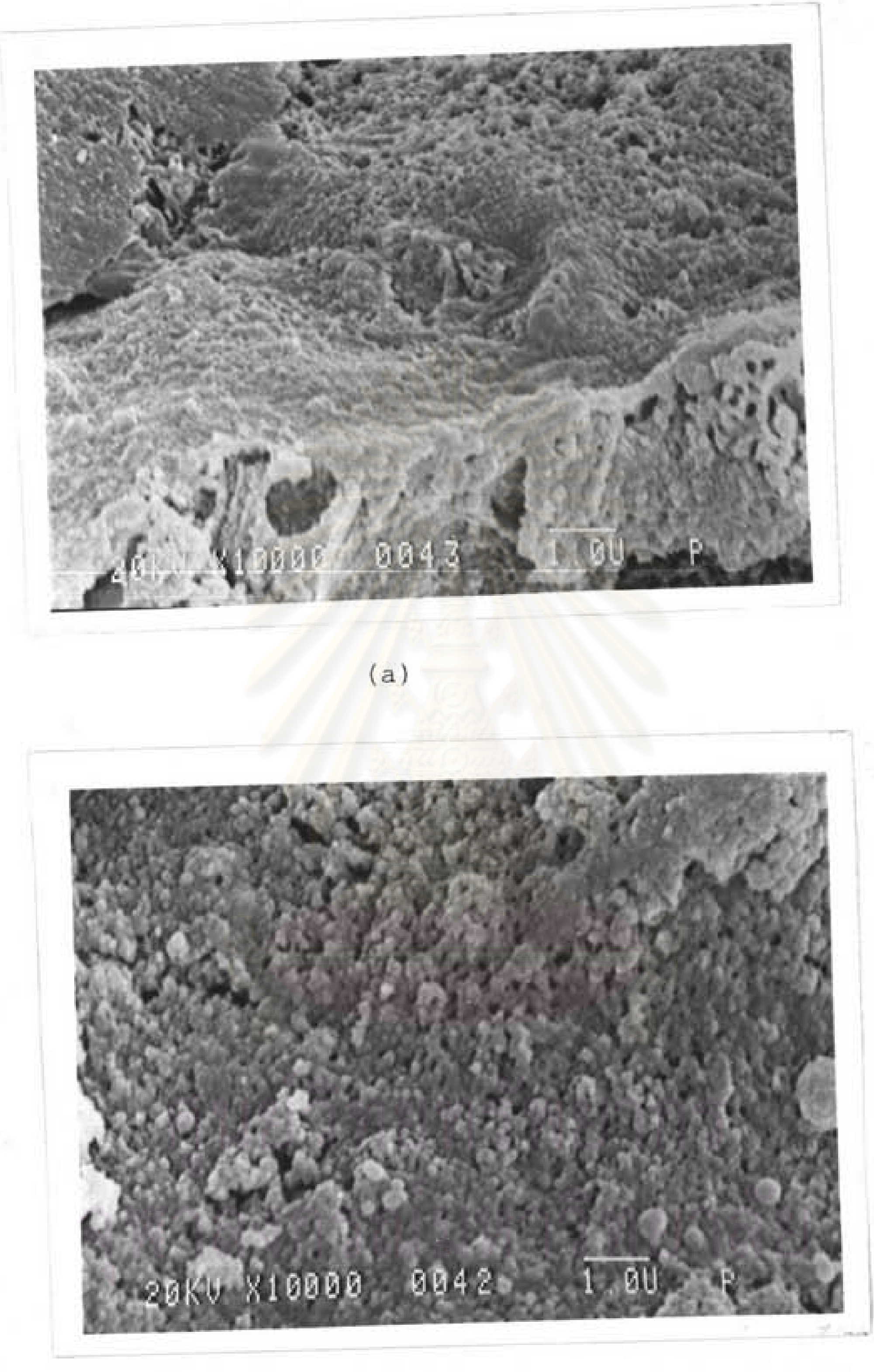
The thermogravimetric scans in nitrogen of polypyrrole , polythiophene and poly (3-methylthiophene) are shown in Figure 4.21 . From the curve , polypyrrole suffer about 90% loss of their original weight when heated from room temperature to temperature as high as 1000 °C. Polypyrrole also exhibits the thermal stability below 125 °C. The thermal stability of the present polypyrrole differs significantly from the thermal behaviour of polythiophene and poly (3-methylthiophene) which are stable up to the decomposition temperature of about 240 °C. However, they are thermal stable more than polyacetylene which shows a rather poor thermal stability and suffers a weight loss immediately upon heating at room temperature [41].

However, among all the polymers studied , they suffer the weight loss when exposed to higher temperature (>100 ^{o}C). The results from Table 4.23, we can conclud that polythiophene and poly (3-methylthiophene) have better thermal stability than polyacetylene.

4.4.4 Scaning Electron Microscropy

The SEM of polypyrrole is shown in Figure 4.22. It shows clusters of globulus with small space in between. These apparently account for the fragile nature of polymers, since there are void space and no networklike structure throughout. Figure 4.23 shows the SEM of polythiophene which large spaces in between. This structure disintegrates into granules. The SEM of poly (3-methylthiophene) shown in Figure 4.24 mainly composes of loosely packed granules of several micrometres in dimension with a void space larger than void space in polypyrrole.

In summary, based on SEM comparision, partially the difference in conductivity of three types of the heterocyclic polymers may be due to the size of void space (insulating gaps) between conducting powder particles in the pressed disc.



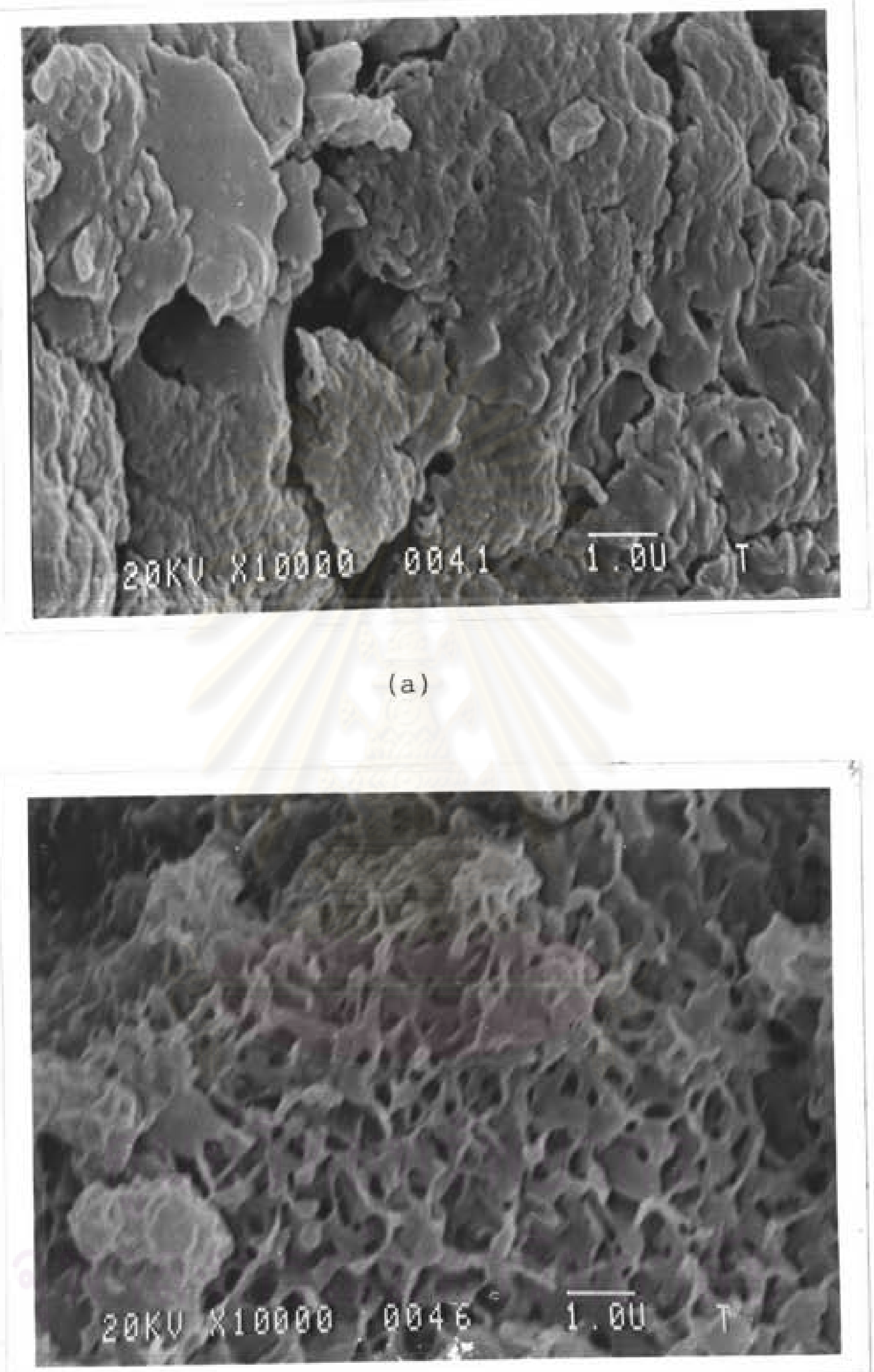
(a)

(b)

Figure 4.22 Scaning electron micrographs of polypyrrole

(a) PP_6 : 133.02 Scm^{-1}

(b) PP_{20} : 85.87 Scm^{-1}



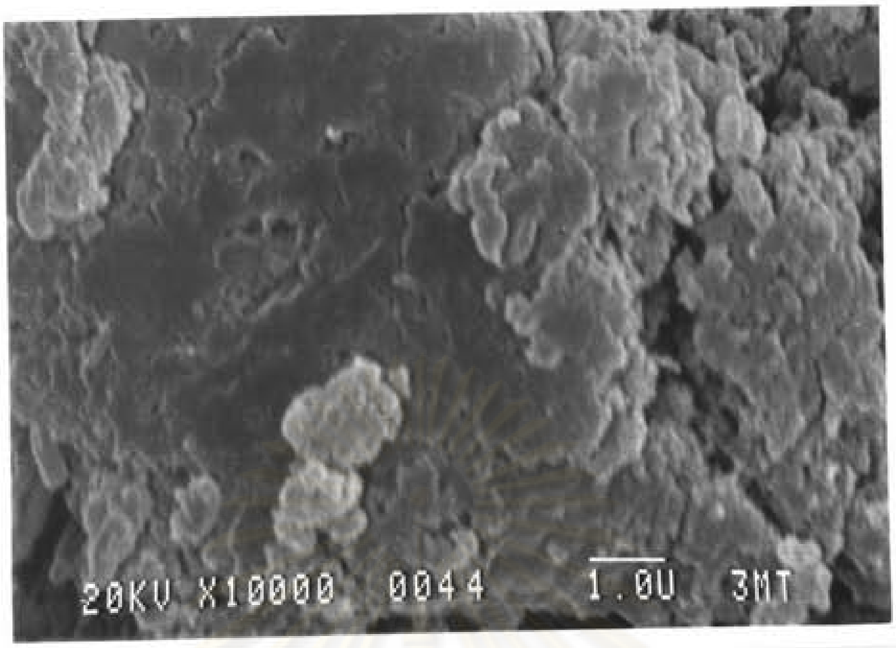
(a)

(b)

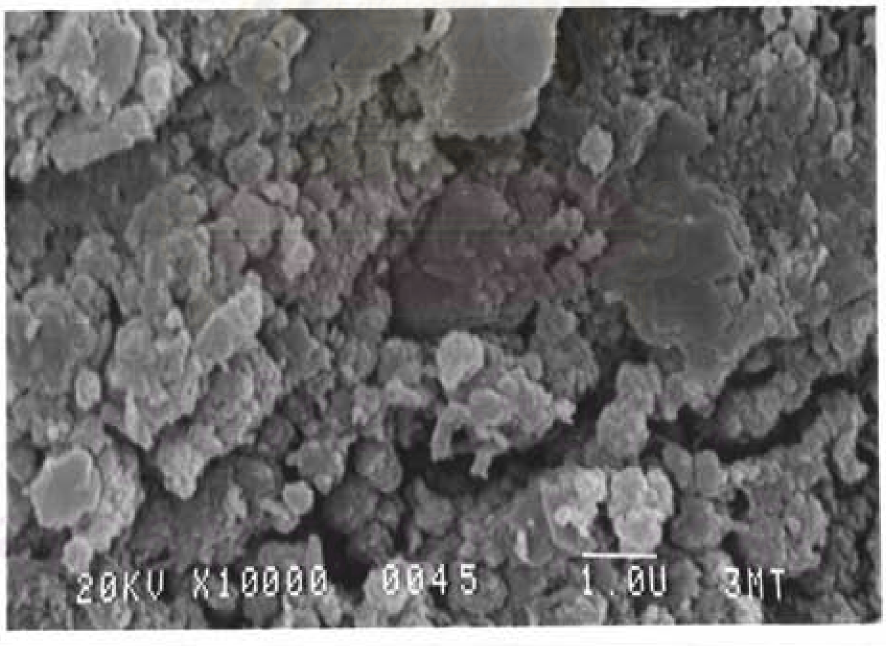
Figure 4.23 Scaning electron micrographs of polythiophene

(a) PT_{44} : $5.2*10^{-5}$ Scm^{-1}

(b) PT_{43} : $<10^{-5}$ Scm^{-1}



(a)



(b)

Figure 4.24 Scaning electron micrographs of poly(3-methylthiophene)

(a) $P3MT_{41}$: $2.26*10^{-5}$ Scm^{-1}

(b) $P3MT_{43}$: $<10^{-5}$ Scm^{-1}

APPENDIX