CHAPTER III

RESULTS AND DISCUSSION

3.1 Synthesis of PT and P3HT

The synthesis of PT by using $FeCl_3$ was found to give varied percent yields depending on the amount of $FeCl_3$ used as shown in **Table 3.1.** Entry 9 gave the highest yield of 100%, however, the resulting PT was formed as lump of product instead of powder. It was assumed that excess $FeCl_3$ was trapped in the PT lump, causing the flocculation of PT, which was more difficult to handle for later usages. Therefore, the more moderate condition was chosen for synthesizing PT at the mole ratio of thiophene : $FeCl_3$ = 3:4, stirring at 0 °C for 6 h and 18 h at room temperature (entry 8). Since PT cannot be dissolved in any solvents, the products were analyzed only by IR spectroscopy (**Table 3.2**) and compared to the IR spectrum from literature.[50]

Table 3.1 Synthesis of polythiophene

Entry	Mole ratio thiophene : FeCl$_3$	Condition	Yield (%)
1	3:1	24 h, RT	31.3
2	3:1	24 h, RT, N$_2$ purge	27.8
3	3:2	45 h, RT	43.3
4	3:2	6 h, 0 °C, 18 h, RT	71.6
5	3:2	6 h, 0 °C	66.4
6	3:2	24 h, RT	42.3
7	3:3	6 h , 0 °C, 18 h, RT	85.3
8	3:4	6 h , 0 °C, 18 h, RT	91.9
9	3:5	6 h , 0 °C, 18 h, RT	100.0

Table 3.2 The assignments of the IR spectrum of polythiophene[a]

Assignments	PT ν (cm^{-1})	PT from reference 50 ν (cm^{-1})
Aromatic CH stretching	3070	3080
C=C stretching	1640	1690
C=C stretching	1430	1440
C=C stretching	1390	1340
C–C stretching	1110	1040
C–C stretching	1030	1040
Aromatic CH bending	790	790

[a] **Figure A-1**, Appendix A

P3HT was obtained as sticky lump like a rubber. The percent yields of the P3HT varied according to the amount of FeCl$_3$. This was similar to what was observed in the synthesis of PT as shown in **Table 3.3**. However, the maximum percent yield was less than that of PT when using its best condition, which is at mole ratio of 3-hexylthiophene : FeCl$_3$ = 3:7, stirring at room temperature for 24 h (entry 8). By increasing the portion of FeCl$_3$, it would increase the product yield but might reduce the purity of the product. P3HT has the λ_{max} at 440 nm.

From ^{1}H-NMR spectrum (CDCl$_3$), (**Figure A-3**, Appendix A) ; P3HT showed characteristic signals of the hydrogens at the α-position of the hexyl group at δ 2.8 ppm, and the aromatic protons of thiophene rings from four possible environments appeared as four resonances at δ 6.97 ppm. (**Figure 3.1**)

In IR spectrum, P3HT showed peaks similar to PT but had strong peaks at 2920 and 2850 cm^{-1} (**Table 3.4**) corresponding to C-H stretching of alkyl groups at β-positions of thiophene rings. P3HT partially dissolved in THF, toluene, chloroform and almost entirely in CH$_2$Cl$_2$. It did not dissolve in methanol, acetone, acetonitrile, DMF, and DMSO.

Table 3.3 Synthesis of poly(3-hexylthiophene)

Entry	Mole ratio monomer : FeCl$_3$	Condition	Yield (%)
1	3:5	Acetonitrile, RT, 24 h	8.4
2	3:5	CHCl$_3$, RT 24 h	44.3
3	3:5	CHCl$_3$, RT 24 h, N$_2$ purge	39.8
4	3:5	CH$_2$Cl$_2$, 0 °C , 24 h	52.7
5	3:5	CH$_2$Cl$_2$, RT, 24 h	60.0
6	3:5	CH$_2$Cl$_2$, RT 24 h, N$_2$ purge	49.6
7	3:6	CH$_2$Cl$_2$, RT 24 h	61.8
8	3:7	CH$_2$Cl$_2$, RT 24 h	68.3
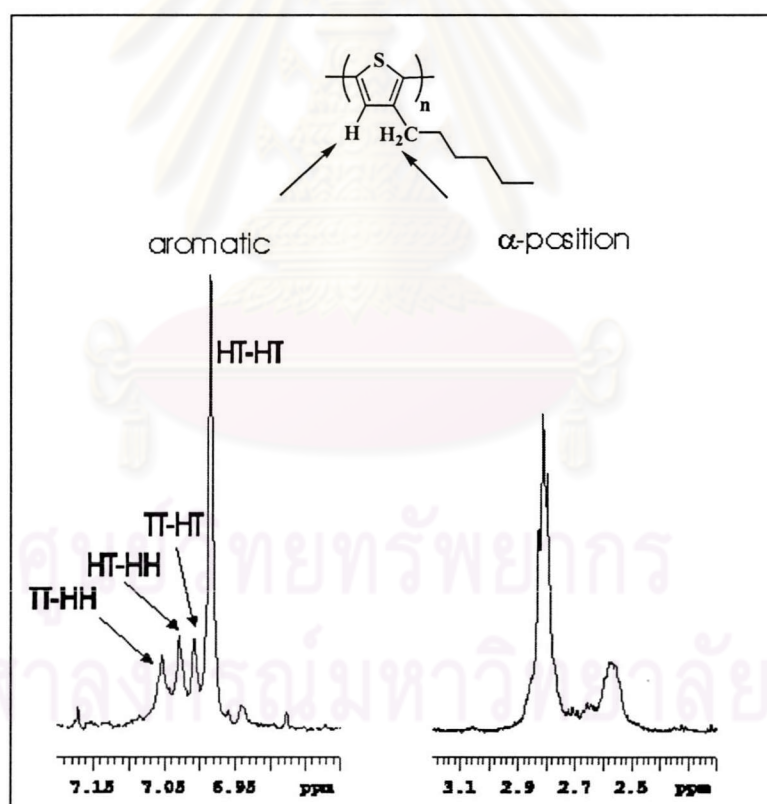
Figure 3.1 ^{1}H-NMR spectrum of P3HT

Table 3.4 The assignments of the IR spectrum of poly(3-hexylthiophene)[a]

Assignments	P3HT ν (cm^{-1})
Aromatic CH stretching	3070
Aliphatic CH stretching	2920
Aliphatic CH stretching	2855
C=C stretching	1510
C=C stretching	1460
C=C stretching	1380
C–C stretching	1190
C–C stretching	1100
Aromatic CH bending	825
Aromatic CH bending	725

[a] **Figure A-2**, Appendix A

3.2 Oxidation of PT

3.2.1 One-pot Method

This method was carried out by adding polymerizing agent (FeCl$_3$) and oxidizing agent (*m*CPBA) together in the reactor. The products were generally obtained in lower yields comparing to using polymerizing agent alone. From entries 9-11 (**Table 3.5**), the percent yield increased with the amount of FeCl$_3$, probably because of better polymerization. The relatively low yields suggested that *m*CPBA might somehow block the polymerization process of FeCl$_3$. In IR spectrum, sulfone S=O stretching peaks at 1135 and 1305 cm^{-1} were not observed, indicating that there was perhaps no oxidation during the reaction.

Table 3.5 Oxidation of PT by One-pot method

Entry	Mole ratio monomer : FeCl$_3$: mCPBA	Solvent	Condition	Yield (%)
1	3 : 1 : 4	Acetone	24 h, RT	0
2	3 : 1 : 4	Acetone	72 h, RT	0
3	3 : 1 : 4	CH$_2$Cl$_2$	72 h, RT	18.06
4	3 : 1 : 3	CHCl$_3$	24 h, RT, N$_2$ purge	6.23
5	3 : 1 : 3	CH$_2$Cl$_2$	24 h, RT, N$_2$ purge	29.71
6	3 : 1 : 3	CH$_2$Cl$_2$	24 h, RT	27.57
7	3 : 1 : 2	CH$_2$Cl$_2$	24 h, RT, N$_2$ purge	36.15
8	3 : 1 : 2	CH$_2$Cl$_2$	6 h, 0°C, 18 h, RT, N$_2$ purge	20.08
9	3 : 1 : 2	CH$_2$Cl$_2$	24 h, RT	33.02
10	3 : 2 : 2	CH$_2$Cl$_2$	24 h, RT	46.33
11	3 : 3 : 2	CH$_2$Cl$_2$	24 h, RT	77.38

3.2.2 Consecutive method

In this method, the oxidation of thienyl moieties was carried out after polymerization. The prepared PT was oxidized with various oxidizing agents. It was found that for 70% HNO$_3$/CH$_3$SO$_3$H, mCPBA , mCPBA/ FeCl$_3$ and H$_2$O$_2$/CF$_3$COOH, the reaction mixture turned dark at the beginning of the reaction, while color did not change when H$_2$O$_2$ and H$_2$O$_2$/AcOH were used. All oxidizing agents would eventually bleach off the color of the PT powder over a period of time. Upon following the reaction by FT-IR technique, no indication of sulfone group was detected. It was assumed that oxidizing agents probably degraded the polymer chains into shorter saturated fragments without oxidizing the S atoms. Furthermore, the unsuccessful oxidations may arise from the problem that PT was not dissolved in any solvents and made it difficult to initiate the reaction on the entangled, insoluble polymer chains.

3.3 Oxidation of P3HT

Since P3HT can dissolve in some organic solvents, it is possible to follow the oxidation process by using many analytical methods and control the reaction accordingly. Besides, reaction in solution would allow the oxidizing agent to reach the

reaction sites in the polymer chain more easily. The results of the oxidation processes by different oxidizing agents are described as followed:

3.3.1 Oxidation of poly(3-hexylthiophene) by mCPBA

When carrying out the oxidation with *m*CPBA at different reaction times, (**Table 3.6**) only the products sedimented after 30 and 45 min of reactions (entries 3 and 4) showed the two $v(SO_2)$ stretching peaks in IR spectra at 1140 and 1307 cm^{-1}, indicating that there is a presence of thienyl *S,S*-dioxide functional group.

Table 3.6 Oxidation of P3HT by mCPBA

Entry	Reaction time (minute)	% sedimented products	The presence of sulfone peaks in IR
1	0	93	No
2	15	94	No
3	30	90	Yes
4	45	85	Yes
5	60	70	No

For the products in entries 1 and 2, the reaction time may be too short for thiophene to be oxidized to sulfone group. For the product in entry 5, however, the absence of the sulfone peaks along with the discoloring and the decrease in the amount of sedimented product was observed. It is assumed that the polymer chain had been degraded because of the overoxidation. This overoxidized degradation stemmed from the fact that the formation of sulfone group destroyed the aromaticity of the thiophene ring to give the prominent diene feature. Normally, double bond would be oxidized more easily and could eventually be cleaved resulting in the chain scission. Low temperature could reduce the rate of the oxidative cleavage but would retard the S-atom oxidation as well. The degradation of polymer chain would yield the shortened polymer that lacked the desired conductive property. Furthermore, the molecules of the shortened polymer chain would be small enough to be partially dissolved in methanol and cannot be recovered. From the analysis of the solution of the product in methanol with UV-visible spectroscopy, there was a shift of λ_{max} from 440 nm of the starting material to about 300 nm, showing that the product may have

been degraded to smaller molecules. The ^{1}H-NMR spectrum was too complicate to help identify the structure of the product.

Sedimentation of the reaction mixture with methanol would separate out the left over oxidizing agent and by products and allow the product to be cast into films. However, this precipitated product was found to be unable to redissolve. Therefore, it is impossible to cast film out of this product from the sedimentation. Furthermore, mCPBA could not be totally removed from the product and hence remained as the major impurity.

Reaction progress can be illustrated by the collection of UV-visible spectra. (**Figure 3.2**) As the reaction continued, there was a reduction of the absorbance at λ_{max} of 440 nm with the slight increase of the absorbance at higher wavelength. This increase of the absorbance seemed to level off after longer oxidation times (beyond 60 min) while the absorbance at λ_{max} continued to decline. This was presumably due to the continued degradation of the polymer at the expense of the forming sulfone moieties.
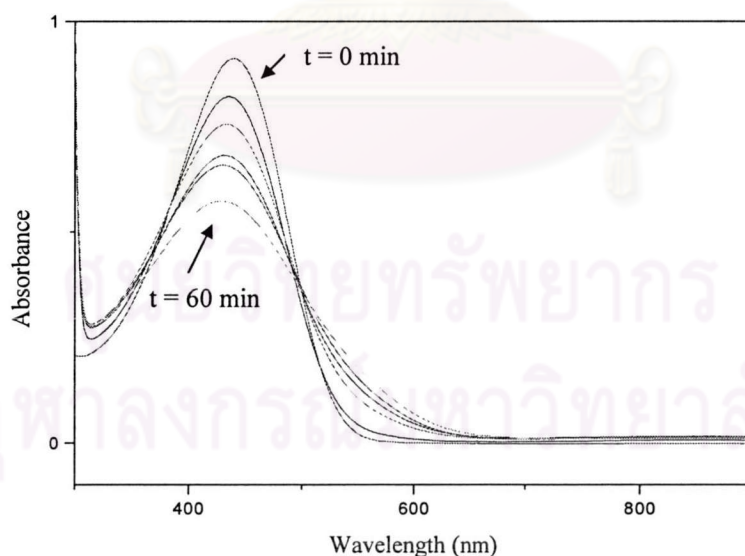
Figure 3.2 UV-visible spectra of poly(3-hexylthiophene) being oxidized by mCPBA at reaction time = 0, 15, 30, 45, and 60 min

3.3.2 Oxidation of poly(3-hexylthiophene) by H_2O_2/TFA

With the oxidation process using H_2O_2/TFA at mole ratio P3HT:H_2O_2:TFA=1:300:30, (**Table 3.7**) the IR spectrum of the product was not as clean as that of the product oxidized by *m*CPBA. Being awere that the reagent could act as doping agent and obscure the UV-visible spectra analysis, the product was further washed with 5% $NaHSO_3$ before UV-visible measurement. (**Figures 3.3** and **3.4**) From these UV-visible spectra, the absorbance at higher wavelengths increased along with the course of the reaction similar to the oxidization by *m*CPBA. The oxidizing agent could be easily removed by aqueous rinse. The films from 30 and 90 min oxidized P3HT looked quite similar to the P3HT. On the other hand, the 120 min oxidized P3HT could not be cast into films, probably due to overoxidation of polymer.

Table 3.7 Oxidation of P3HT by H_2O_2/TFA

Entry	Reaction time (min)	The presence of sulfone peaks in IR (film)
1	30	Yes
2	90	Yes
3	120	No[a]

[a] The oxidized P3HT could not be cast into films

The oxidation by such heterogeneous H_2O_2/TFA was difficult to control and obtain a good reproducibility due to perhaps the limited contact of starting material and the uneven distribution among phases. Higher equivalence of TFA seemed to show an effect on the UV-visible spectra. (**Figures 3.5** and **3.6**) This effect, however, may arise from H^+ doping process rather than permanent oxidation.
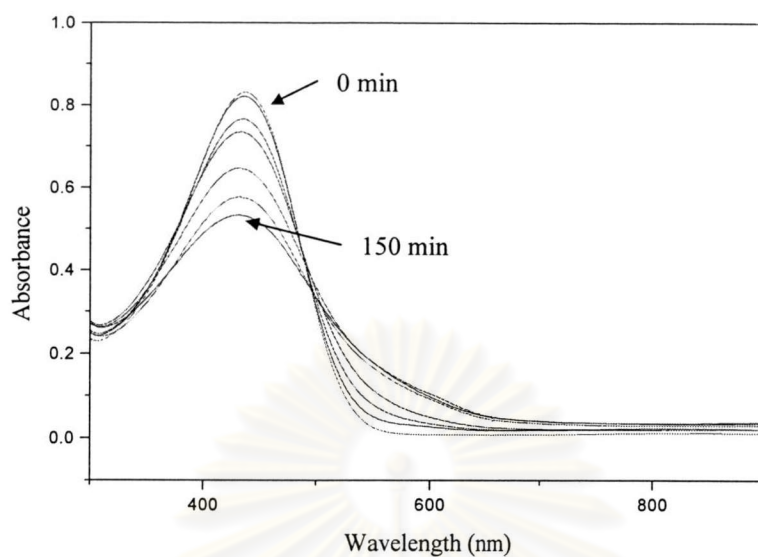
Figure 3.3 UV-visible spectra of poly(3-hexylthiophene) and H_2O_2/TFA oxidized poly(3-hexylthiophene) before washed by $NaHSO_3$ at t = 0, 5, 30, 60, 90, 120, and 150 min
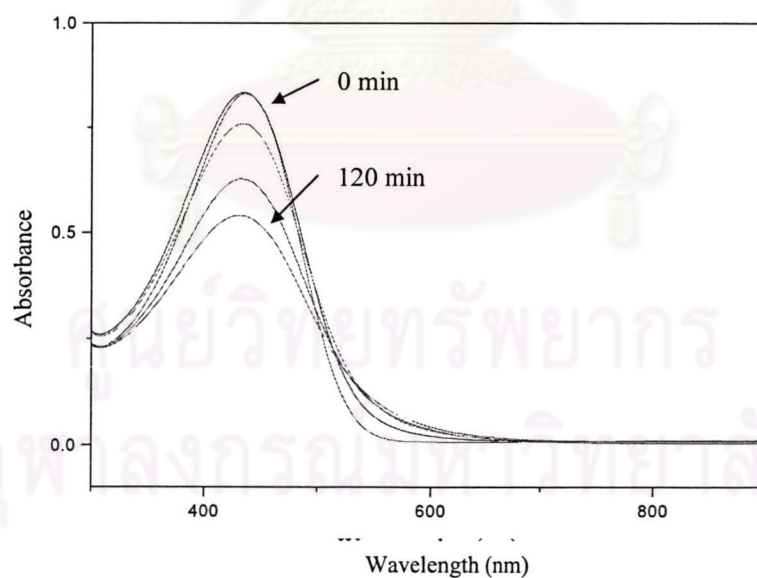

Figure 3.4 UV-visible spectra of poly(3-hexylthiophene) and H_2O_2/TFA oxidized poly(3-hexylthiophene) after washed by 5% $NaHSO_3$ at t = 0, 30, 60, 90, and 120 min

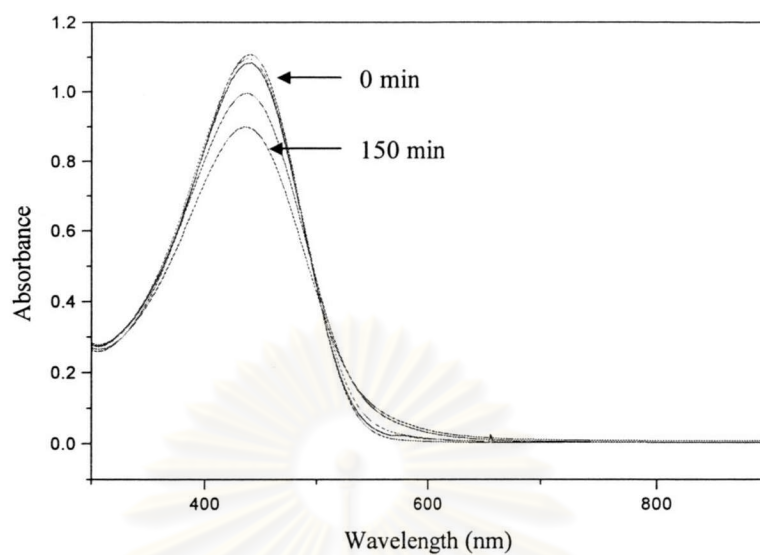**Figure 3.5** UV-visible spectra of poly(3-hexylthiophene) and H₂O₂/TFA oxidized poly(3-hexylthiophene) (mole ratio P3HT:H₂O₂:TFA=1:300:10) at t = 0, 5, 30, 60, 90, 120 and 150 min
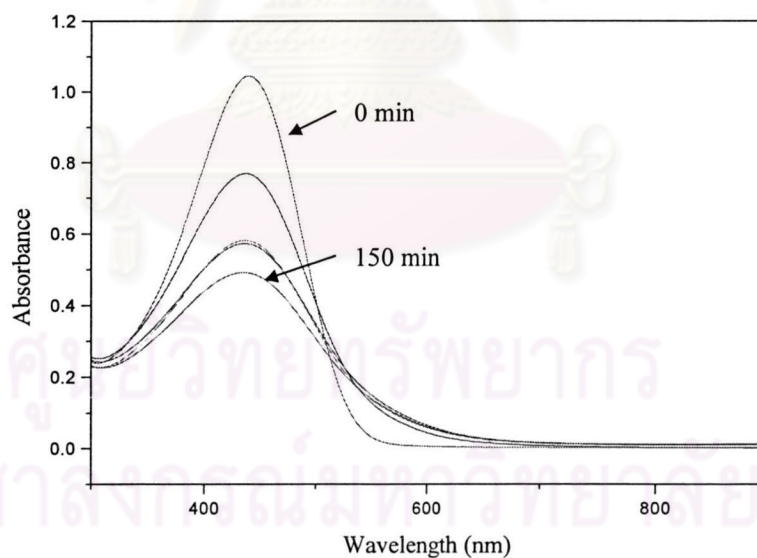
Figure 3.6 UV-visible spectra of poly(3-hexylthiophene) and H₂O₂/TFA oxidized poly(3-hexylthiophene) (mole ratio P3HT:H₂O₂:TFA=1:300:40) at t = 0, 5, 30, 60, 90, 120 and 150 min

3.3.3 Oxidation of P3HT by other oxidizing agents

Attempts had been made to oxidize P3HT with other oxidizing agents. By following the reaction progress with UV-visible Spectrophotometry, it was found that the following oxidizing agents caused the degradation of the polymer: 70%HNO_3/CH_3SO_3H, $KMnO_4$/$CuSO_4.5H_2O$, oxone/tetrabutylammonium sulphate, oxone/benzyltriethylammonium chloride and methylmorpholine *N*-oxide/mCPBA. The usual reduction in intensity of the λ_{max} of the oxidized product without any changes in the higher wavelength region were observed.

The oxidizing agents that showed no effect included H_2O_2, UHP, UHP/TFA, DMSO/H_2SO_4, trimethylamine *N*-oxide dihydrate (MNO), pyridine *N*-oxide, aqueous oxone/*N*-benzylcinchlodinium chloride, methylmorpholine *N*-oxide, UHP/ tetrabutylammonium sulphate, UHP/benzyltriethylammonium chloride, H_2O_2/TsOH, H_2O_2/CH_3COOH, H_2O_2/CH_3SO_3H, oxone, oxone tetrabutylammonium salt and dimethyl dioxirane. The possible reasons behind the non-reactive nature of the oxidizing agents were 1) the oxidizing power of the oxidizing agents were not strong enough 2) their bulkiness and 3) the heterogeneous nature of the mixture.

3.4 Polymer doping

3.4.1 PT doped by $HClO_4$

By comparing IR-spectra between various doping levels of PT, at higher doping level the signal at 1090-1120 cm^{-1} became stronger and the signal at 630 cm^{-1} appeared.
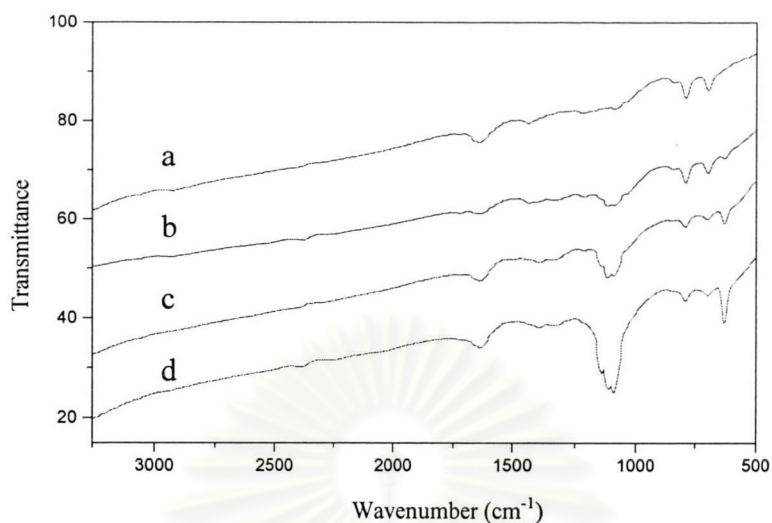
Figure 3.7 FT-IR (KBr) spectra of PT in various doping levels ; a) PT; b) low doped PT; c) medium doped PT; d) high doped PT

3.4.2 P3HT solution doped by $HClO_4$

The P3HT solution was doped with aqueous $HClO_4$ in THF (mole ratio P3HT: acid = 240 : 1). After addition of acid into the P3HT solution, the reaction mixture turned darker. By following the reaction by UV-visible spectroscopy (**Figure 3.8**) the intensity of the absorbance at λ_{max} gradually reduced with the increase of the absorbance at higher wavelength. After 120 min, the doped P3HT was starting to precipitate from the reaction mixture which completed after 130 min. It was assumed that the high polarity of the doped polymer chain induced slow aggregation and precipitation from the reaction.

3.4.3 P3HT solution doped by TFA

From UV-visible spectra of doped P3HT solution in $CHCl_3$ (**Figure 3.9**: mole ratio P3HT:acid = 40:1, and **Figure 3.10**: mole ratio P3HT:acid = 80:1), the absorbance at higher wavelength also slightly increased. The larger amount of TFA added, the larger intensity of the absorbance in higher wavelength was observed with no precipitation of the product. Doping P3HT solution by TFA in THF caused no change in the spectrum, however.
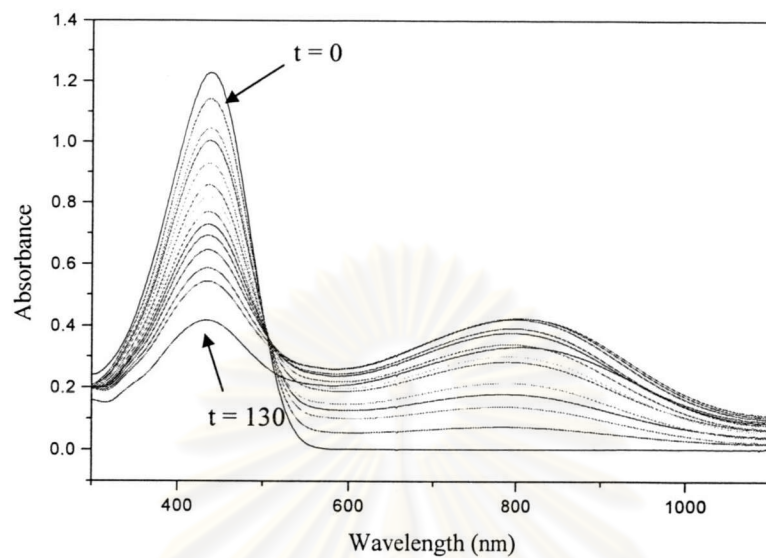
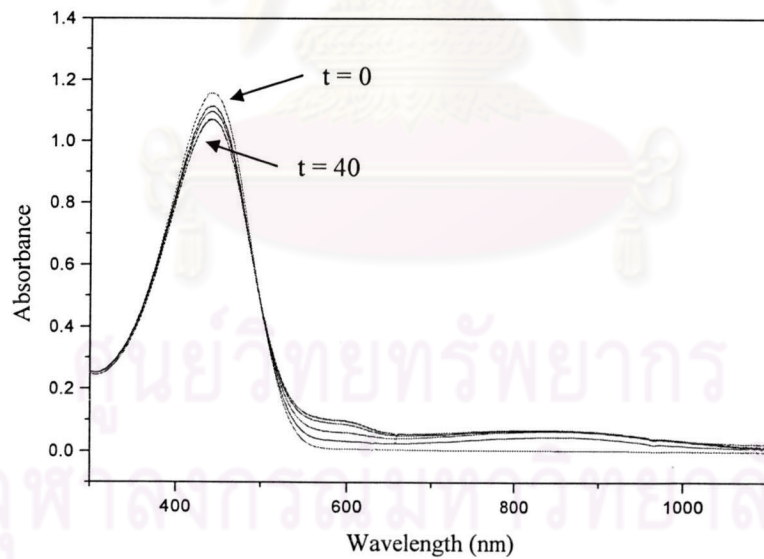**Figure 3.8** UV-Vis spectra of poly(3-hexylthiophene) solution doped by $HClO_4$

Figure 3.9 UV-Vis spectra of poly(3-hexylthiophene) solution doped by TFA; mole ratio P3HT: acid = 40 : 1
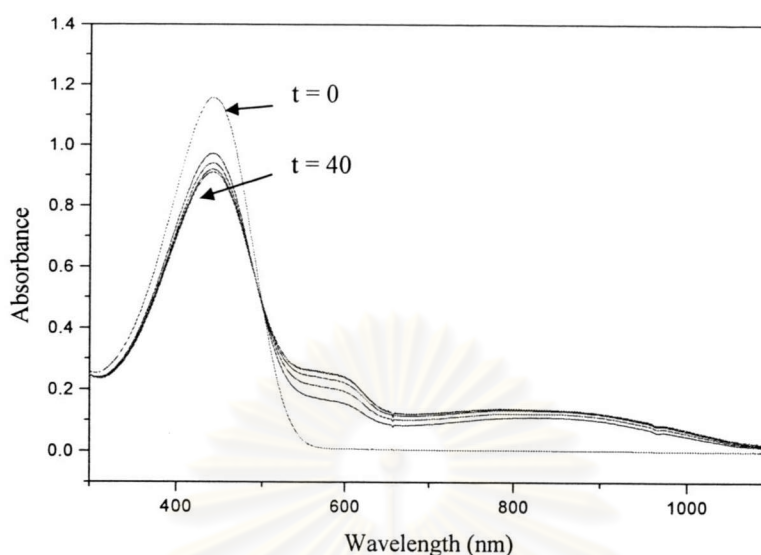
Figure 3.10 UV-Vis spectra of poly(3-hexylthiophene) solution doped by TFA; mole ratio P3HT: acid = 80 : 1

3.5 Absorption-Conjugation-index (AC-index)

In UV-visible spectra, λ_{max} usually corresponds to the main chromophore of a molecule that most absorbs the incoming light. The position and intensity of the absorbance at λ_{max} are generally the characteristic information that can be correlated to electronic properties of the molecule. In macromolecules or polymers, however, the information at λ_{max} may only partly reflect their important characters. This is especially significant for conjugated polymers, when the absorptions at various regions would correspond to many conjugated systems that all variedly contribute to the macroscopic properties of the polymer.

AC-index has been proposed as a "weighed integrative" absorption at a range of wavelengths. The higher λ values were "weighed" to be more important than that of lower values because of their presumed correspondence to the more conjugated systems. The sum of these weighed absorbances normalized over the sum of the unweighed ones are the AC-index : high AC-index would reflect the high effective conjugation length within the polymer chain which could, in turn, correlate to high conductive properties. The equation for the calculation of AC-index is shown below (example for the AC-index calculation is shown in appendix C): [52]

$$\text{AC-index } (a_1 \text{ to } a_{n+1}) = \frac{\Sigma x f(x)}{\Sigma f(x)} \qquad \ldots\ldots\ldots\ldots(1)$$

; where $x = (a_n + a_{n+1})/2$,

$f(x) = (b_n + b_{n+1})/2$,

a = wavelength (nm) in a specified region a_1 to a_{n+1},

b = absorbance at the corresponding wavelength a

3.5.1 AC-index of oxidation of P3HT by *m*CPBA or H$_2$O$_2$/TFA

The AC-index values of the change in UV-visible spectra of P3HT oxidized by *m*CPBA (**Figure 3.2**) were calculated in 2 ranges; 310-700 nm and 310-900 nm. The results of the calculations were shown in **Table D-1** (appendix D) and plotted against reaction time (**Figure 3.11**). The AC-index appeared to rise as the reaction proceeded. When comparing the AC-index (310-700) with AC-index (310-900), it was found that AC-index (310-900) followed the same trend as the AC-index (310-700) except that there was a dip of the value at 40 min. This was assumed to be due to the point where the degradation of the polymer took place faster than the formation of the sulfone groups, where longer conjugations in the polymer chain were expected. The range terminated at 700 nm may not have sufficiently covered the absorbances from the longer conjugation regions.
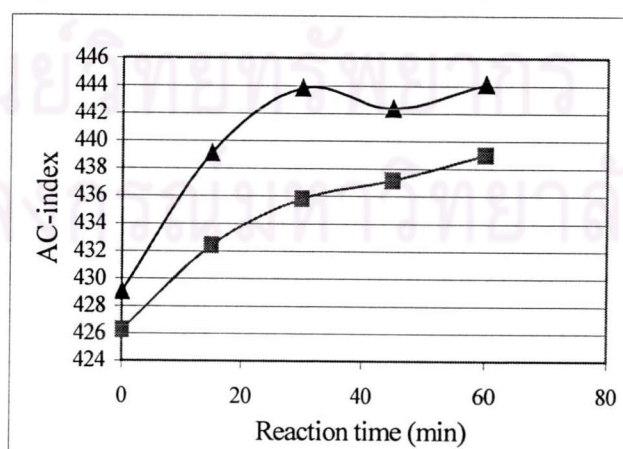

Figure 3.11 AC-index (310-700) (■); and AC-index (310-900) (▲) of P3HT oxidation by *m*CPBA

From UV-visible data of poly(3-hexylthiophene) and oxidized poly(3-hexylthiophene) by H_2O_2/TFA (**Figure 3.3**), AC-index values were calculated as shown in **Table D-2** (appendix D) and **Figure 3.12**. The graph was shown the same trend as that from the oxidation by *m*CPBA. The AC-index (310-900) increased before decreased slightly at 45 min, and increase once again at longer reaction time. Though the dip was not as apparent as the case of *m*CPBA.
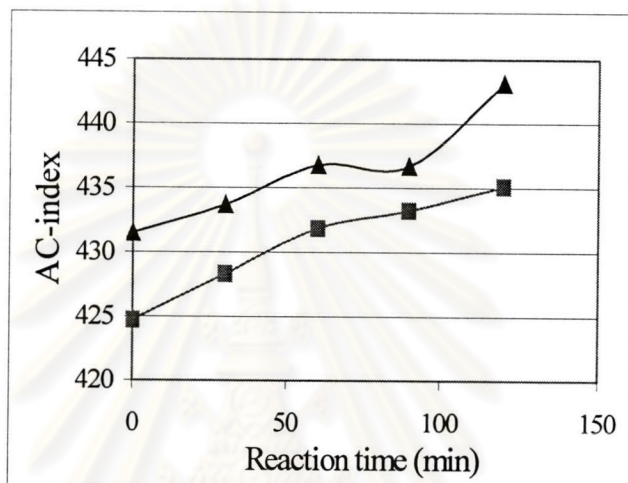

Figure 3.12 AC-index (310-700) (■); and AC-index (310-900) (▲) of P3HT oxidation by H_2O_2/TFA

By comparing *m*CPBA and H_2O_2/TFA, the reaction using *m*CPBA would be faster than the reaction using H_2O_2/TFA, because *m*CPBA is soluble in organic solvent, which could allow the exchange of oxygen with polymer directly. When comparing the AC-index of the oxidation processes on P3HT, the oxidation by *m*CPBA was faster and had higher AC-index values than by H_2O_2.
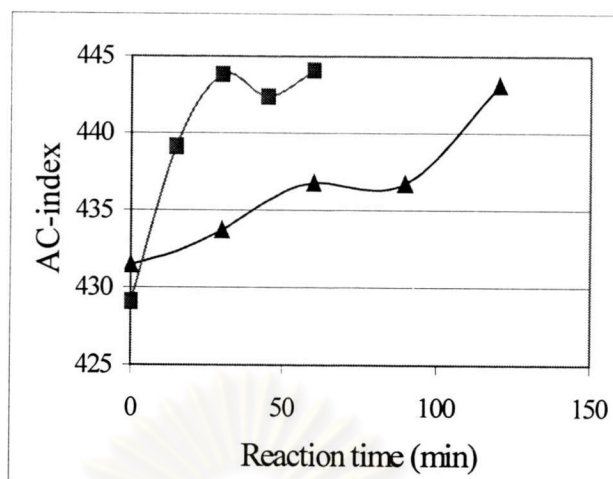
Figure 3.13 AC-index (310-900) of P3HT oxidation by *m*CPBA (■); and by H$_2$O$_2$/TFA (▲)

3.5.2 P3HT solution doping

From AC-index (300-1100) of P3HT solution doped by HClO$_4$ (**Figure 3.14**), its values increased continuously until the precipitation occurred. In contrast, doping by TFA (**Figure 3.15**) gave constant AC-index at 20th-30th min of reaction time without precipitation. Furthermore, the AC-index values are clearly different between the two doping levels of mole ratios P3HT: TFA = 6 : 5 and 3 : 5.
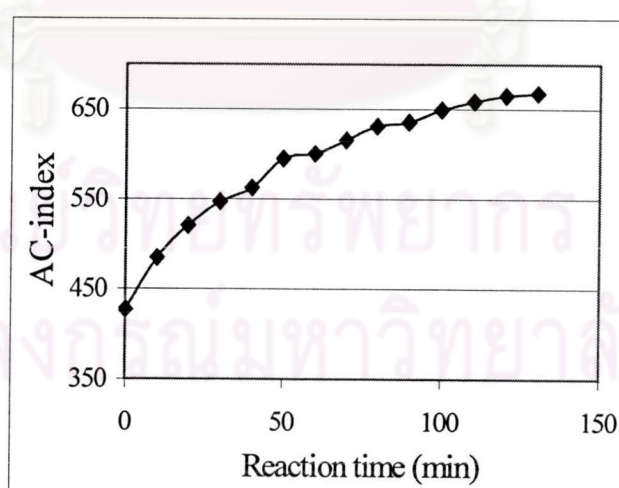

Figure 3.14 AC-index (300-1100) of P3HT solution doped by HClO$_4$; mole ratio P3HT: HClO$_4$ = 7 : 2
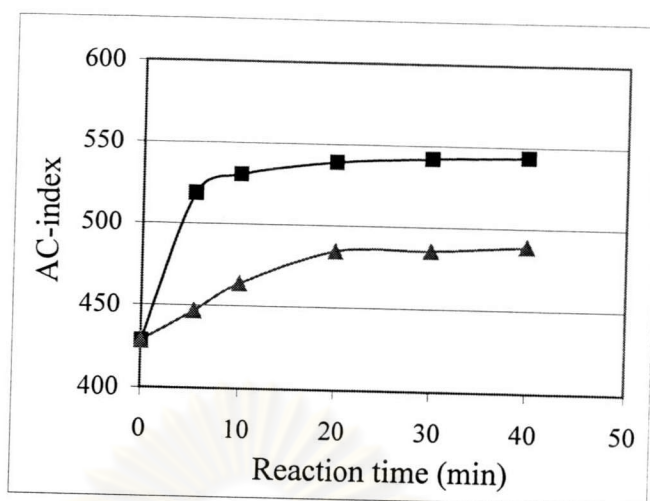
Figure 3.15 AC-index (300-1100) of P3HT solution doped by TFA; mole ratio
P3HT: TFA = 6 : 5(▲); and 3 : 5 (■)

3.6 Conductivity measurement

To measure the conductivity of PT and iodine vapor doped PT, the polymer discs were prepared, the PT powder was ground and pressed in hydraulic press apparatus at 5 tons for 1 min. Unfortunately, the doped PT cannot be pressed into discs even pressing at 12 tons for 10 min.

The conductivity of PT, P3HT and their oxidized products are shown in **Table 3.8**. The non-doped PT (entry 1) and P3HT (entry 2) had too low conductivity to be measured by four-point probe method. For P3HT film doped by iodine vapor at 60 min, 90 min, 120 min and 24 h (entries 3-6), their conductivity started at high values but quickly decreased until steady after 3 min. However, the conductivity of the films of the doped oxidized P3HT by H_2O_2/TFA (from **Table 3.7**) remained constant throughout the measurements. The conductivity of the doped P3HT oxidized at longer time was lower (entry 8), probably due to the over oxidation of P3HT previously discussed in section 3.3.1. The conductivity of the doped $P3HTOX_1$ (entry 7) was higher than all the doped parent P3HT, indicated the electrical properties improvement of P3HT by the oxidation process, possibly through the transformation of thienyl groups to thenyl S,S-dioxides.

Table 3.8 Conductivity of PT and derivatives of PT

Entry	Sample	Doping Time	Thickness (cm)	Conductivity (S.cm^{-1})
1	Pressed PT disc	0	0.01	0
2	P3HT film	0	0.002	0
3	I$_2$-doped P3HT	60 min	0.0025	0.12
4	I$_2$-doped P3HT	90 min	0.003	0.12
5	I$_2$-doped P3HT	120 min	0.003	0.12
6	I$_2$-doped P3HT	24 h	0.002	0.37
7	I$_2$-doped P3HTOX$_1$[a]	24 h	0.002	0.6
8	I$_2$-doped P3HTOX$_2$[b]	24 h	0.002	0.06

[a] Taken from the 30 min oxidation of P3HT by H$_2$O$_2$/TFA (entry 1, **Table 3.7**)

[b] Taken from the 90 min oxidation of P3HT by H$_2$O$_2$/TFA (entry 3, **Table 3.7**)