CHAPTER III

RESULTS AND DISCUSSION

3.1 Synthesis of PT and P3HT

The synthesis of polythiophene by oxidative polymerization using ferric chloride followed the method used by Tepveera [8]. Polythiophene was obtained in 90 % yield in the form of brown powder that cannot be dissolved in any solvents. It was analyzed by IR spectroscopy that gave the spectrum (Table 3.1 and **Figure A-1**, Appendix A) which was consistent with the literature [52].

Table 3.1 The assignments of the IR spectrum of polythiophene

Assignments	wavenumber (cm^{-1})
Aromatic C-H stretching	3065
C=C stretching	1660, 1430
C–C stretching	1040
Aromatic C-H bending	790. 700

The synthesis of poly(3-hexylthiophene) using anhydrous ferric chloride yielded 84 % of the product higher than those reported in literature [16] (74 % yield) using the same method. Poly(3-hexylthiophene) was obtained as sticky lump like rubber. Its chloroform solution has the λ_{max} at 440 nm. The ^{1}H-NMR spectrum of poly(3-hexylthiophene) (**Figure A-3**, Appendix A) showed the characteristic signal of the protons at α-position of the hexyl group from Head-to-Tail and Head-to-Head regioisomers at δ 2.7 and 2.5 ppm respectively, and the aromatic protons of thiophene rings from four possible environments appeared as four resonances at δ 6.9–7.0 ppm. (**Figure 3.1**) The IR spectrum of poly(3-hexylthiophene) is quite similar to polythiophene, but with stronger peaks at 2920 and 2850 cm^{-1} (**Table 3.2** and **Figure**

A-2. Appendix A) corresponding to C-H stretching of the hexyl groups at β-positions of thiophene rings. Poly(3-hexylthiophene) dissolved in tetrahydrofuran, toluene, chlorobenzene, chloroform, and dichloromethane.
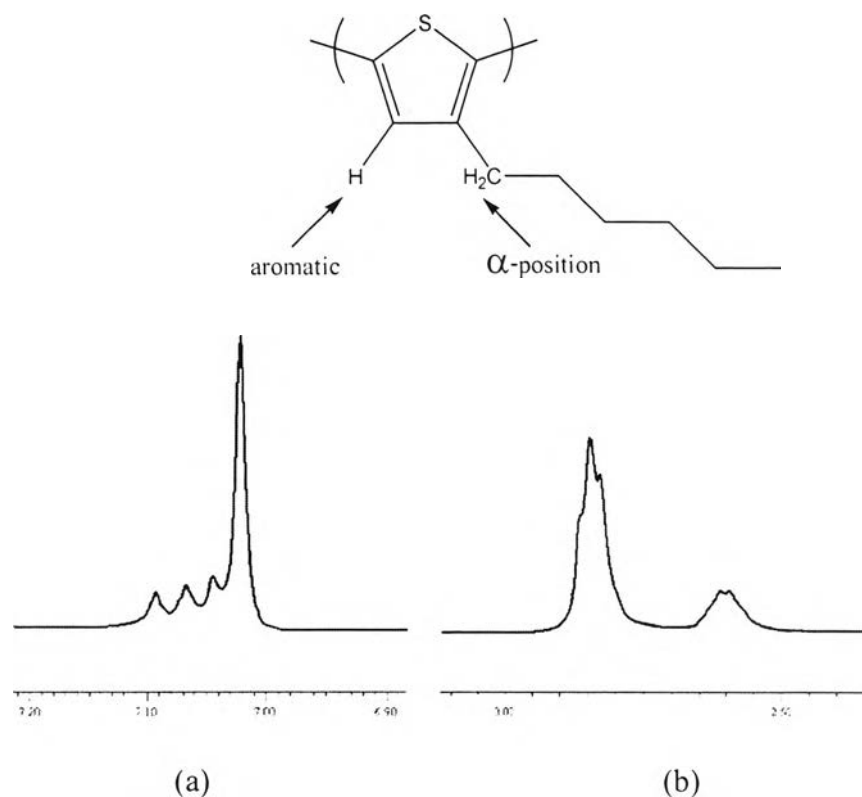

Figure 3.1 Characteristic signals in ^{1}H-NMR spectrum of P3HT (a) aromatic protons and (b) α-methylene protons.

Table 3.2 The assignments of the IR spectrum of poly(3-hexylthiophene).

Assignments	wavenumber (cm^{-1})
Aromatic C-H stretching	3065
Aliphatic C-H stretching	2925, 2855
C=C stretching	1510, 1460
C–H bending	1370
C–C stretching	1185
Aromatic C-H bending	825, 726

3.2 Bromination of thiophene and polythiophene derivatives

Bromination of thiophene using the method of Kellogg and coworkers [41] successfully yielded relatively pure 2,5-dibromothiophene in about 60% yield. Its ^{1}H-NMR spectrum was consistent with the previous report (**Figure A-4**, Appendix A). Attempting to further brominate onto β-positions of the thiophene using longer time and more vigorous conditions was not successful, probably due to the much less reactivity towards electrophiles of the already brominated thiophene. Small yield of tribrominated and other isomeric dibrominated products have been reported in other study [54].

Bromination of polythiophene gave a dark brown powder that was insoluble in organic solvent. The weight of the product was 167% relative to the starting polymer, suggesting possible incorporation of bromo substituents onto polythiophene. Due to its insolubility, the product could not be firmly identified to be poly(3-bromothiophene).

Bromination of poly(3-hexylthiophene) gave products that were soluble in dichloromethane, chloroform, and tetrahydrofuran. All the brominated products showed hypsochromic shifts of the λ_{max} of their UV-Vis absorption spectra (**Figure A-11**, Appendix A) in relation to 440 nm of original P3HT (**Table 3.3**). The hypsochromic shifts of the λ_{max} in UV-Vis spectra of the products were attributed to shorter effective conjugation length of the polymer after the incorporations of bulky bromo groups. The disappearance of aromatic proton signal at δ 7.0–7.1 ppm in ^{1}H-NMR spectra indicated that bromo groups were readily incorporated onto the β-positions of thiophene units. The characteristic signal of the protons at α-positions of the hexyl groups at δ 2.8 and 2.6 ppm also disappeared and became one broad peak at δ 2.7 ppm in fully brominated P3HT. (Entry 2, 5, and 6, **Table 3.3**)

From **Table 3.3**, both Entry 1 and 2 showed significant degradation of the polymer chains. This suggested that the incorporation of bromo groups not only occurred at the β-positions, but also the α-positions of thiophene units that led to the degradation of the product. The possible mechanisms of the substitutions at β- and α-positions in the presence of acid and polar solvent such as acetic acid are shown in **Scheme 3.1b**.

Table 3.3 The characterization and percent degradation of brominated P3HTs.

Entry	solvent	conditions	λ_{max} (nm)	M_n of starting P3HTs	M_n of brominated P3HTs	substitution (%)	degradation[a] (%)
1	CH_2Cl_2/ CH_3COOH	reflux 1h	342	16777	6115	87	74
2	CH_2Cl_2/ CH_3COOH	reflux 2h	339	16777	4266	100	83
3	$CHCl_3$	RT 2h	360	20010	23748	91	17
4	$CHCl_3$	RT 4h	345	20010	24329	99	18
5	$CHCl_3$·	RT 9h	338	20010	24157	100	18
6	$CHCl_3$	RT 12h	336	20010	22062	100	26

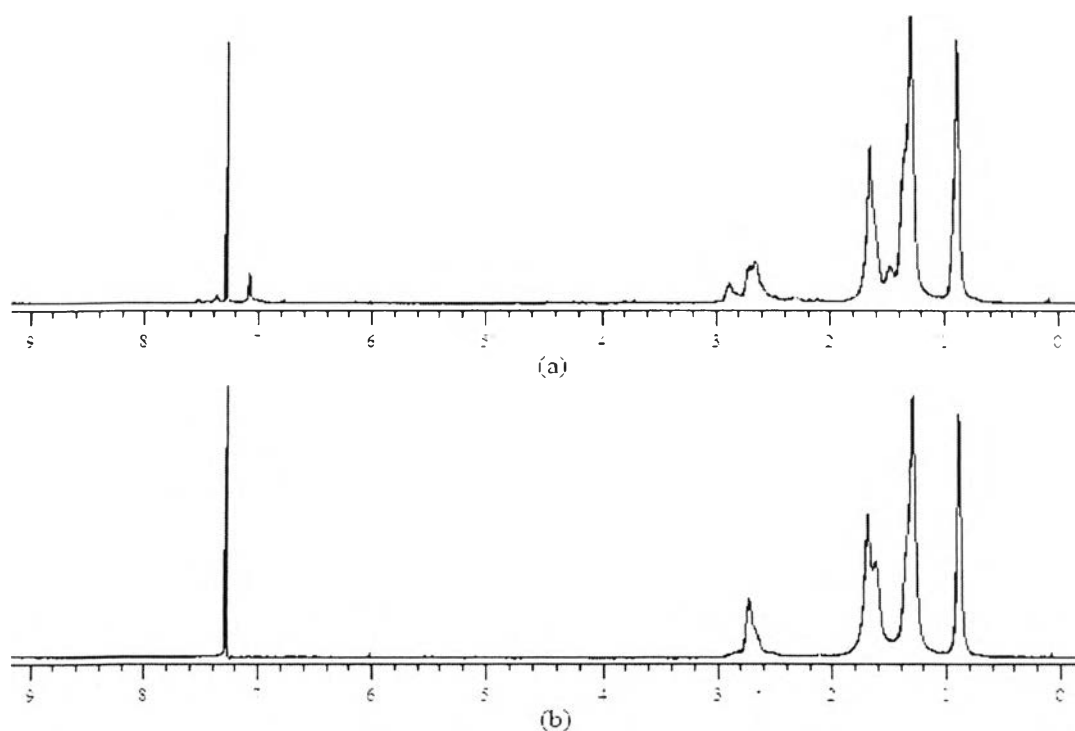[a] The calculations of the degradation percentage are shown in Appendix B

Figure 3.2 The disappearance of the characteristic signals of aromatic and α-methylene protons of thiophene units in P3HT bromination (a) Entry 1, **Table 3.3** (b) Entry 2, **Table 3.3**.

Holdcroft and coworkers have reported a milder procedure that has been successfully reproduced with much less degradation [42] (Entry 3-6, **Table 3.3**). In these cases, the values of molecular weight (M_n) of the brominated P3HTs, measured by GPC, were slightly higher than those of their original P3HTs, yet when taking the weight from bromo groups into account, the product chains were considered being shortened. The integration of proton signals at β-positions of aromatic thiophene units

and the α-methylene protons of the hexyl groups revealed an almost entirely replacement of aromatic protons up to 91–100% depending on the duration of the reaction (**Figure 3.3**, full spectra are shown in **Figures A-11** to **A-14**, Appendix A). The fully brominated P3HT should gain about 50% more weight onto the unsubstituted P3HT. The fact that the molecular weight of the brominated P3HTs only increased slightly suggested that some degradation of the chains occurred, which became more significant when using more polar solvent.
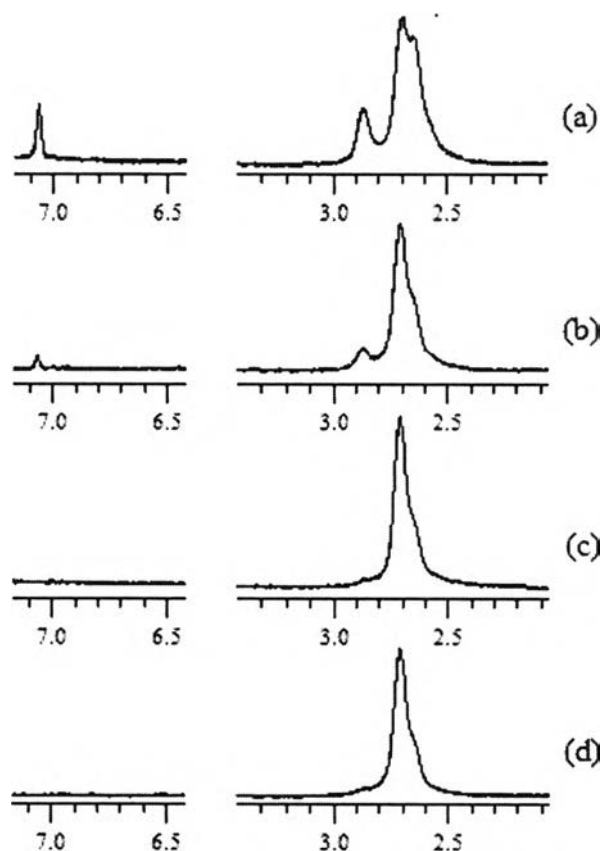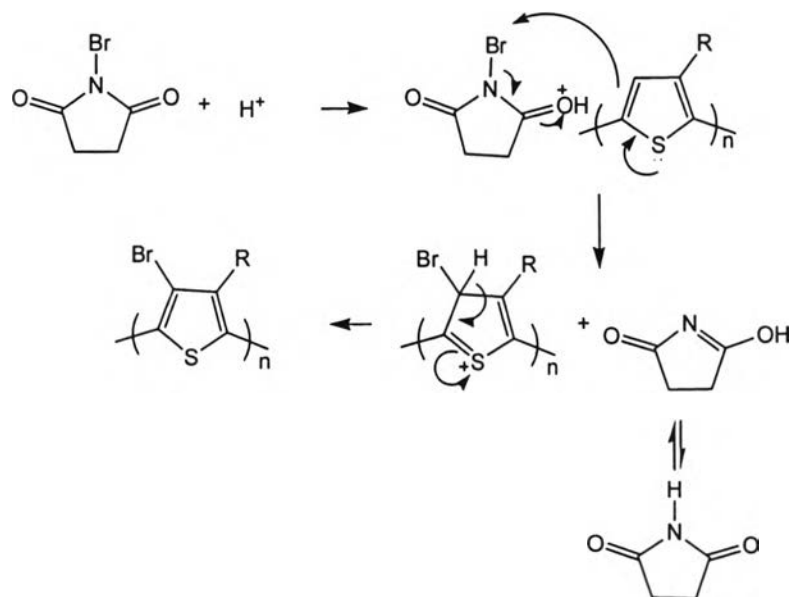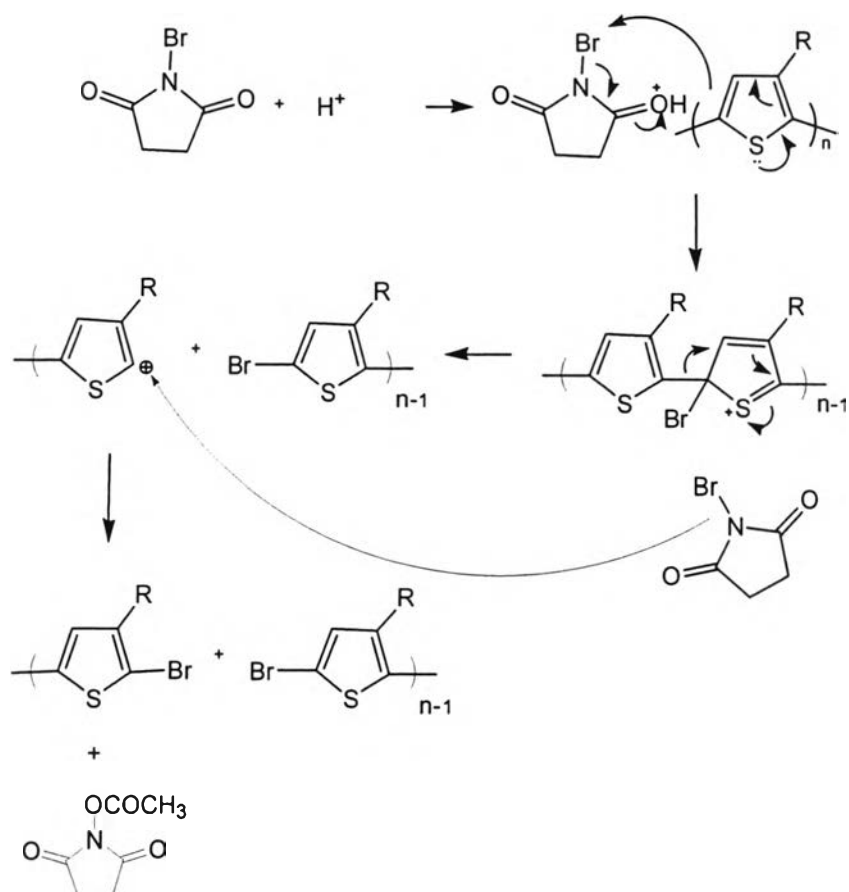

Figure 3.3   The disappearance of the characteristic signals of aromatic and α-methylene protons of thiophene units in P3HT bromination (a) Entry 3, **Table 3.3** (b) Entry 4, **Table 3.3** (c) Entry 5, **Table 3.3** (d) Entry 6, **Table 3.3**.

(a) β-positions of thiophene units

(b) α-positions of thiophene units

Scheme 3.1 Possible mechanisms of P3HT bromination in the presence of acid and polar solvent (R=Hexyl).

In relatively lesss polar solvent, the mechanism of the bromination reaction is more likely to be initiated through radical process (Entry 3–6, **Table 3.3**). The radical-based single electron transfer (SET) mechanisms for the brominations at α- and β-positions of thiophene units of the polymer are shown in **Scheme 3.2**

(a) β-positions of thiophene units

(b) α-positions of thiophene units
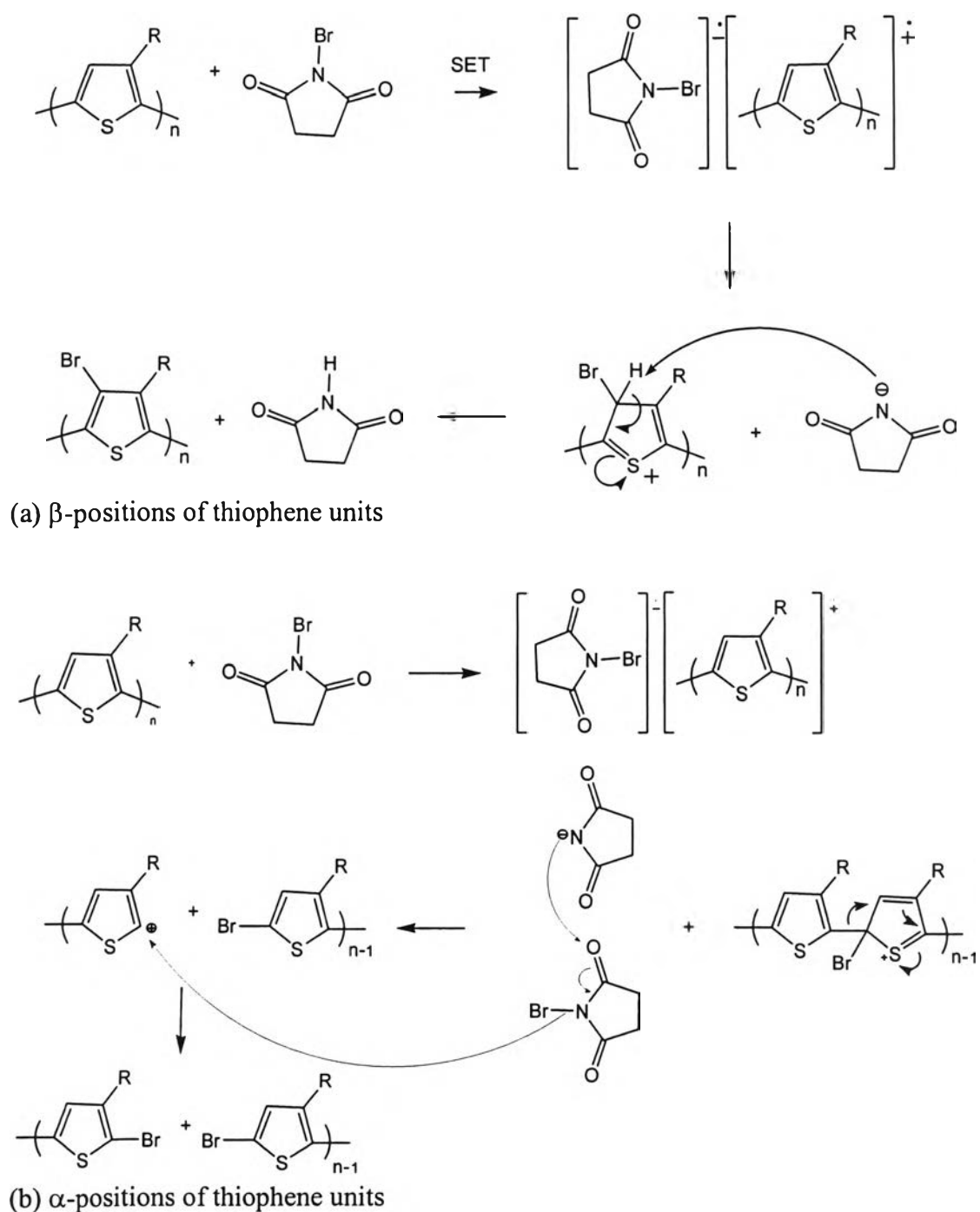
Scheme 3.2 mechanisms of P3HT bromination in non-polar solvent (R=Hexyl).

3.3 Acylation of thiophene and polythiophene derivatives

Acetylation of thiophene gave a complex mixture that showed the proton signal of acetyl group in ^{1}H-NMR spectrum (**Figure A-12**, Appendix A). However, the mixture could not be firmly purified and identified to be the desired product. Due to such difficulty in purification and characterization, the reaction condition applied in this experiment appeared to be unsuitable for a general preparation of acetylthiophene.

Acetylation of polythiophene gave insoluble brown powder that could not be firmly characterized except the weak acetyl carbonyl signal in IR spectrum (**Figure A-14**, Appendix A). Octanoylation of polythiophene gave a soluble mixture, together with the perhaps unreacted insoluble polythiophene. The soluble part of the mixture was characterized by IR and ^{1}H-NMR spectrophotometry (**Figures A-15 and A-16**, Appendix A). In IR spectrum, the product could only be characterized by the weak carbonyl signal at 1710 cm^{-1}. From NMR spectrum, the signal of the alkyl side chain protons of the carbonyl group appeared, but the signals of thiophene protons were unobservable. The molecular weight of octanoylated polythiophene was approximately 1100 measured by GPC, which showed that this soluble product was roughly an oligomer containing 5–6 monomer units, assuming 100% substitution based on the absence of the thiophene ring protons.

Acetylation of poly(3-hexylthiophene) gave products that were soluble in dichloromethane, chloroform and tetrahydrofuran. All the acetylated products showed hypsochromic shift of the λ_{max} of their UV-Vis absorption (**Figure A-27**, Appendix A) in relation to 440 nm of the original P3HT (**Table 3.4**). The hypsochromic shifts of the λ_{max} in UV-Vis spectra of the products were attributed to shorter effective conjugation length of the polymer after the incorporations of acetyl groups. Such degradation of polymer chains also reflected in the lower M_n of the products compared to the starting P3HT, assuming no acetylation on the ring occurred. AlCl$_3$ with vigourous condition degraded the polymer considerably. (Entry 1, **Table 3.4**) Such chain shortening was still observed even using the mildest condition without AlCl$_3$ (Entry 3). To get a clearer evidence of acetyl group incorporation in the polymer, a smaller oligomer was needed. In this case, a sample of P3HT fraction that has been extracted by acetone from the original as-synthesized

mixture was subjected to the reaction condition and characterized [53, 55] (Entry 4). The ^{1}H-NMR spectrum of this latter product (**Figure A-26**, Appendix A) clearly showed the presence of extra α-methylene protons of carbonyl groups despite lower average molecular weight and insignificant change of the carbobyl signal in IR spectrum (**Figures A-23 and A-24**, Appendix A).

Table 3.4 The characterizations and percent degradation of acetylated P3HTs.

Entry	conditions	λ_{max} (nm)	M_n of starting P3HT	M_n of acetylated products	substitution (%)	degradation[a] (%)
1	AlCl$_3$, reflux 1h	405	20148	12661	80	47
2	AlCl$_3$, RT 4 h	429	26401	19552	26	30
3	RT 15 h	427	26401	22521	13	17
4	AlCl$_3$, reflux 1h	[b]	1444	1204	88	32

[a] The calculation of the degradation percentage are shown in Appendix B

[b] Showed no obvious λ_{max} due to broad and complex absorption between 250–500 nm.

From the above results of P3HT acetylation, it could be concluded that the incorporation of acetyl groups onto thiophene rings should mainly occur at the α-positions of the thiophene rings followed by chain degradation as the desired major pathway rather than the β-positions. Therefore, most acetyl groups present in the products were expected to situate only at the terminal ends of the polymeric chains, corresponding to the unobserved α-methyl protons of the carbonyl group signal in ^{1}H-NMR spectra. In exception, the signals of these protons from the product of the reaction on the smaller oligomer, where the acetyl groups at the terminal ends of the oligomeric chain were more visible in ^{1}H-NMR spectrum. The mechanisms of the degradation with and without AlCl$_3$ were proposed as shown in **Scheme 3.3**
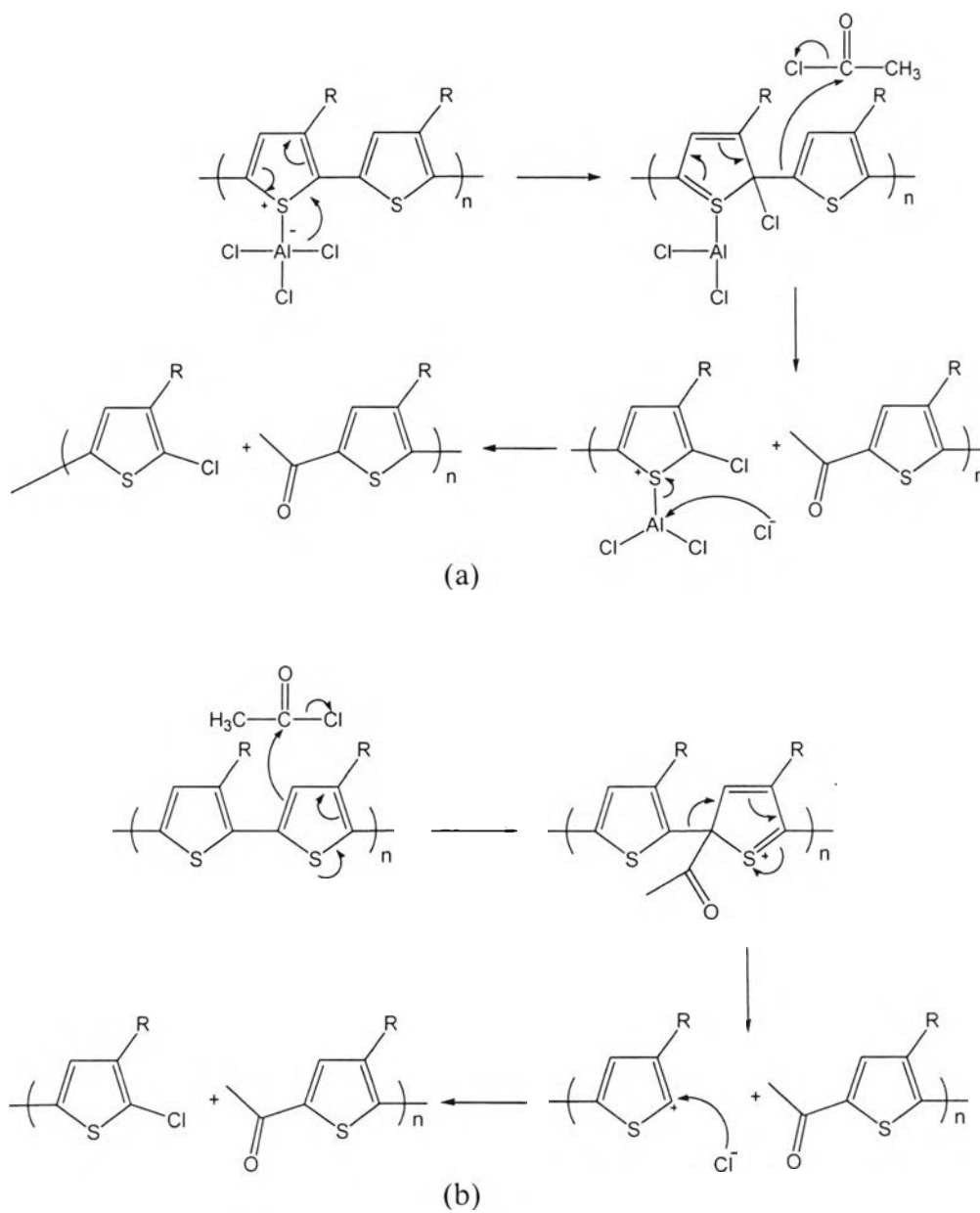
Scheme 3.3 Mechanisms of P3HT upon acetylation (a) with $AlCl_3$ and (b) without $AlCl_3$ (R=Hexyl).

3.4 *S*-Arylation

Arylation of thiophene and polythiophene derivatives carried out through two methods: trapping of a benzyne intermediate and using diphenyliodonium salt reagent with a catalyst.

3.4.1 *S*-Arylation by trapping during the formation of biphenylene

After the reaction between anthranilic acid and isoamylnitrite in a catalytic amount of CF_3COOH, a yellowish precipitate of diazonium carboxylate occurred. The wetted precipitate was then transfered into a solution of thiophene in dichloroethane. After 5 min, the solution turned red and the precipitate slowly dissolved after heating and remained red and clear for three hours. Evaporation of solvent gave red solid which was identified to be mainly biphenylene (15), (**Figure A-33**, Appendix A) with the characteristic ^{1}H-NMR signals at δ 6.6 and 6.7 ppm together with other products (**Figure A-32**, Appendix A). Apart from the usually heating of the solution for quick generation of benzyne, the solution was left stirring at room temperature for three hours to gradually generate benzyne. Nevertheless, the exact similar was observed.

The same condition was applied to P3HT in place of thiophene. The obtained result was identified to mostly the unreacted P3HT from ^{1}H-NMR spectroscopy (**Figure A-34**, Appendix A). Similar to the case of thiophene, there were some ^{1}H-NMR signals that could not be exactly identified. The expected character of the monosubstituted benzene attached to S^+ atom in NMR spectrum was still absent.

Attempt to follow the progress of the reaction was done by an *in situ* method. P3HT was added during the preparation of diazonium carboxylate. When diazonium carboxylate was formed, it was not filtered but was left to decompose slowly at room temperature assuming that P3HT could trap out the generated benzyne *in situ*. The ^{1}H-NMR spectrum of the crude product (**Figure A-35**, Appendix A) showed the presence of biphenylene and unknown monosubstituted benzene with an electron withdrawing substituent. However, the aromatic signals of P3HT remained the same as unreacted P3HT, suggesting no or only little arylation at the S-atoms.

There was still a possibility that the reaction might have yielded the desired arylated species as an intermediate and quickly decomposed before it could be

detected. To investigate this possibility, two sets of reactions were introduced and monitored by UV-Vis spectroscopy: the decomposition of diazonium carboxylate in UV quartz cells with and without P3HT. The diazonium carboxylate was prepared as a diluted solution in 1,2-dichloroethane. Without P3HT, diazonium carboxylate began to dimerize into biphenylene within 15 minutes and continued to generate this product rapidly after heating (**Figure A-36**, Appendix A). In the presence of P3HT, diazonium carboxylate still decomposed into biphenylene at a similar pace and left P3HT unreacted (**Figures A-37–A-38**, Appendix A), supporting the above result which showed slow decomposition of the precipitate at room temperature and also showed the same result in the UV-Vis spectra (**Figures A-39–A-40**, Appendix A). From all these experiments, it could be concluded that the benzyne intermediate cannot be trapped by S-atoms of the thiophene rings and preferred to react with themselves.

3.4.2 *S*-Arylation by using diphenyliodonium salts

The *S*-Arylation of thiophene using diphenyliodonium salt was adapted from Kitamura's method [49]. Diphenyliodonium chloride (DPIC) was used first as the arylating agent. The result showed that with the addition of $Cu(OAc)_2$ in catalytic amount (0.01 equivalent), the reaction did not yield the expected thiophenium salt product. The reason attributed to this could be the lack of catalyst in the reaction because of the excess amount of Cl^- (1 equivalent) that might turn Cu^{2+} into the inactive $CuCl_2$ when 1.01 equivalent of $Cu(OAc)_2$ was used the reaction with either 3-hexylthiophene or P3HT, large amount of insoluble green precipitate of $CuCl_2$ was formed. DMSO-d_6 was added to the precipitate to perhaps dissolve the desired product to be investigated by ^{1}H-NMR spectroscopy whether there was any thiophenium salt present in the green precipitate. Unfortunately, the ^{1}H-NMR spectrum showed no sign of product and characterization of the identified the unreacted 3-hexylthiophene starting material in ^{1}H-NMR spectrum. Similar result were found with P3HT. The obtained precipitate was purely $CuCl_2$ and the its filtrate showed only original P3HT signals in ^{1}H-NMR spectroscopy.
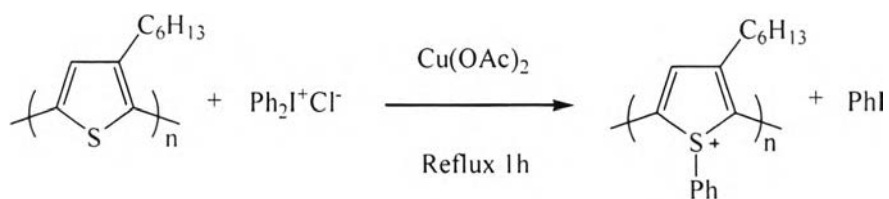
Figure 3.4 The expected products of the *S*-arylation of P3HT using DPIC.

This reaction was monitored in NMR tubes to examine if the thiophenium salt might have been generated, but quickly decomposed before it could be isolated. Pure DPIC in $CDCl_3$ showed the signals of phenyl group at δ 8.0, 7.5 and 7.4 ppm (**Figure A-41**, Appendix A). After addition of P3HT the usual signals of P3HT appeared (**Figure A-42**, Appendix A). When the reaction was left at room temperature for 1.5 hours, there was an occurrence of signals at δ 7.7, 7.3 and 7.1 ppm from the iodobenzene product (**Figure A-43**, Appendix A) whereas P3HT signals showed no significant change. After three hours the mixture showed more dominant peaks of iodobenzene while there was still no change of P3HT peaks (**Figure A-44**, Appendix A). Even after heating the reaction for two more hours, in which DPIC was completely consumed (**Figure A-45**, Appendix A). In another NMR tube, 1 equiv of AgOTf was used in place of $Cu(OAc)_2$ as the catalyst, similar results were observed (**Figures A-46–A-48**, Appendix A). From these results it could be concluded that *S*-arylation of thiophenes did not take place using DPIC as the arylating reagent either with $Cu(OAc)_2$ or AgOTf as a catalyst.

The *S*-arylation of P3HT using diphenyliodonium triflate (DPIT) gave a precipitate after triturated by ether confained to what observed by Kitamura [49]. However, the precipitate was insoluble in any solvent and could not be characterized by ^{1}H-NMR spectroscopy while the filtrate was identified to contain only the unreacted P3HT from ^{1}H-NMR spectroscopy. The IR spectrum of the precipitate (**Figure A-49**, Appendix A) showed aliphatic C–H stretching of hexyl group around $2850-2950\ cm^{-1}$ and aromatic C=C stretching around $1630\ cm^{-1}$, but could not firmly identified to be the expected S-aryl thiophenium salt product. From solid-state UV-Vis spectrum (**Figure A-51**, Appendix A), it showed a slightly bathochromic shift of the the λ_{max} (395 nm) compared to original P3HT (415 nm) (**Figure A-50**, Appendix A) and an occurrence of another maximum at 695 nm, which is similar to P3HT being doped. This UV-Vis spectrum suggested that the P3HT might have been arylated

using DPIT giving different optical property from the original P3HT, and especially the absorbance at higher wavelength. This reaction, however, could not be always repeated consistently. The yields of the precipitate were very low and sometimes none, made it impractical to prepare sample for further tests.
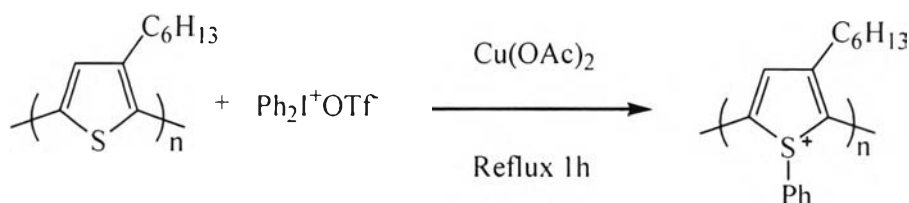

Figure 3.5 The S-arylation of P3HT using DPIT.

3.5 S-Methylation of thiophene and polythiophene derivatives

The S-methylation of thiophene was conducted using Acheson's procedure [48] with an alternative catalyst, silverperchlorate hydrate. The reaction time was doubled to ensure the formation of product.
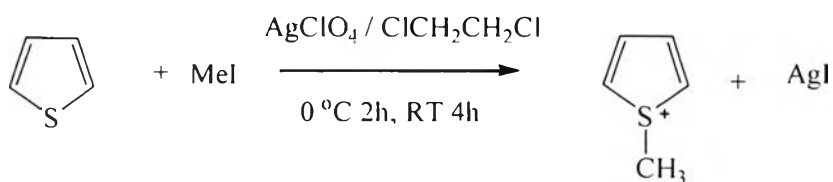

Figure 3.6 The S-methylation of P3HT using Methyliodide.

The polarity of the thiophenium product might make it insoluble by the solvent used in this reaction, dichloroethane, therefore it would be mixed with insoluble yellow precipitate of AgCl. To identify the thiophenium salt, crude mixture was rinsed with dichloroethane several times to remove unreacted thiophene and methyl iodide. Then DMSO-d_6 was added to the precipitate to dissolve the thiophenium salt from the mixture. From ^{1}H-NMR spectrum, there were signals at δ 7.5 and 7.1 ppm which could be identified as α and β proton of thiophenium salt, respectively (Figure A-52, Appendix A and Figure 3.4). The result was similar to what has been reported in the literature [48].
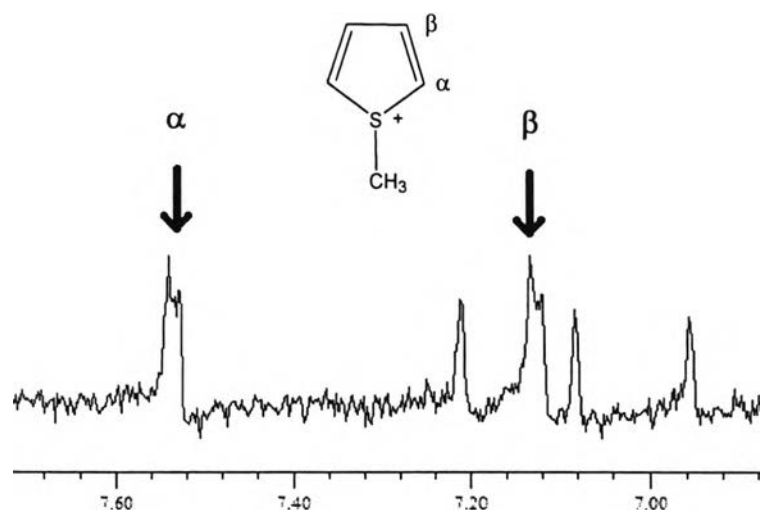
Figure 3.7 Expanded ¹H-NMR signals of methylated thiophene in aromatic region.

The *S*-methylation of P3HT yielded insoluble green precipitate just like what observed in the case of the earlier arylation of P3HT, making it difficult to characterize. The reaction with P3HT was also monitored in NMR tubes using methyl iodide (**Figures A-53 to A-54**, Appendix A) and dimethyl sulfate (**Figures A-55 to A-56**, Appendix A). Unfortunately, it was observed no detectable products, the same result as *S*-arylation in NMR tubes. The signals of P3HT in these ¹H-NMR spectra remained unchanged. The reaction might still take place but only gave an insoluble product that precipitated out of the solution, make it unable to detect.