CHAPTER IV

CONCLUSION

Polythiophene (PT) and poly(3-hexylthiophene) (P3HT) has been successfully prepared by polymerization of 3-hexylthiophene with anhydrous ferric chloride, providing both polymers 90 and 74 % yields respectively. Bromination on thiophene yielded the expected 2,5-dibromothiophene in 60 % yield. Attempts to further brominate onto β-positions of the dibromothiophene were not successful, probably due to the much less reactivity towards electrophiles of the already brominated thiophene. Bromination of polythiophene gave a dark brown powder that was insoluble in most 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 showed hypsochromic shifts of the λ_{max} in UV-Vis spectra of the products attributed to shorter effective conjugation length of the polymer after the incorporations of bulky bromo groups. Moreover, these brominated products also showed polymer chain degradation up to 83 %, especially in polar solvent. This suggested that the incorporation of bromo groups not only occurred at the β-positions of PT, but also at the α-positions of thiophene units that led to the degradation.

Acetylation of thiophene gave a complex mixture that has the proton signal of acetyl group present in ^{1}H-NMR spectrum, but the mixture could not be firmly purified and identified to be the desired product. Acetylation of polythiophene gave insoluble brown powder that cannot be firmly characterized except the weak appearance of acetyl carbonyl signal in IR spectrum. Octanoylation of polythiophene gave a soluble mixture, together with the perhaps unreacted insoluble polythiophene. The soluble mixture has the signal of the alkyl sidechain protons of the carbonyl group appeared, but the signals of thiophene protons were unobservable in ^{1}H-NMR spectrum. Acetylation of poly(3-hexylthiophene) gave products that showed hypsochromic shifts of the λ_{max} in UV-Vis spectra, together with other evidences of chain degradation. The incorporation of acetyl groups onto thiophene rings could mainly occur at the α-positions of the thiophene rings followed by chain degradation as the major pathway. Therefore, the small number of acetyl groups present in the products were expected to situate only at the terminal ends of the polymeric chains, corresponding to the relatively unobserved α-methyl protons of the carbonyl group signal in ^{1}H-NMR spectra.

The *S*-arylation through benzyne trapping by either thiophene or P3HT obtained mostly the unreacted thiophene or P3HT from ^{1}H-NMR spectroscopy. 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. The study of decomposition of diazonium carboxylate in UV quartz cells with P3HT showed that the decomposition occurred but left P3HT unreacted. It could be concluded that the benzyne intermediate cannot be trapped by S-atoms of the thiophene rings and preferred to react with themselves.

The *S*-Arylation of 3-hexylthiophene and P3HT using diphenyliodonium chloride gave crude mixture identified to be the unreacted substrates. By using diphenyliodonium triflate, the attempted arylation of P3HT gave dark precipitate that was insoluble in all tested solvent. Its solid state UV-Vis spectrum showed a small absorption maximum around 700 nm. The *S*-methylation of thiophene using methyl iodide gave a mixture containing the desired product. The *S*-methylation of P3HT, however, yielded an insoluble dark precipitate that could not yet be firmly identified.

For further works, the replacement of the 4-position of 4-bromo P3HT could be done by derivatization into other useful functional groups through coupling reactions. This should provide a useful strategy to tailor the structure and the band gap of the polymers and therefore control their electrooptical properties. Products from the functionalizations at S-atoms of P3HT suffered from their lack of solubility, hindering them from further characterizations and functionalizations. Nevertheless, they could still be investigated on a few of their other physical properties, such as surface conductivity of the pressed pellet form.