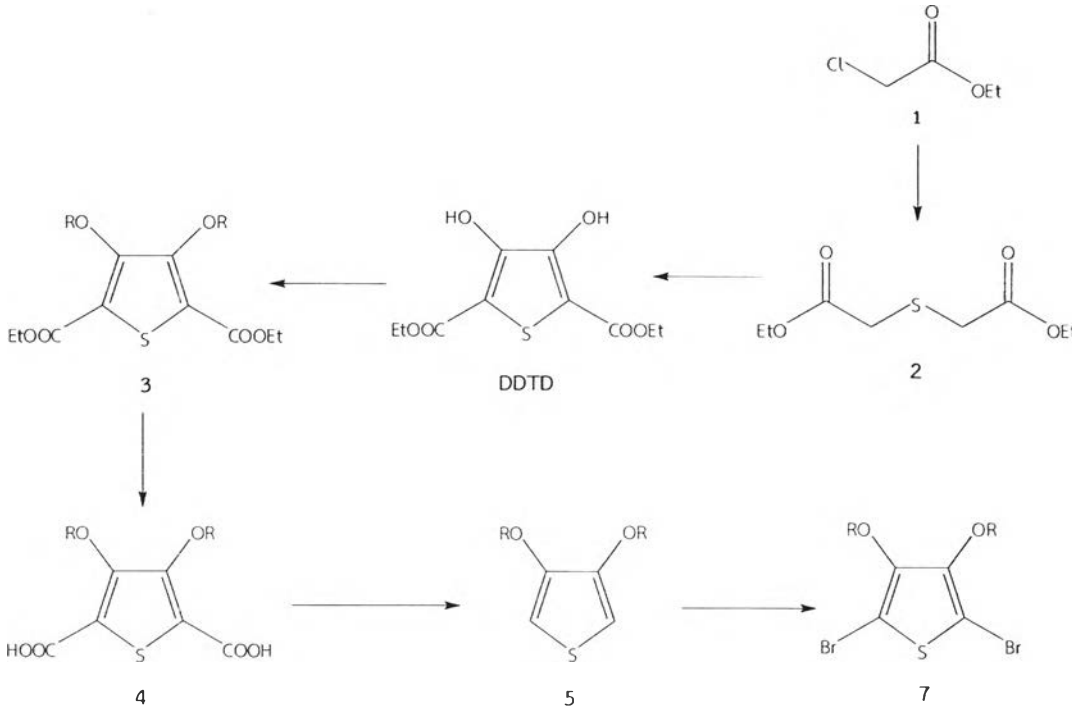
CHAPTER IV

CONCLUSION

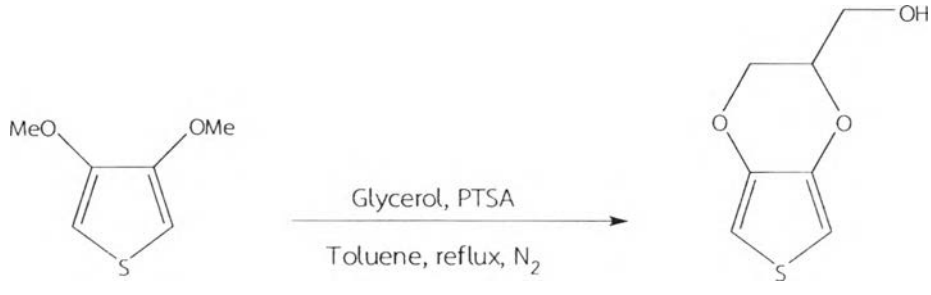
The synthesis of 2,5-dibromo-3,4-dioxythiophene derivatives **7** were first carried out via the traditional synthetic route as shown in **Scheme 4.1** [34-41].



Scheme 4.1 Synthesis of compound **7** (**3a**, **4a**, **5a**: R = Me ; **3b**, **4b**, **5b**, **7b**: R = $-CH_2CH_2-$; **3c**, **4c**: R = $-CH_2CH(CH_2OH)-$; **4d**, **5d**: R = H)

Substitutions of ethyl chloroacetate **1** with sodium sulfide nonahydrate yielded diethyl thioglycolate **2** in 45%. Diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate DDTD was obtained via Hinsberg reaction of diester **2** and diethyl oxalate in 68%. Methylations of DDTD with dimethyl sulfate gave compound **3a** in 73%. Compound **3b** was synthesized via the similar double Williamson etherification of DDTD and 1,2-dibromoethane in 87%. Compound **3c** was synthesized from DDTD and epichlorohydrin in 57%. Up to 80% yield from hydrolysis of diethylester derivatives **3** was achieved, affording 3,4-dialkoxythiophene-2,5-dicarboxylic acid **4a**, **4b**, and **4d**. Unfortunately, compound **4c** could not be isolated.

The diacids **4** were decarboxylated to obtain **5a** and **5b** (EDOT) in 63% and 70%, respectively. **5d** was supposedly decomposed during column chromatography purification. Because of the unsuccessful diester hydrolysis, compound **6** was instead synthesized from ether exchange reactions between **5a** and glycerol in 42%. Brominations of thiophene derivatives with NBS gave the corresponding compounds **7** mostly in excellent yields (77-98%). Furthermore, one pot synthesis of **7b** from **4b** by combining the decarboxylation and bromination steps was carried out giving the product in 77% yield, which was superior to 68% yield obtained from separated steps.



Scheme 4.2 Ether exchange reactions of 5a to compound 6

The facile solid state polymerization (SSP) processes of **7b** monomers surrounding the template molecules to give an unprecedented MIPs from imprinted PEDOT have been achieved. The binding experiments of these MIPs, monitored by UV-Vis spectroscopy technique, were carried out with 3 templates. We found that TPP-MIPs showed only small imprinting effects, possibly due to the large size of TPP and altered cavities during template removal. Noticeable imprinting effects of TNP-MIPs and TNT-MIPs could be observed. The results showed that the specific adsorption values (ΔQ) of TNP and TNT molecules bound to the MIPs were 128.41 μmol/g and 103.63 μmol/g, respectively. After using Soxhlet extraction with methanol, the rebinding capacities of the TNP-MIPs and TNT-MIPs were calculated from the extracted TNP and TNT templates to be 38.64% and 28.63%, respectively. In the rebinding experiments, the vacant reused MIPs displayed the diminished specific adsorption values (ΔQ) to 63.76 μmol/g for TNP-MIPs and 12.37 μmol/g for TNT-MIPS. This means that these MIPs for TNP and TNT were not suitable to be reused.

The cross binding experiments have shown that the prepared MIPs gave no specific response to the mismatched templates, similar to the observed results from NIPs. This confirmed that these MIPs are selective to their respective template molecules.

According to the results above, it indicated that PEDOT prepared through SSP, could be imprinted and used for later recognizing its template. MIPs of TNP showed better sensitivity and specificity than MIPs of TNT. These results suggested that PEDOT could be developed further into specific sensors for given template molecules.