

CHAPTER IV

CONCLUSION

New 3,4-dialkoxythiophene derivatives were successfully synthesized via the five step route. Substitution of ethyl chloroacetate **1** with sodium sulfide nonahydrate gave diethyl thioglycolate **2** in 49.0%. Diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate **3** was synthesized from diethyl thioglycolate **2** and diethyl oxalate through Hinsberg reaction in 63.0%. Compound **3** was used as the starting material for the synthesis of new diethyl 3,4-dialkoxythiophene-2,5-dicarboxylates **3** and **4**. All of the syntheses in acidic conditions failed to give the desired products. The reaction of compound **3** with chloroacetyl chloride obtained the expected product **4j** in 16.7%. The product **4k** was synthesized from compound **3** and trans-1,4-dibromo-2-butene through double nucleophilic substitutions in 53.2%. The reactions of compound **3** and 2,3-dichloroquinoxaline obtained either **4l** or **4m** in 10.0% and up to 61.1% respectively. The product **4n** was synthesized from compound **3** and 3,4-dichloro-1,2,5-thiodiazole in poor yield. It is possible that the product **4n** not stable and lost during workup and purification processes. In another case, the product **4p** was synthesized by bromination of compound **4k** with pyridinium tribromide, yielding the product **4p** in 89.4%.

Hydrolysis of the dicarboxylate **4k** afforded the dicarboxylic acid **5k** in 92.5%. Unfortunately, compound **4m** and **4p** could not be synthesized using the same process. The dicarboxylic acid **5k** was decarboxylated to give the new 3,4-dialkoxythiophene **6** in 59.5%. Bromination of thiophene monomer **6** with *N*-bromosuccinimide gave the dibromothiophene **7** in excellent yield (96.0%). The tetrabromothiophene **8** could also be synthesized from compound **6** using pyridinium tribromide in 23.7% yield.

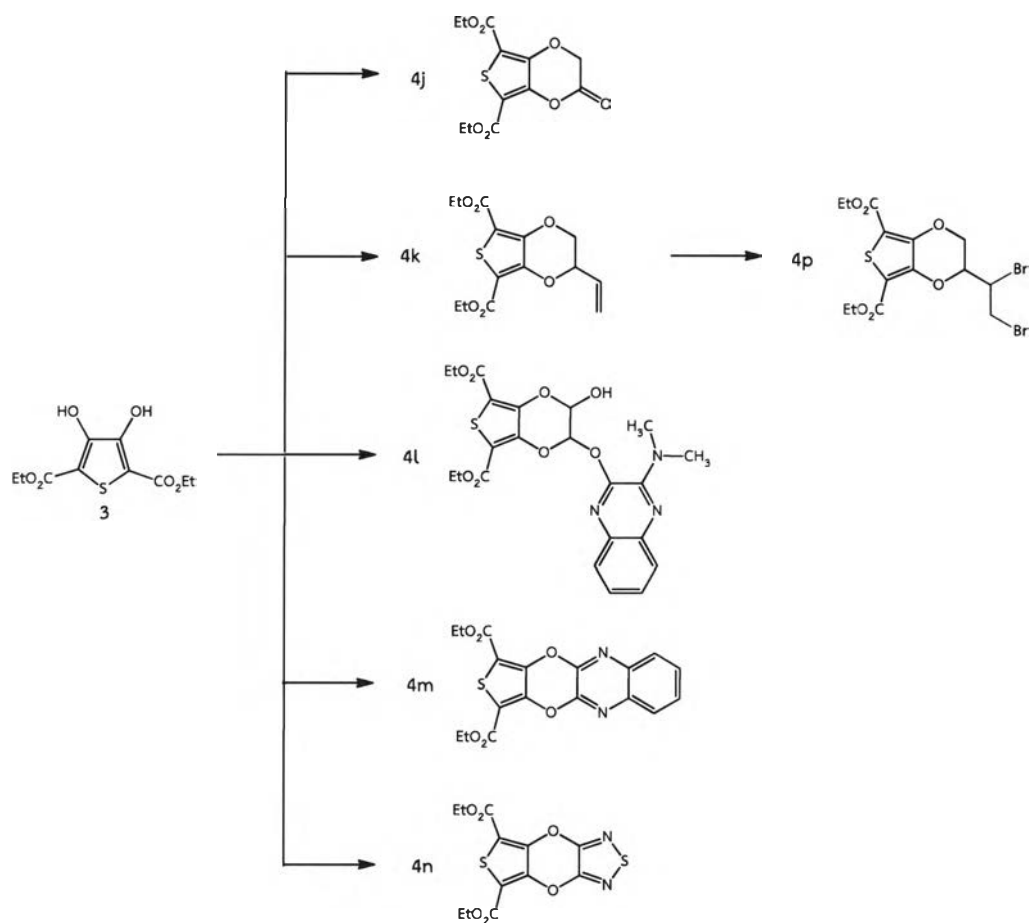


Figure 4.1 Synthesis diagram of diethyl 3,4-dialkoxythiophene-2,5-dicarboxylates 4

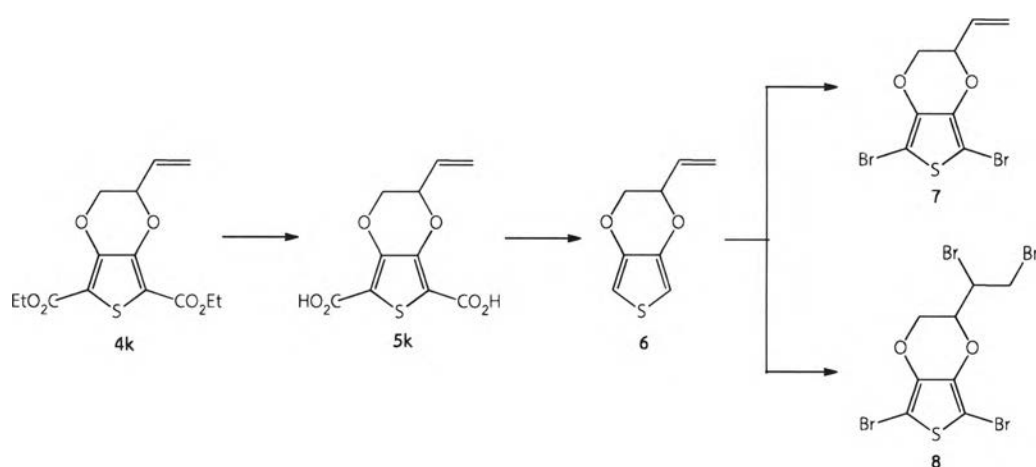


Figure 4.2 Synthesis diagram of thiophene monomer



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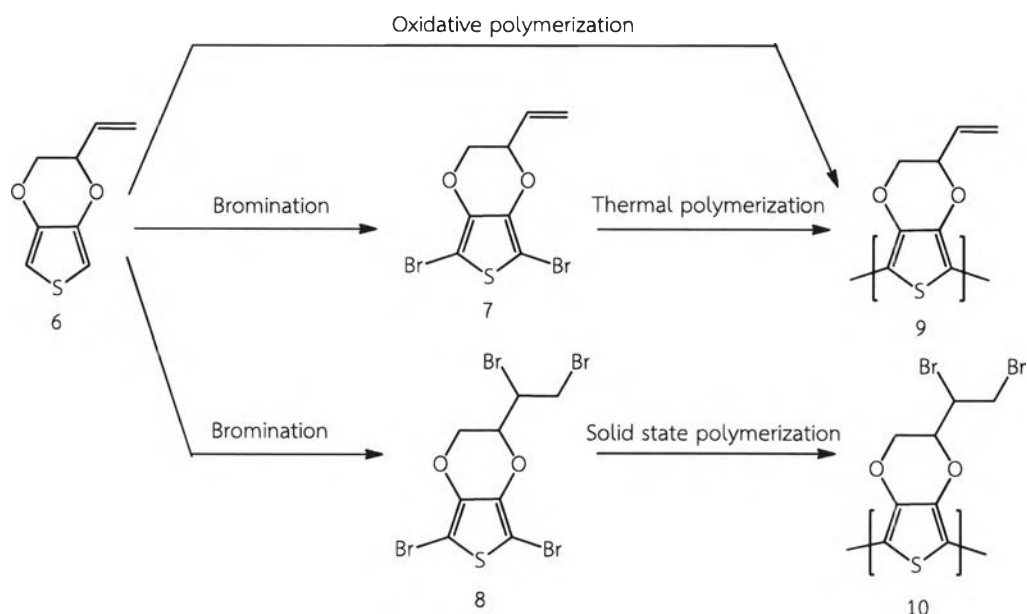


Figure 4.3 Synthesis diagram of polythiophene derivatives

The synthesis of new polymer **9** was achieved by both oxidative and thermal polymerization. The oxidative polymerization of thiophene monomer **6** using anhydrous ferric chloride as the oxidizing agent in chloroform, obtained polymer **9** in 72.2% yield. Thermal polymerization, modified from reported solid state polymerization, on liquid dibromothiophene **7** also gave polymer **9** in 68.4% yield. Unfortunately, the polymer **9** was insoluble in all organic solvents and hence could not be characterized as solution. The optical property of the solid polymer **9** synthesized from thermal polymerization exhibited a large bathochromic shift compared to that of polymer **9** derived from oxidative polymerization, indicating more extended conjugation within the polymer chain.

The solid state polymerization of tetrabromothiophene **8** to polymer **10** was successfully performed in 45.4% yield. Polymer **10** could not be dissolved in any common solvents. The optical property of polymer **10** was measured as pressed solid film which showed a maximum wavelength absorption (λ_{max}) at 688 nm, indicating large extended conjugation along the chain of polymer **10**.