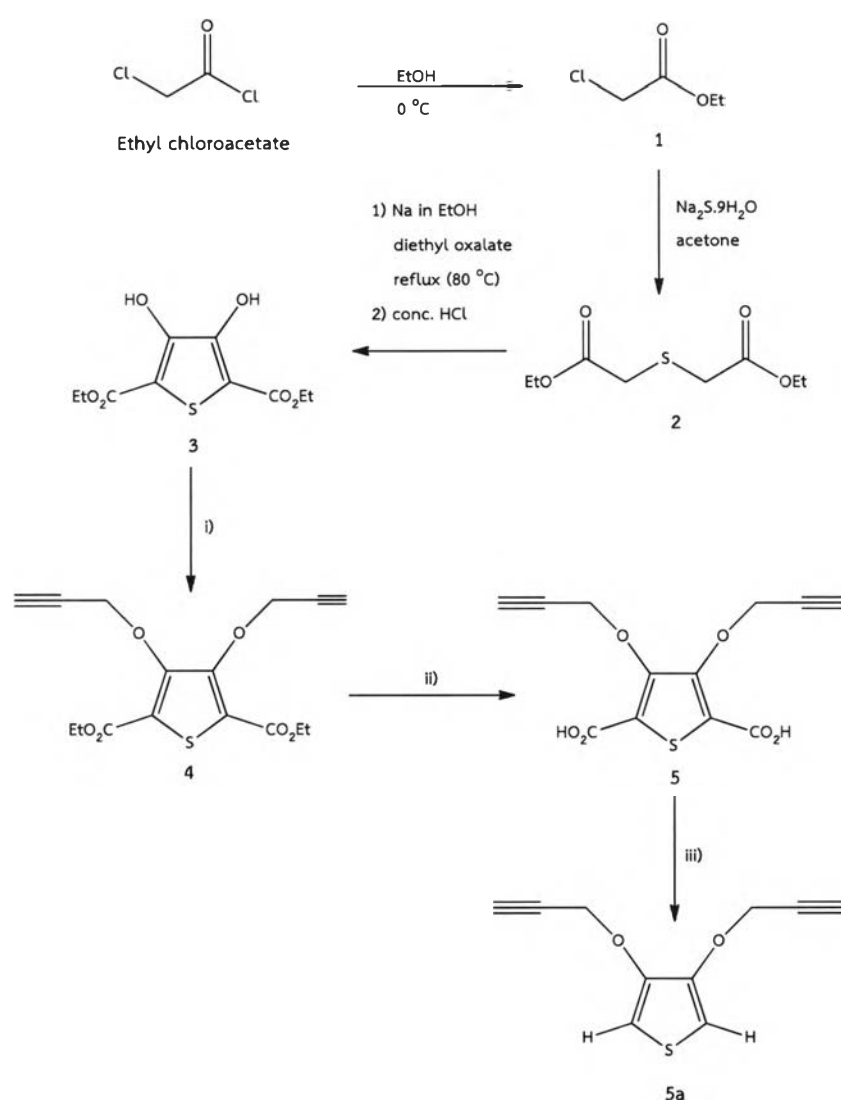


CHAPTER IV

CONCLUSION

The synthetic scheme of dialkyne monomers (**4**, **5** and **5a**) is showed in Scheme 4.1.

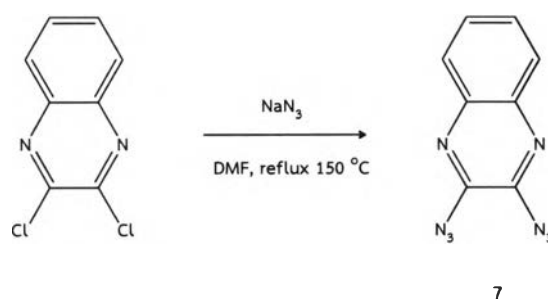


Scheme 4.1 The synthesis route of compound **4**, **5** and **5a** *Reagents and conditions:*
i) propargyl bromide, K₂CO₃, DMAP, CH₃CN:DMF, 80 °C, 4 h; ii) NaOH, EtOH, 80 °C, 4 h; iii) Cu₂O, quinoline, 150 °C, 5 h.

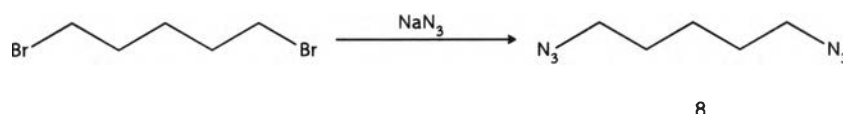


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The dialkyne monomers, diethyl 3,4-bis(2-propynyloxy) thiophene-2,5-dicarboxylate (**4**) and diethyl-3,4-bis(2-propynyloxy)thiophene-2,5-dicarboxylic acid (**5**) were synthesized from the key intermediate, diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate (**3**). Substitutions of ethyl chloroacetate (**1**) with sodium sulfide obtained diethyl thiodiglycolate (**2**) in 60%. Compound **3** was synthesized via the Hinsberg reaction of compound **2** with diethyl oxalate in 55% yield. Double nucleophilic substitution reaction of compound **3** with propargyl bromide gave compound **4** in 76%. The hydrolysis of compound **4** afforded compound **5** in 84%. Compound **5** was decarboxylated to obtain 3,4-bis(2-propynyloxy)thiophene (**5a**), which was, however, could not be isolated.



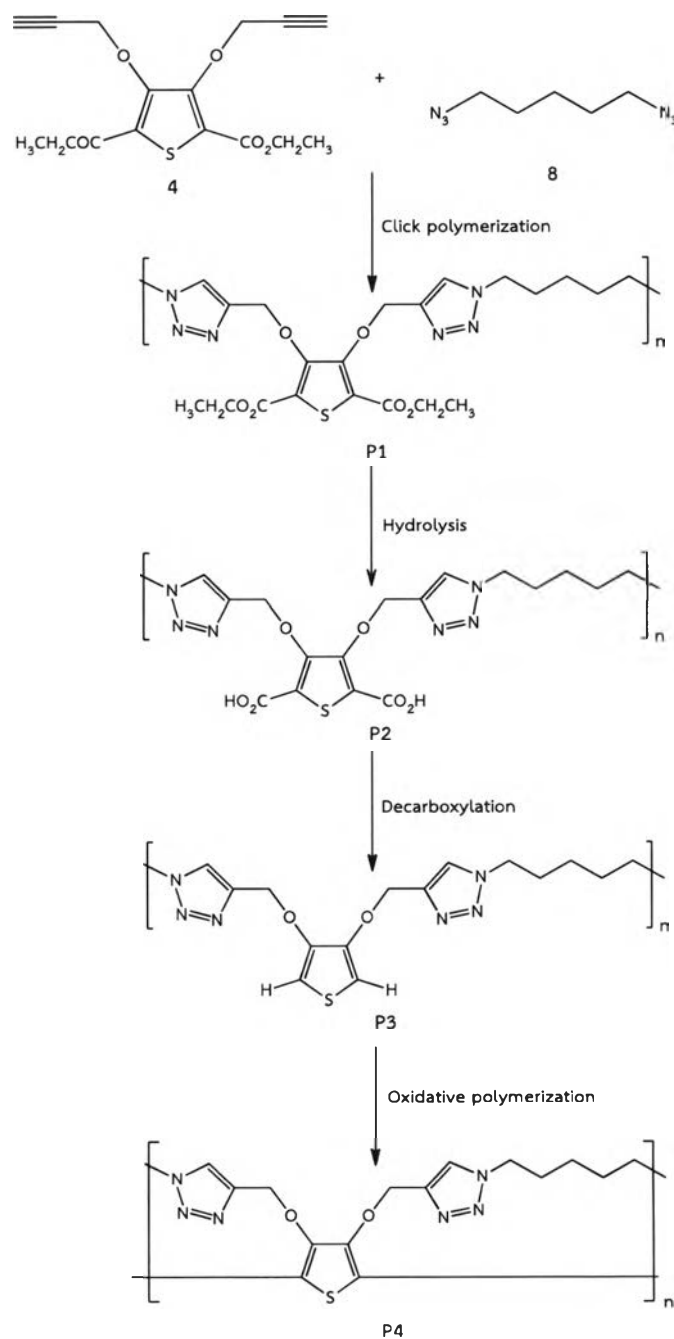
Scheme 4.2 Synthesis of 2,3-diazidoquinoxaline (**7**)



Scheme 4.3 Synthesis of 1,5-diazidopentane (**8**)

In attempts to make diazide monomers, diethyl 3,4-bis(2-hydroxyethoxy)thiophene-2,5-dicarboxylate (**6**) was synthesized from double nucleophilic substitution reactions of compound **3** and 2-bromoethanol in 74%. Unfortunately, tosylations of compound **6** did not give a complete reaction. Other diazide monomers was also synthesized through nucleophilic substitutions of corresponding halogen compounds with sodium azide to obtain 2,3-diazidoquinoxaline (**7**) and 1,5-diazidopentane (**8**) in 72% and 83%, respectively (**Scheme 4.2-4.3**).

The CuAAC click reaction of compound **8** with phenylacetylene afforded 1,5-bis(4-phenyl-1,2,3-triazoly)pentane (**9**) in 37% and confirmed the success of this reaction on diazides. Nevertheless, reaction **7** did not obtain the expected product under similar condition.



Scheme 4.4 The synthesis route of double strand polymer **P4**



The synthesis of polymer **P1** was performed by CuAAC click polymerization using copper (II) acetate as a catalyst between compounds **4** and **8**, obtaining up to 32% with the range of M_w up to 4484. The polymer **P2** could be obtained via similar CuAAC click polymerization of compounds **5** and **8**, this polymer could be more efficiently synthesized by hydrolysis of polymer **P1**, which obtained polymer **P2** in 69%. Decarboxylations of polymer **P2** afforded polymer **P3** in 45%.

A new synthetic approach to the synthesis of double strand polymer **P4** was achieved by oxidative polymerization using anhydrous ferric chloride, giving the double strand polymer in 72%. Characterizations of the resulting polymer was performed by NMR, FT-IR, solid UV-Vis techniques. Solid UV-Vis spectrum showed the absorption maximum at around 630 nm, indicating its high coplanarity structure. The thermal properties of this polymer was analyzed by TGA technique. The DTG thermogram showed the thermal decomposition about 298.5 °C and 437.4 °C and only moderate amount of mass loss was observed at 500 °C.

