

CHAPTER I

INTRODUCTION

1.1 A Brief History of click chemistry

Terms of materials, polymer sciences and biotechnology, limitations of these researches were ligation strategies that can be effectively used in the presence of a wide range of different functional groups typically encountered in these fields. For ligation strategies have requirements high selectively, orthogonality to other functional groups, compatibility with water and other protic solvent and high yields. The concepts of organic synthesis can be improved the ligation reaction by using click chemistry [1].

Click chemistry is a new approach to the synthesis of new substances by efficiently and reliably joining small units together with heteroatom links (**Figure 1.1**). In 2001, click chemistry was discovered by Sharpless and co-workers [2] which described click chemistry as a *'set of powerful, highly reliable and selective reactions for the rapid synthesis of useful new compounds and combinatorial libraries through heteroatom links (C-X-C)'*. Click reaction must be high efficiency such as giving consistently high yields, simple reaction conditions, readily available starting materials and reagent, simple purification methods without chromatographic methods such as crystallization or distillation, physiologically stable, stereospecific and wide in scope [3].

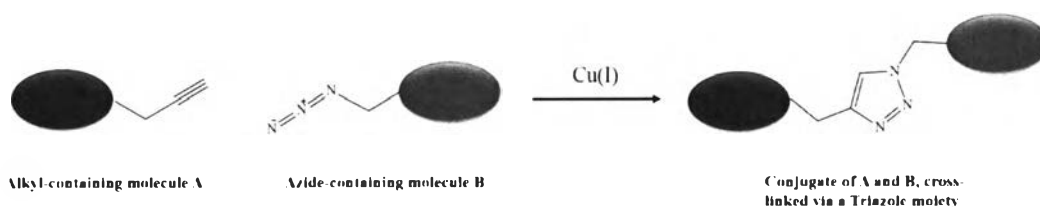


Figure 1.1 Joining small units together by click reaction



The concepts of click chemistry was introduced to polymer sciences in 2004 by Hawker, Shapless and co-workers [4] which reported the preparation of triazole dendrimers. The high efficiency of click reaction has been used to synthesize in terms of polymers as well as hyperbranched poly([1,2,3]-triazole)s was prepared by click polymerization [5] which developed from click reaction of small molecules. The traditional methods of synthesis polymer were step-growth polymerizations such as condensation and coupling polymerization that are slow because of the sluggish reactivity of monomers and have poor atom economy [6]. In contrast to click polymerizations, monomers can be readily activated to generate highly reactive species. To use click chemistry for polymerization of polymers can theoretically be very fast and give polymeric product with high molecular weights.

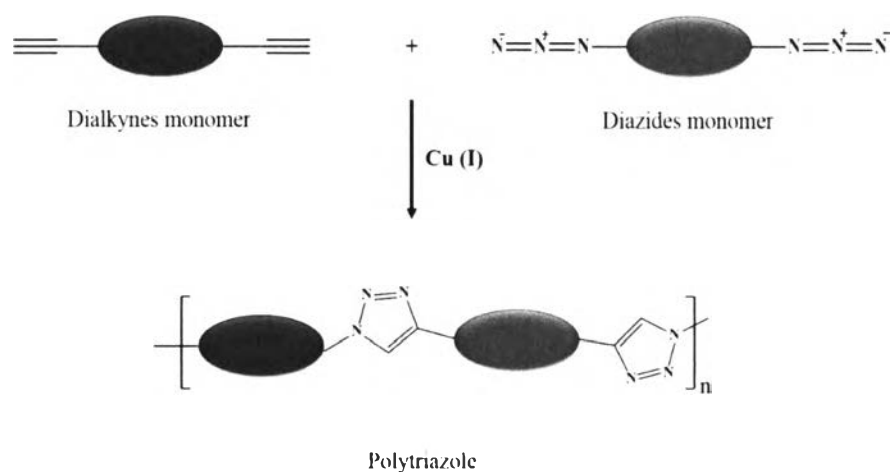


Figure 1.2 Click polymerization of dialkyne and diazide monomers

1.2 Click Chemistry Reaction Types

1.2.1 Nucleophilic Opening of Spring-Loaded Rings

The S_N2 ring opening of three membered ring heterocycle is a type of click reaction. Epoxide, aziridines, cyclic sulfate, episulfonium ions and aziridinium ions are substances, which was used in the S_N2 ring opening reaction [2]. The common substances for this reaction are heterocycles epoxides and aziridines.

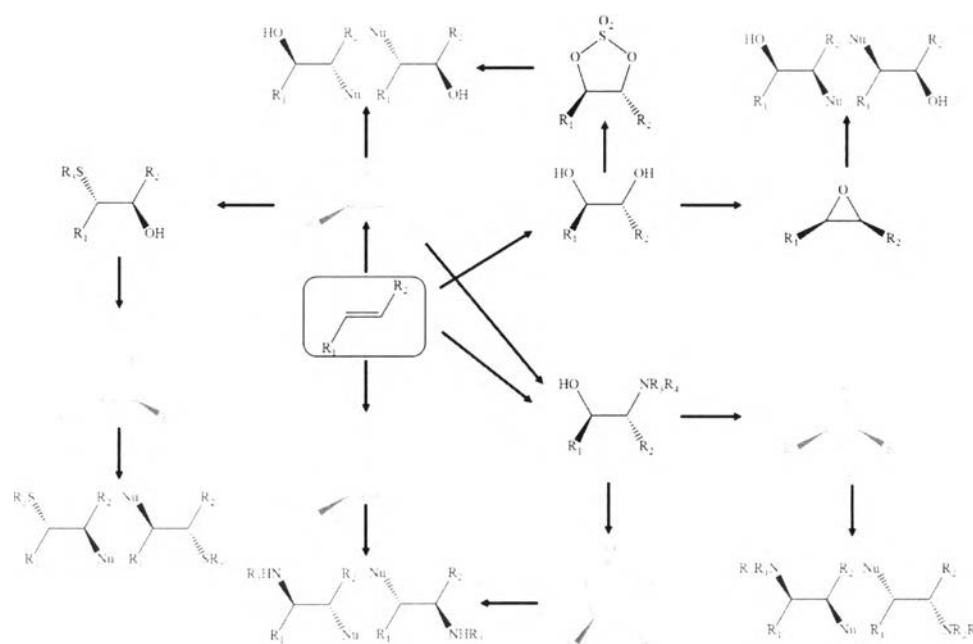


Figure 1.3 Generation and opening of spring-loaded cyclic electrophiles from olefins or their oxidation products

All ring opening reactions are shown in **Figure 1.3**. The reaction can be accomplished in many solvents such as alcohol, water, mixture of alcohol and water and absence of solvents. The regioselectivity of reaction was controlled by solvents used. The example of ring opening reaction of *cis*-1,4-cyclohexadiene epoxide with benzylamine shows in **Figure 1.4**. In the absence of solvent, the reaction gives a product as a 1,3-diol in 94% yield. While in case of methanol as a protic solvent, the reaction gives a different product as a 1,4-diol in 90% yield. The product from this reaction can be purified by crystallization from the crude solution [2].

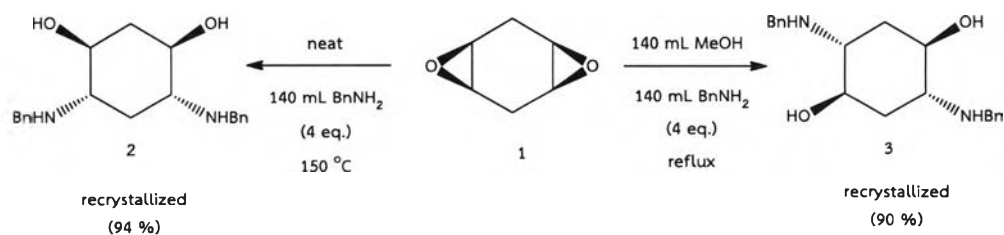


Figure 1.4 Regioselectivity of Oxirane Opening

1.2.2 Protecting Group Reaction

The acid-catalyzed reactions of aldehydes and ketones obtain cyclic 1,3-dioxolane rings in high yields. It is generally stable at physiological pH, has already appeared as components in orally available drugs, contribute several hydrogen bond acceptor sites and interesting dipole effects, provide constrained scaffolds with well-defined projections and spatial orientations of their substituents, are assembled from modular and abundant components, and represent one of the rare click chemistry modules based on reversible carbonyl chemistry [2].

1.2.3 Cycloaddition reaction

The most popular reaction of click chemistry is cycloaddition reaction which concerns heteroatom such as hetero-Diels-Alder and 1,3-dipolar cycloadditions. This reaction merges the organic molecules of two unsaturated reactants to generate the product as a variety of five and six-membered heterocycles. For click chemistry, cycloaddition reaction was mentioned to the Huisgen 1,3-dipolar cycloaddition between azides and alkynes to form triazoles.

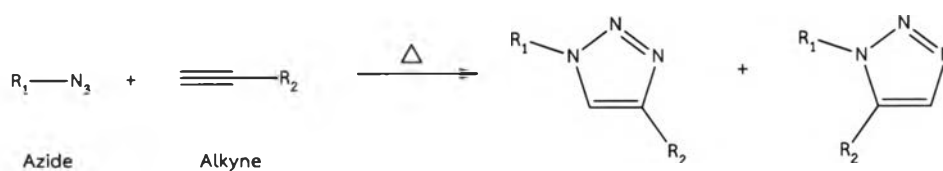


Figure 1.5 The Huisgen 1,3-dipolar cycloaddition of azides with alkynes gives mixture of regioisomer of 1,4-disubstituted and 1,5-disubstituted triazoles [7].

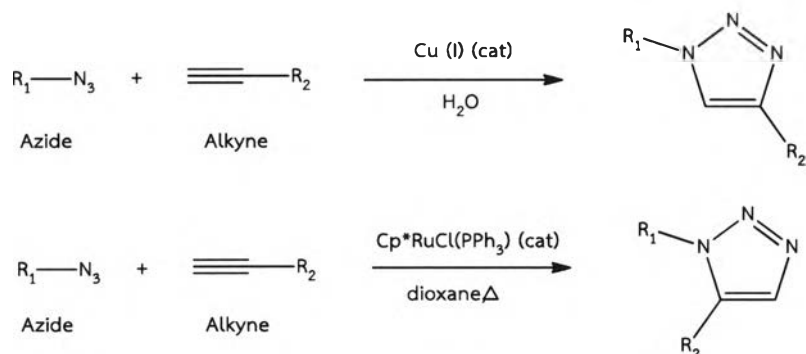


Figure 1.6 The Huisgen 1,3-dipolar cycloaddition of azides with copper catalyzed and ruthenium-catalyzed

The traditional of Huisgen 1,3-dipolar cycloaddition of azides with alkynes requires high temperature and generates the products as a mixture of two regioisomers of 1,4-disubstituted and 1,5-disubstituted triazoles as shown in **Figure 1.5** [7]. The regioselectivity of triazoles can be controlled by the catalyst to use in the reaction. The copper-catalyzed reaction generates the product as a 1,4-disubstituted regioisomer specifically of triazoles, while the ruthenium-catalyzed reaction generates the product as a 1,5-disubstituted triazoles. (**Figure 1.6**) Comparison of the traditional cycloaddition by thermal reaction with copper-catalyzed cycloaddition between phenyl propargyl ether (A) and benzyl azide (B), the traditional cycloaddition by thermal reaction was achieved the two disubstituted triazole isomers as products. While the copper-catalyzed cycloaddition of phenyl propargyl ether (A) with benzyl azide (B) was completed by the use conditions of reaction as a 5 mol% of sodium ascorbate and 1 mol% of copper (II) sulfate in the mixture of water and tert-butyl alcohol (2:1) to obtain the product as a 1,4-disubstituted triazole (91% yield). In this reaction, sodium ascorbate is the reducing agent to generate copper (I) catalyst (**Figure 1.7**) [8].

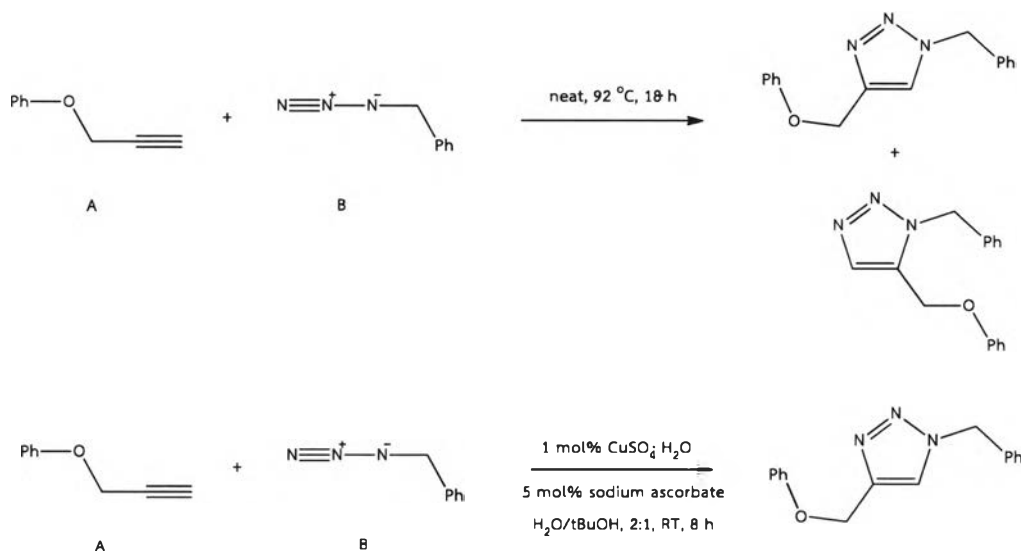


Figure 1.7 Thermal and Huisgen 1,3-dipolar cycloaddition of phenyl propargyl ether (A) with benzyl azide (B)

1.2.3.1 Copper-Catalyzed Azide-Alkyne Cycloaddition (CuAAC)

The copper-catalyzed azide-alkyne cycloaddition (CuAAC) was introduced by Sharpless and co-workers in 2002 [8]. The CuAAC reaction of azide and terminal alkyne obtained the 1,4-disubstituted triazole as a product. The rate of CuAAC reaction is as enormous as 10^7 - 10^8 when compared to the uncatalyzed 1,3-dipolar cycloaddition. CuAAC reaction uses copper (I) catalyst from copper (I) salts such as copper (I) bromide or copper (I) iodide, or copper (II) salts and reducing agents such as sodium ascorbate to reduce Cu from (+2) to (+1) oxidation state. Copper (II) sulfate (CuSO₄) is a common catalyst to be used in the CuAAC reaction. This reaction can be performed in a variety of solvent, and mixture of water with a variety of miscible organic solvents including alcohol, DMSO, DMF, t-BuOH and acetone.

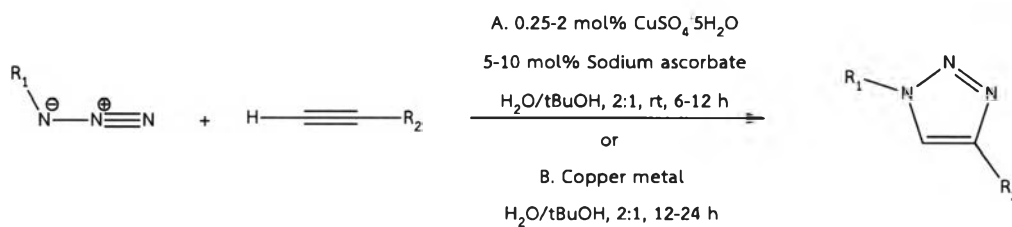


Figure 1.8 Copper (I)-Catalyzed Synthesis of 1,4-Disubstituted 1,2,3-Triazoles

In 2005, Fokin and co-workers reported the synthesis of azoles by Huisgen 1,3-dipolar cycloadditions. The product was achieved from organic azides with terminal alkynes to give 1,4-disubstituted 1,2,3-triazoles, and the catalyst of this reaction used copper (II) sulfate (procedure A) or copper metal from the copper wire or shaving (procedure B) (**Figure 1.8**). Copper (II) sulfate was converted to copper (I) by sodium ascorbate or ascorbic acid as a reducing agent. In procedure B, the copper metal was used when the substrates do not tolerate ascorbate. Product mixtures were isolated by simple filtration [9].



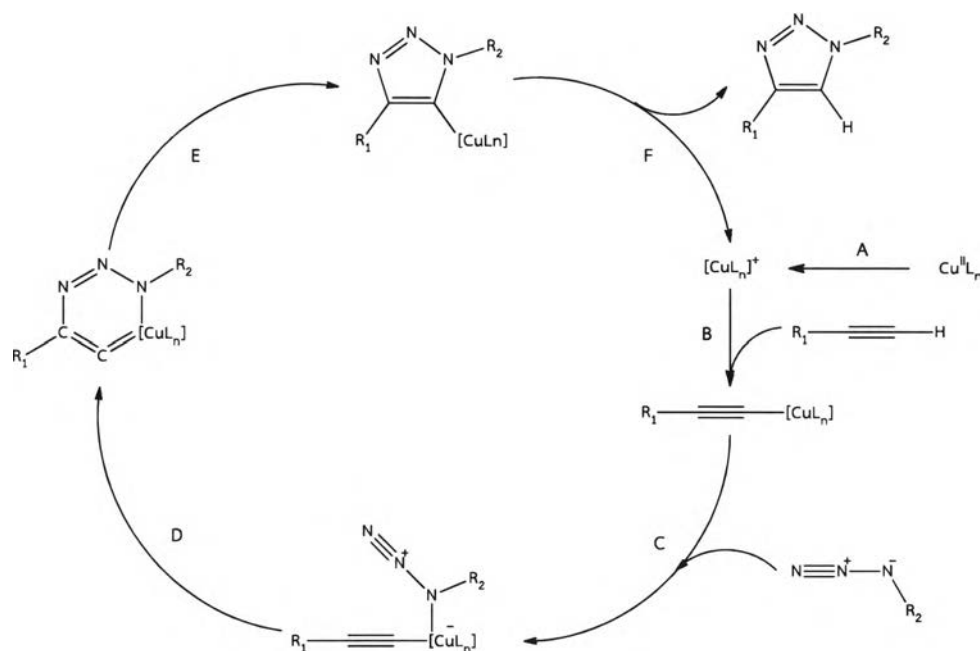


Figure 1.9 The mechanism of CuAAC L: ligand or a counterion associated with copper (I/II)

The mechanism of CuAAC reaction shows in **Figure 1.9**. In the first step, the copper (I) catalyzed is generated in an induction period or the copper (II) catalyzed is generated by reducing agent to obtain Cu (I) catalyzed (step A). The formation of copper (I) catalyzed with triple bond of terminal alkyne (step B) is bonded to give copper (I) acetylide. After that, the copper (I) acetylide is bonded with azide to generate a copper-azide-acetylide complex (step C). The ring closing, formed to the six-membered metallacycle (step D). The six-membered metallacycle converts to copper (I) triazolide (step E). The product is formed by dissociation of copper and the copper complex is generated to reaction cycle [10].

1.3 Click Chemistry in Polymer and Materials Science

Over the past decades, chemists have discovered novel synthetic approaches for the preparation of functional polymers. In the past, anionic polymerization was the approach for the synthesis of well-defined complex (co)polymer structure. Since the discovery of living/controlled radical polymerization, these reactions have made complex macromolecule structure. Nevertheless, all of the above methods cannot be constructed linear block copolymers. The approaches of generating block structures and star polymer has limits and cannot obtained all desired structures. The limitation of block copolymer formation has three the reasons [1].

- The reactivity and type of monomer are used to synthesize may be very different.
- It is often desirable to obtain block copolymers, which are a hydrophobic and a hydrophilic component or amphiphilic block copolymer. However, the synthesis of amphiphilic block copolymers has often limitation to prepare by identification of a common solvent in which the synthesis of block copolymer can be carried out.
- For nonlinear block copolymer such as block-stars or combs, this is not only two listed problem from above but also with additional complication, which depended on the method to use for their construction.

However, the approach of polymerization requires chemical transformations of high efficiency as well as the tolerance against a variety of functional groups and reaction conditions. Click chemistry can be the concept for requirement that are perfectly facilitated by the characteristic of these reaction and this reaction can theoretically be very fast and give polymer with high molecular weights. Click chemistry was introduced to the applications of polymer science in 2004 by Hawker, Shapless and co-workers [4]. The approach of polymerization by click polymerization is well-established approach for synthesis of well-defined macromolecule architectures. The ability of click chemistry has emerged in the synthesis of complex polymer structures, which achieved the block, star and comb structure of polymer with molecular weight ranges to have thus far been used as building blocks in the generation of larger and



more complicated structures and the mainly synthetic methods has been the CuAAC click polymerization.

1.3.1 Polymerization via CuAAC

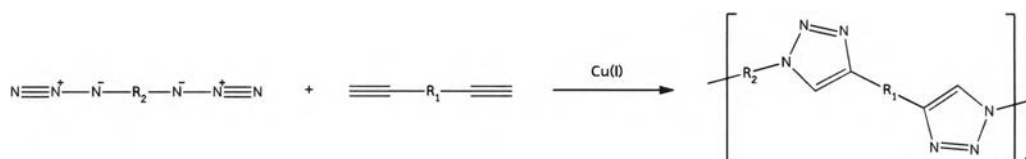


Figure 1.10 The copper (I) catalyzed azide-alkyne cycloaddition of bifunctional azide and alkyne monomers

The most of click polymerization is similar system of click reaction. The copper (I) catalyzed azide-alkyne cycloaddition of bifunctional azide and alkyne containing monomers (**Figure 1.10**) can be key step in the synthesis of variety of polymers that result in the formation of triazole in the main chain. CuAAC click polymerization was introduced to polymer by synthesis of triazole dendrimers or polytriazoles (PTAs) [4, 5]. The example of the synthesis of PTAs by CuAAC click polymerizations show in Figure 1.12 (a-f), which show the variety of synthetic PTAs polymer from various monomers such as AB_2 , $A_2 + B_3$, $A_2 + B_2$, and AB [6].

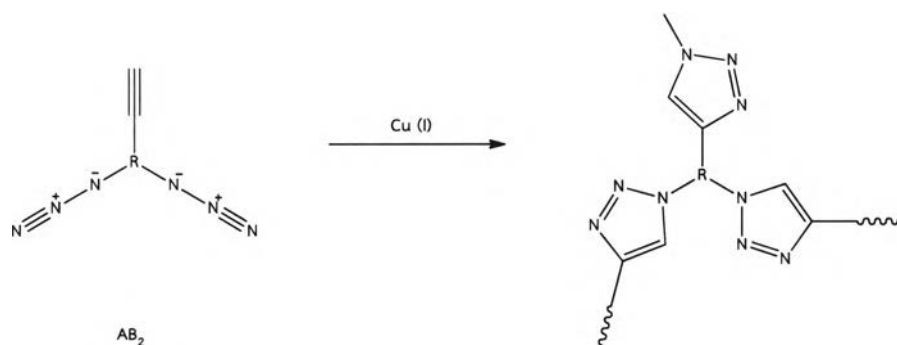


Figure 1.11 a) Synthesis of 1,4-Regioregular Hyperbranched PTA by Copper(I)-Mediated Click Polymerization of Ethynylene Diazides (AB_2) Monomer [11]

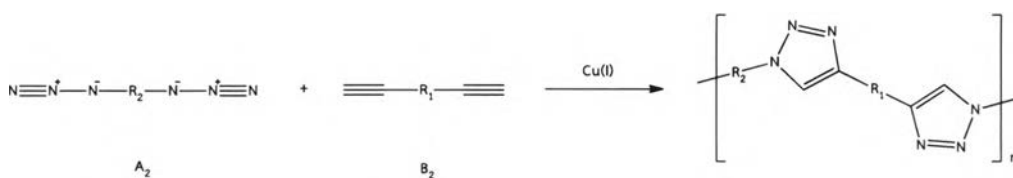


Figure 1.12 b) Synthesis of 1,4-Regioregular Linear PTA by Cu (I)-Catalyzed Click Polymerization of Diazides (A_2) and Diyne (B_3) Monomers [12]

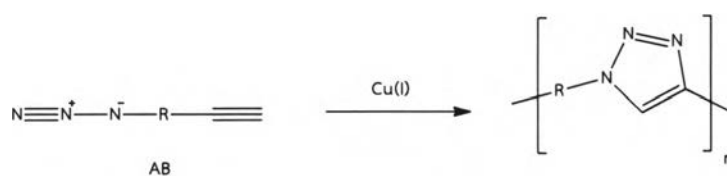


Figure 1.13 c) Synthesis of 1,4-Regioregular Linear PTA by Cu (I)-Catalyzed Click Polymerization of Azidoacetylene (AB) Monomers [13, 14]

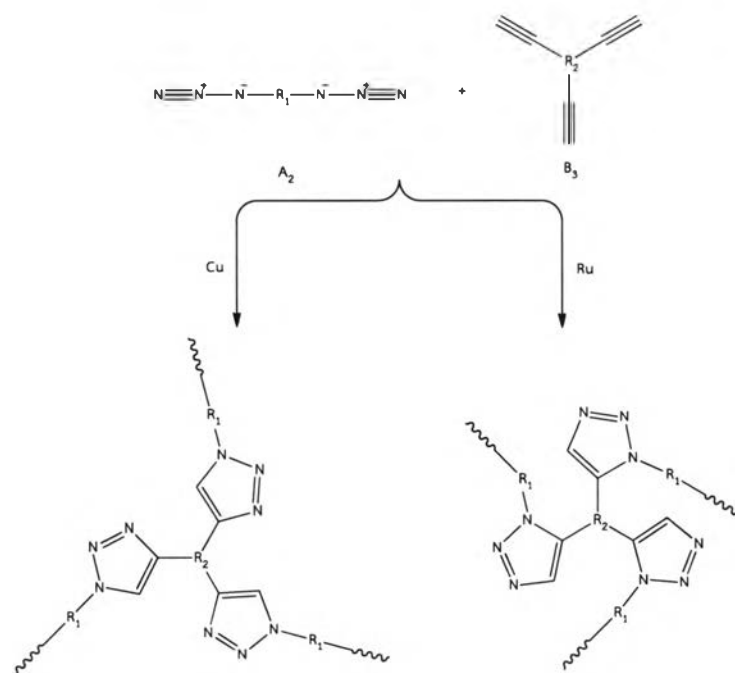


Figure 1.14 d) Synthesis of 1,4-Regioregular Hyperbranched PTA by Cu- and Ru-Catalyzed Click Polymerization of Diazides (A_2) and Triyne (B_3) Monomers [15]

The catalyzed system of CuAAC is CuSO_4 with sodium ascorbate as a standard conditions and the most widely to use in click reaction but the polymerization of this condition was accomplished in very long time. While the Cu(I) catalyzed compound of $\text{Cu}(\text{PPh}_3)_3\text{Br}$ was used in click polymerization to finish in few hours, which this catalyzed is a soluble in common organic solvents and dramatically accelerate the reaction rate. For Cu and Ru catalyzed to prepare in CuAAC click polymerization can achieved 1,4- and 1,5-regioregular polymers, the Ru compound of $\text{Cp}^*\text{Ru}(\text{PPh}_3)_2\text{Cl}$ is good catalyst and obtains 1,5-regioregular PTAs.

1.4 Advantages of Click Chemistry

Click chemistry has gained much interest among researcher and has published numerous research because of several advantages such as:

- Rapid and quantitative
- Mild reaction conditions
- Almost no byproducts
- Easy product isolation
- No side reactions
- Multiple and broadly applications
- High yields
- Functional group tolerant
- Reagent readily available

1.5 Applications of Click Chemistry

According to the high efficiently of click chemistry has led to use in many applications such as:

- Biotechnology
 - Modification of peptides, peptoids, oligonucleotide
 - Modification of natural products



- Synthesis of carbohydrate clusters and carbohydrate conjugation
- Protein/Peptide-Polymer conjugates
- Labeling of DNA
- Construction of fluorescent oligonucleotides for DNA sequencing
- Medical biotechnology
 - Drug discovery
 - Pharmaceuticals
- Dendrimer
 - Synthesis and modification of dendrimer
 - Design structure of dendrimer
- Nanotechnology
 - Nanoscale electronics
 - Functionalization of inorganic nanoparticles
- Materials science
 - Coating for glass, metal, plastics and other surface
 - Anti-coatings for medical implants
- Polymers
 - Synthesis of variety polymers such as polytriazole
 - Synthesis of polymer-protein bioconjugates
 - Click reaction on surface and resin materials

1.6 Conductive Polymers

Conductive polymer was discovered by Hatano and coworkers [16] which originated since the discovery of conductivity in polyacetylene with an order of 10^{-5} S/cm. In 1977, the high levels of conductivity in polymer was first observed when Shirakawa, MacDiarmid and Heeger discovered that oxidation with halogen vapor made polyacetylene film 10^9 times more conductive than they were originally [17] which was awarded the Nobel Prize in Chemistry in 2000 “for the discovery and development of



electrically conductive polymers". The conductive polymer was developed in conjugated poly(heterocycles) such as poly(pyrrole) or poly(thiophene) [18]. In field of conductive polymers as organic electronics or plastic electronics have unique properties which are interesting for this new technology [19]. Organic electronics or plastic electronics are different from conventional electronics which use inorganic materials such as silicon or gallium arsenide in many aspects. Organic semiconductor materials offer several advantages over their inorganic such as: low weight, low cost, tenability, flexibility and solubility/processability.

Conductive polymers are organic macromolecules that consist of one backbone chain of alternating single and double bonds between carbon-carbon or carbon-nitrogen atoms. Polymer chain of conductive polymers consist the sp^2 -hybridized orbitals of the carbon atoms which forms the delocalized π -orbitals of the alternating single and double bonds. Furthermore, the π -electrons can be easier moved from one bond to the other which makes conductive polymers as the semiconducting properties. Conductive polymers not only have the electronic properties of semiconductor but also the mechanical flexibility and ease of production of plastics. Furthermore, they are good materials to be used in the fabrication of electronic devices because their properties can be fine-tuned by external parameters during chemical synthesis within a certain band width and the intrinsic flexibility of their polymer enables new and low-cost manufacturing techniques of flexible roll-up displays, flexible sensors, large photovoltaic arrays and many others. The widespread interest in electrically conductive polymers is a consequence of the possibility that these material can be used as lightweight and easily fabricated replacements for semiconductor chips and integrated circuits, lightweight wiring, electrode materials in fuel cells and batteries, and components in wide variety of optoelectronic devices [20].



1.7 Band Theory

The band theory of organic semiconductors, the bonding and antibonding π -orbitals of the sp^2 hybridized π -electron materials generate energy bands, which are fully occupied π -band and empty π^* band. The band theory of conjugated polymers generate distinct energy band as the valence band (VB) and the conduction band (CB). The valence band is the highest occupied band electronic levels and the conduction band is the lowest unoccupied levels, which the difference of energy between valence band and conduction band is called the band gap [21]. The effect of HOMO-LUMO gap of a linear π -conjugated system depends on various structural of conjugated polymer such as chain length, bond length alternation, planarity, and the presence of electron-acceptor or electron donor substituents and the resonance stabilization energy of the aromatic cycles [22].

The design low band gap systems, there are a variety of methodologies which can be used to obtain polymers with band gaps. Five basic approaches have been used to reduce band gap that include controlling bond-length alternation (Peierls distortion), creating highly planar systems, inducing order by interchain effects, resonance effects along the polymer backbone, and using donor-acceptor effects.

1.8 Effective conjugation length (ECL)

The ideal of conducting polymer should has its π electrons in the conjugated unsaturated bonds even by distributing all through the whole chain. This requirement usually does not hold due to the formation of defects in polymer and twisting of planar structure out of conjugation in the polymer.



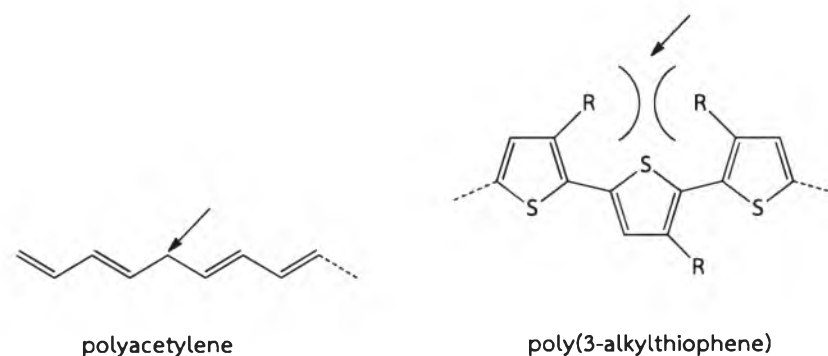


Figure 1.15 A defect in polyacetylene and steric induced structural twisting in poly(3-alkylthiophene).

The examples of the two reasons above are showed in **Figure 1.15**. The formation of a defect in polyacetylene as a saturated sp^3 -hybridized methylene caused the disruptive effect in the flow of electrons on polymer chain. In another reason, the steric incumbent between adjacent R groups on HH thienyl units in irregular poly(3-alkylthiophene) brought about the twisting of the thienyl ring planes out of coplanarity, causing an increase in the energy needed to allow the flow of electrons through the polymer chain, hence making the polymer chain less conductive.

Furthermore, another possible reason would be the twisting of polymer chain that occurs randomly at the single bonds and divided the polymer into separated sections with their own coplanarity (**Figure 1.16**). Twisting of polymer chain would also cause the reduction of conjugation in the polymer.

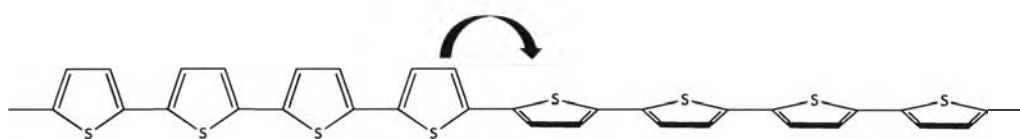


Figure 1.16 Twisting of polythiophene

1.9 Polythiophene

Polythiophene is constructed from thiophene monomer that composed of repeating five-membered heterocyclic monomeric unit. It is one of the attention in the field of conducting polymers for technological used. Polythiophene with an ideal extended π -conjugated is possible only in polymers with perfectly 2,5-linked repeating units but 2,4-and 2,5-couplings as well as hydrogenated thiophene units can also be found in the polymers.

Polythiophene is attributed to its good environmental stability in neutral form, its structure utility which allow their electronic and electrochemical properties to be modified by chemical means, the ease of derivatization and its ability to be polymerized by various methods. For these reasons, polythiophene and derivatives have been used in the widely and variety of applications such as transistors, hole injection layer in polymer LEDs, electrical conductors, environmental sensors, and solar cells [23].

1.10 Synthesis of polythiophene

Polythiophene is generally synthesized by mean of two main routes that are the electrochemical synthesis by applying a potential across a solution of the monomer to be synthesized and the chemical synthesis by using oxidants or cross-coupling catalyts.

1.10.1 Electrochemical polymerization

Polythiophene can be prepared by electrochemical polymerization that a potential is applied across a solution containing thiophene monomer and an electrode to be produce polymer film at the anode surface after electropolymerization, the obtain polymer are not easily processible. This method is appropriate for the preparation of polymers such as polythiophene and poly(3-methylthiophene). [24] Electrochemical polymerization is very useful method for preparing polymers such as polythiophene, poly(3-methylthiophene), and poly(3-phenylthiophene) which are



insoluble and infusible. When these polymers are obtained in the form of powder they cannot be processed into a film or other useful forms [25].

Polythiophene is not stable at the potentials used for the electrochemical polymerization of thiophene, so polythiophene deposited on the anode at the earlier stage of the polymerization is overoxidized and has been damaged, while the process continues to produce new polymer.

1.10.2 Oxidative coupling polymerization

The oxidative coupling polymerization is a typical of chemical polymerization by using synthesis by using oxidants or cross-coupling catalysts. The oxidative coupling polymerization with iron (III) chloride is relatively high yield in contrast to electrochemical polymerization. Furthermore, the molecular weight of polymer synthesized via this method is sufficiently high to be cast into a film. Polymers was synthesized from this method are soluble in common organic solvents and their films can be formed by simply casting its solution on a solid substrate.

Sugimoto and coworker [26] elaborated transition metal halides as oxidizing agent for polymerization of 3-hexylthiophene and found that iron (III) chlorides were the effective one (**Figure 1.17**). The films was fabricated by casting a solution of the resulting poly(3-hexylthiophene) on substrate and the results showed similar characteristics to those prepared by the electrochemical method.



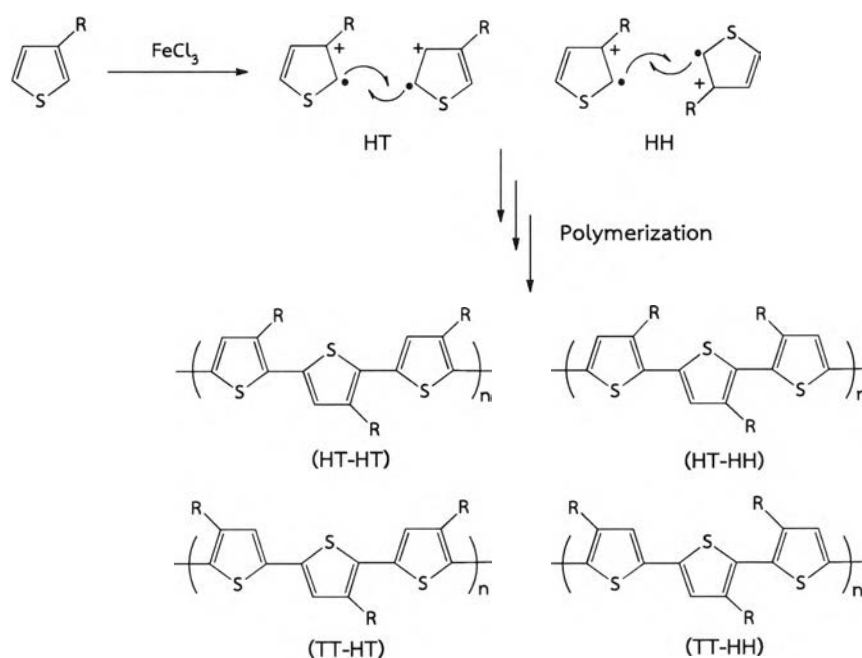


Figure 1.17 The oxidative coupling reaction of 3-alkylthiophene by FeCl_3 .

Niemi performed a detailed study on the polymerization mechanism of 3-alkylthiophene with iron (III) chloride. The results showed that only solid iron (III) chloride was active as an oxidative polymerization agent for 3-alkylthiophene while the soluble part of iron (III) chloride was inert [27]. The solubility of iron (III) chloride in chloroform and the consuming effect of evolved hydrogen chloride gas explained the extra amount of iron (III) chloride that was initially necessary to obtain high conversion in polymerization. A plausible polymerization mechanism of 3-alkylthiophene was proposed to proceed through a radical mechanism, developed on the basis of the crystal structure of iron (III) chloride and quantum chemical computations of thiophene derivatives [26].

Chemical polymerizations show several advantages such as large scale production possible, post-covalent modification of bulk conjugated polymer possible, more option to modify conjugated polymer backbone covalently and the ability to synthesize perfectly regioregular substituted polythiophenes.

1.10.3 Other polymerization

Moreover, polythiophene can be polymerized by various methods such as metal-catalyzed cross-coupling polymerization, solid state polymerization and acid-assisted-polycondensation.

Polymerization using a metal-catalyzed cross-coupling technique has been extensively investigated [28, 29]. The reaction is supposed to proceed by an oxidative addition of an organic halide with a metal catalyst and then transmetallation between the catalyst complex and a reactive Grignard or other organometallic reagent (or disproportionation) generates a diorganometallic complex. The last step involves reductive elimination of the coupled product with regeneration of the metal catalyst. Numerous organometallic species (including organomagnesium, organozinc, organoboron, organoaluminum, and organotin) have been demonstrated to be used in cross-coupling reactions with organic halides.

Solid state Polymerization is a process in production of polymer by heat. This reaction is driven by temperature, pressure, and the diffusion of by-products from the interior of the pellet to the surface. The advantages of solid-state polymerization including low operating temperatures, which restrain side reactions and thermal degradation of production, while requiring inexpensive equipment, and uncomplicated and environmentally sound procedures. However, at solid-state polymerization low temperatures, rate of the reactions are slow compared to polymerization in the melt phase because of the reduce mobility of the reacting species, and the slow diffusion of the by-products [30].

Recently, the researchers [31] have found that derivative of polythiophene as a PEDOT was prepared by acid-assisted-polycondensation based on 5-bromo-2,3-dihydro-thieno[3,4-b][1,4]dioxine (BEDOT). Under the exposure to ambient atmosphere, the formed PEDOT polymer is in doped state to some extent, showing poor conductivity of lower at 10^{-6} S/cm while improved to 0.3 S/cm along with further iodine doping. Such finding provides another alternative for the synthesis of conjugated polymers through simple acid-assisted-polycondensation.



1.11 Literature reviews

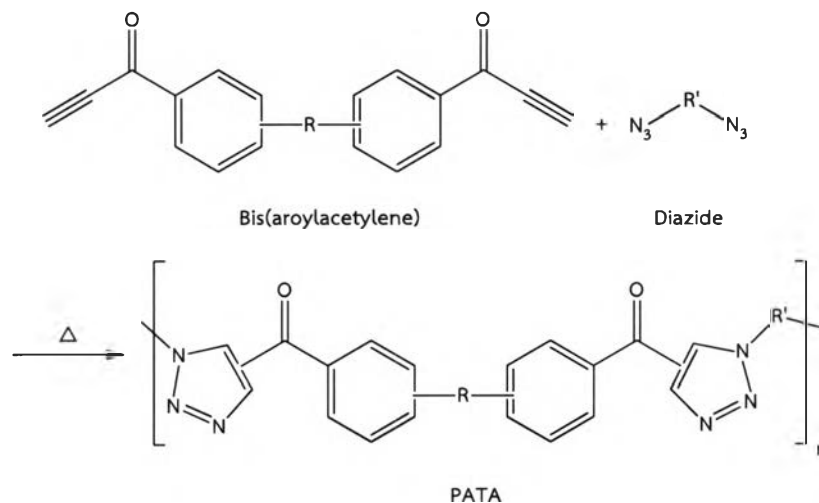


Figure 1.18 The metal-free click polymerizations of bis(aroylacetylene) with diazide

Qin et al. reported the synthesis new polymer as a linear poly(aroyltriazole)s (PATAs) by the thermal 1,3-dipolar cycloaddition reaction of bis(aroylacetylene)s and diazides as show in **Figure 1.18**. The conditions of this reaction was prepared in polar solvents such as DMF/toluene at a moderate temperature of 100 °C in the absence of catalysts to give the product with high molecular weights (M_w up to 26700) in high yields (up to ~98%). The PATAs polymers are all soluble in common organic solvents and thermally stable, losing little of their weights when heated to temperatures of ~360 °C [32].

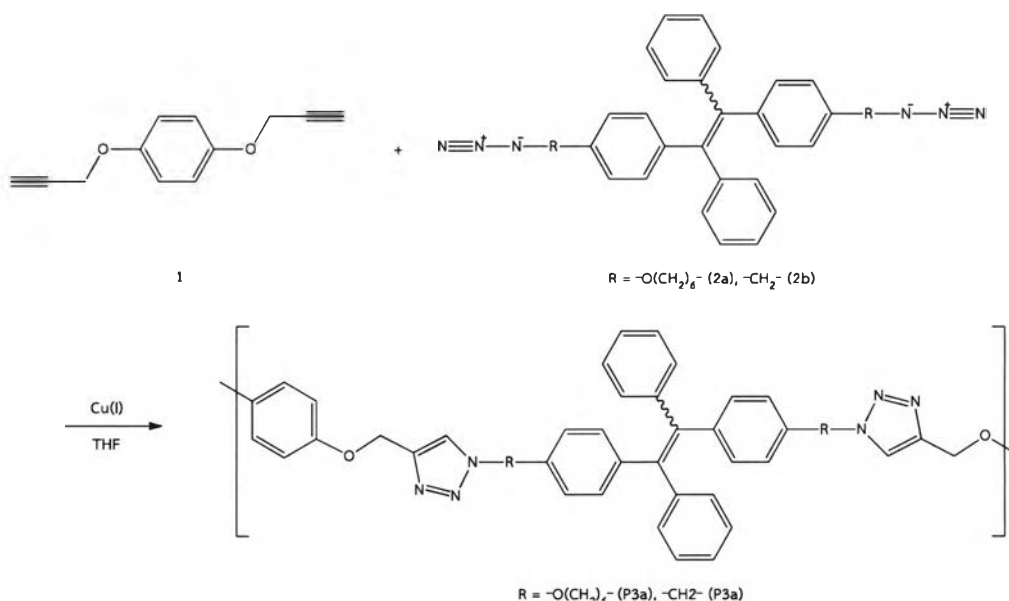


Figure 1.19 Synthetic Route to Polytriazoles **P3** via click polymerization of Diyne **1** with Diazides **2**

In 2009, this group researcher has recently reported a group of new tetraphenylethene (TPE)-containing polytriazoles by click polymerization of diyne with diazides in the present of catalyst. The researchers have previously succeeded in the catalyst-free click polymerization by heating of bis(arylacetylene)s with diazides. The catalyst-free click polymerization was accomplished in THF for 101 h which used longer time due to the low activity of diyne. In this report presented the click polymerization by using copper as a catalyst to synthesize the TPE-containing polytriazoles with high molecular weight in high yields and thermal stable ($T_d \geq 340 \text{ }^\circ\text{C}$) as show in **Figure 1.19**. The reaction time of click polymerization to use Cu(I) as a catalyst was decreased when compared with catalyst-free click polymerization. The application of polytriazole are used as chromosensors for detection of explosives in the aggregate and solid states [33].

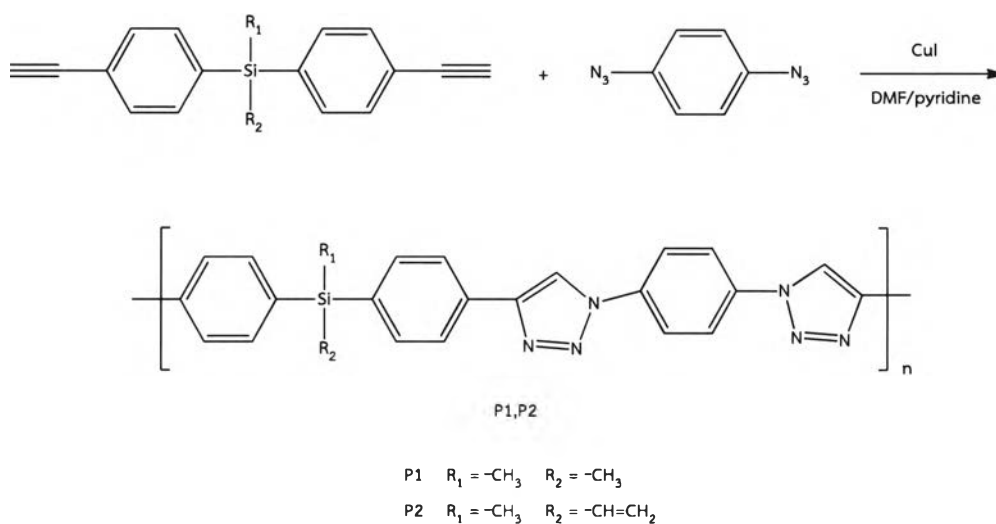


Figure 1.20 Synthesis of poly[silylene-1,4-phenylene-(1,2,3-triazole-4-yl)-1,4-phenylene]s by step-growth click coupling polymerization

Wang et al. reported the synthesis of poly[silylene-1,4-phenylene-(1,2,3-triazole-4-yl)-1,4-phenylene]s by step-growth click coupling polymerization of bis(*p*-ethynylphenyl)silanes and 1,4-diazidobenzene (Figure 1.20). Click coupling polymerization was accomplished in the mixture of DMF/pyridine by using copper iodide (CuI) as a catalyst at 60 °C for 24 h to obtain the polymer with high molecular weight and high thermal stability. The containing of the organosilicon units in the backbones can be improved the solubility of these polymers. The σ - π conjugated organosilicon polymers were observed in visible blue region (ca. 440 nm) in the fluorescence emission spectrum and these polymers could be used for potential optical materials in OLEDs [34].

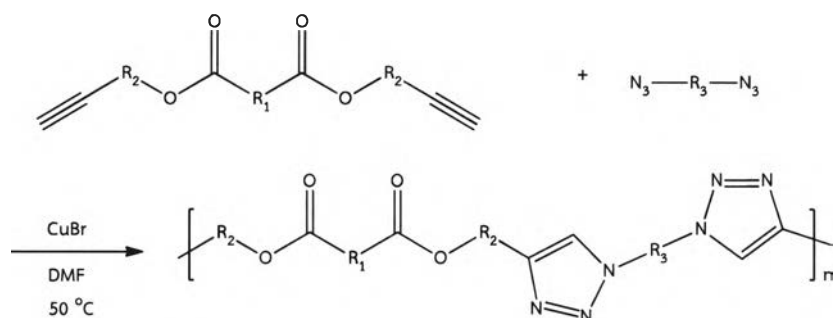
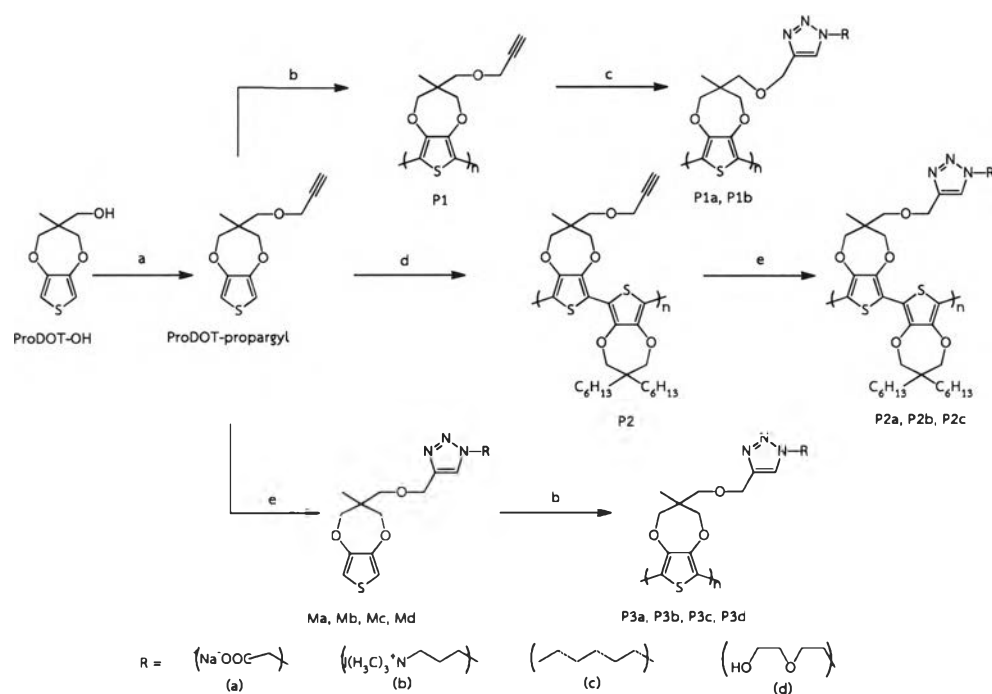


Figure 1.21 Synthesis of click polyesters

In 2010, Nagao and coworkers reported the synthesized of polyesters that contained main-chain 1,4-disubstituted triazoles through click Cu (I)-catalyzed polymerizations of dialkynes containing ester linkages and diazides as show in **Figure 1.21**. These reaction was obtained polyester with high molecular weights as a $[(1.0\text{-}7.0) \times 10^4]$ in high yields and triazole backbone can be improved the thermal properties of polyesters and magnified the even-odd effect of the methylene chain length [35].



a) Propargyl tosylate, NaH, DABCO, THF; b) i: FeCl_3 , CHCl_3 ii: $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$ c) RN_3 , $\text{DMSO}/\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, Sodium Ascorbate;
 d) i: dihexyl ProDOT, FeCl_3 , CHCl_3 ii: $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$ e) RN_3 , Acetone/ H_2O , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, Sodium Ascorbate, 80 °C

Figure 1.22 Synthesis Routes for “Click” able Monomer and Polymers

Sinha et al. reported the synthesis and characterization of ‘click’ able monomer and polymers based on 3,4-propylenedioxythiophene (ProDOT). This polymer can be functionalized at the monomer stage or the polymerization. Propargyl-functionalized ProDOT (ProDOT-propargyl) was polymerized by chemical polymerization to obtain insoluble polymer, which can be made water-soluble by reacting click reaction of it with 1-azido-ethanoic acid sodium salt or 3-azidopropyltrimethylammonium iodide. The chemical copolymerization of ProDOT-propargyl with 25 mol % of dihexyl-ProDOT obtained the organic soluble polymer which resulted in the reversal solubility from water-soluble to organic-soluble. The electrochemical properties of poly(ProDOT-propargyl) were prepared by electrochemical polymerization to obtain thin film polymer on the electrode surface and in situ conductance of these polymer showed a maximum conductance of 0.03 S [36].

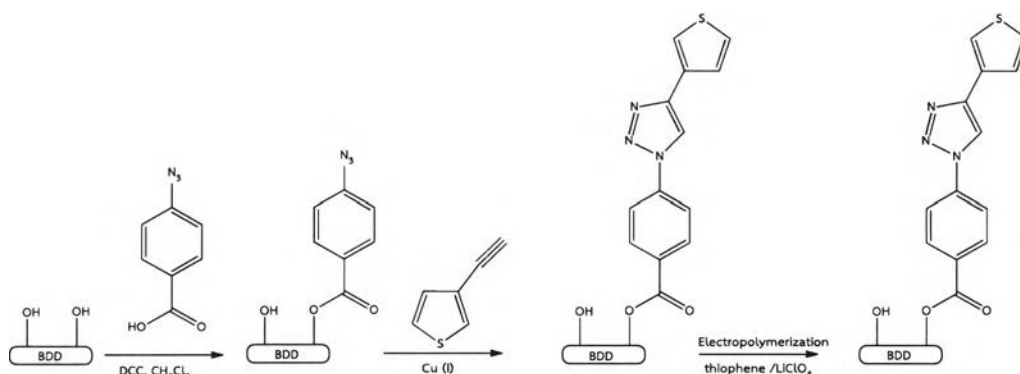


Figure 1.23 The preparation of a conducting polythiophene polymer covalently bonded onto thiophene-terminated boron doped diamond surface.

Wang et al. presented the preparation of a conducting polythiophene polymer covalently bonded to a thiophene-terminated boron-doped diamond (BDD). Azide-terminate was produced by esterification reaction of photochemically oxidized diamond with 4-azidobenzoic acid and thiophene was introduced to azide-terminate BDD surface electrode by click chemistry. Polythiophene film on the BDD surface was prepared from thiophene monomer by electropolymerization. The BDD film can be used in the applications in areas ranging from electronic/photovoltaic devices to chemical/biological sensing [37].

Polythiophene has moderate conductivity. The conductivity of polythiophene may be dropped due to twisting out of coplanarity of thiophene units on the main chain, resulting in high energy band gap. The rotation at the single bonds occurred randomly caused the twist out of coplanarity. The connection of thiophene units on both α or β positions would eliminate such twist of single bonds. In the present design, at α positions of thiophene monomer are being connected by the process of oxidative chemical polymerization, which at β positions are being connected by click polymerization process. This latter approach has never been applied to the synthesis of polythiophene. Thus, a newly designed of this double strand polythiophene to improve coplanarity of the conjugated system could be created.

1.12 Objectives

- To synthesize an improved coplanar polythiophene by connecting both α and β positions of thiophene monomers through two processes of polymerizations to become a double strand polymer.
- To synthesize the dialkyne and diazide monomers as the precursors of CuAAC click polymerization.

