

İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

**SYNTHESIS AND CHARACTERIZATION OF POLYSTYRENE WITH SIDE
CHAIN PYRROLE GROUPS BY COMBINATION OF NMRP AND
CLICK CHEMISTRY**

**M.Sc. Thesis by
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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**PIROL YAN GRUPLARI İÇEREN POLİSTİRENİN NMRP VE KLİK
KİMYASI İLE SENTEZLENMESİ VE KARAKTERİZASYONU**

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FOREWORD

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Polymer Science and Technology

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ABBREVIATIONS

PE	: Polyethylene
PP	: Polypropylene
PS	: Polystyrene
PMMA	: Polymethylmethacrylate
NMP	: Nitroxide Mediated Radical Polymerization
SFRP	: Stable Free Radical Polymerization
TEMPO	: 2,2,6,6-tetramethyl-1-piperidinyloxy
AIBN	: Azoisobutyronitrile
IUPAC	: International Union of Pure and Applied Chemistry
FTIR	: Fourier Transform Infra-red
NMR	: Nuclear Magnetic Resonance Spectroscopy
CuAAC	: Copper-Catalyzed Azide–Alkyne Cycloaddition
AIBN	: Azoisobutyronitrile
PS-<i>co</i>-CMS	: Polystyrene- <i>co</i> -chloromethylstyrene
DMF	: N,N-dimethylformide
CMS	: Chloromethylstyrene

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SYNTHESIS AND CHARACTERIZATION OF POLYSTYRENE WITH SIDE CHAIN PYRROLE GROUPS BY COMBINATION OF NMRP AND CLICK CHEMISTRY

SUMMARY

Recently, many researchers have developed synthetic methods to control polymer architecture and tailor a material's properties for a specific application. For this purpose, post-functionalization of a polymer is a useful technique in which a specific polymer is post-synthetically derived. This approach allows introduction of molecular diversity in the final step.

Novel side-chain pyrrole functional polystyrene (PS) was synthesized by using "Click Chemistry" strategy. This procedure involves the preparation of polymer and pyrrole possessed with the appropriate click components. First, 1-(4-(prop-2-ynoxy)phenyl)-1H-pyrrole (*propargylpyrrole*) terminal groups was synthesized as an electroactive click component. A new procedure for the Clauson-Kaas pyrrole synthesis was used to synthesize *propargylpyrrole*. The other component, namely azido group functional polystyrene (PS- N_3) was synthesized independently in the presence of NaN_3 /DMF. Finally, azido functionalized PS was coupled to *propargylpyrrole* with high efficiency by click chemistry. The spectral analysis confirmed the presence of pyrrole functionality in the resulting polymer. The strategy adopted in this study appears to be entirely satisfactory in terms of efficiency and simplicity. Further work is in progress to expand this approach to other functionalities.

PİROL YAN GRUPLARI İÇEREN POLYSTİRENİN NMRP VE KLİK KİMYASI İLE SENTEZLENMESİ VE KARAKTERİZASYONU

ÖZET

Son zamanlarda, bir çok araştırmacı, polimer mimarisini control etmek ve belirli bir amaca uyarlamak için sentetik metodlar geliştirmiştir. Bu amaçla, polimerin önceden işlevselleştirilmesi kullanışlı bir metoddur.

Bu çalışmada, “Klik kimyası” yöntemi kullanılarak, pirol yan grupları içeren polistiren sentezlenmiştir. Bu yöntem hazırlanan polimerin ve pirolun uygun klik bileşenleri ile etkileşimi ile olmaktadır. İlk aşamada, 1-(4-(prop-2-ynoxy)phenyl)-1H-pirol (*propargilpirol*) sonlandırıcı grupları elektroaktif klik bileşenleri olarak sentezlenmiştir. *Propargilpirol* yeni bir yöntem olan Clauson-Kaas metodu ile sentezlenmiştir. Diğer bileşen olan, azid grubu içeren polistiren (PS- N_3) bağımsız olarak, NaN_3/DMF varlığında sentezlenmiştir. Son olarak azidlenmiş polistiren klik kimyası yöntemi ile *propargilpirol* ile yüksek verimle birleştirilmiştir. Son elde edilen polimerdeki pirol fonksiyonel gruplarının varlığı yapılan spektral analizler ile kanıtlanmıştır. Bu çalışmada elde edilen verim çalışma kolaylığı memnun edicidir. Bu yaklaşımı, diğer fonksiyonel gruplara uygulamak için çalışmalar devam etmektedir.

1. INTRODUCTION

Polymers are widely used in all walks of human life and play a vital role in shaping modern man's activities to be as important and comfortable as they are today. The advances in science and technology made in recent decades owe much to development of polymer science. The synthesis and design of new polymeric materials to achieve specific physical properties and specialized applications, and attempt to find interesting applications involving advanced structures and architectures, are in continuous development in the period of the polymer science.

Basically, a polymerization process is based on a repetitive reaction in which a monomer is converted into polymer segment. To achieve such a goal, polymer chemists have a variety of synthetic processes to choose from reactions with very high selectivity when planning a particular synthesis. However, each method has its strengths and its weaknesses, and often requires high-purity reagents and special conditions. Indeed, the need high-purity monomers and solvents, reactive initiators and pure conditions have dramatically limited the industrial application of many techniques.

Electrically conducting polymers such as polyacetylene, polypyrrole, polythiophene and polyaniline have been the subject of intensive research due to their useful electronic properties and for their application in optoelectronic and display devices, and as active electrode materials in primary and secondary batteries. The factor that has motivated much of the work on the synthesis of conducting polymers is the need to find newer materials having a wide range of physical properties such as flexibility and processibility, and conductivity close to that of metals to suit many technological applications.

The two key developments in the early stages of conducting polymer research were the discovery of synthetic, free standing, high quality films of polyacetylene and the discovery that these films could be doped by electron donors or acceptors to conductivity levels (~ 1000 S/cm) approaching those of some metals. A significant breakthrough occurred in 1979 with the discovery that poly(p-phenylene) could also

be doped to high conductivity. It demonstrated that polyacetylene is not unique in exhibiting high conductivity and led to a number of new polyaromatic based conducting systems, including poly(P-phenylene sulfide), polypyrrole, polythiophene and polyaniline.

The incorporation of electroactive sites into polymers is proposed to be a vesetalie route to improve the physical properties of the conducting polymers . Various controlled polymerizations has been previously used for the preparation of such macromonomers. Obviously, these macromonomers were further used in electropolymerization in conjunction with the low molar mass monomers such as pyrrole and thiophene.

In this thesis, we described the novel synthetic methodology to incorporate pyrrole units into polystyrene as side chains. The precursor polymers were prepared by NMRP which allows control over molecular structure and chain lengt. The subsequent click chemistry step provided quantitative functionalization of the polymers with electroactive groups.

2. THEORETICAL PART

2.1 Conducting Polymers

2.1.1 History of Conducting Polymers

Conducting polymers are a relatively new class of materials whose interesting metallic properties were first reported in 1977, with the discovery of electrically conducting polyacetylene [1]. This chance discovery occurred when a researcher accidentally added too much catalyst while synthesising polyacetylene from acetylene gas, resulting in a shiny metallic like substance rather than the expected black powder. This shiny semi-conducting material was subsequently partially oxidised with iodine or bromine vapours resulting in electrical conductivity values of up to 10^5 s.cm^{-1} , which is in the metallic range [2]. The importance of this discovery was recognised in 2000 when the Nobel Prize for Chemistry was awarded to the scientists who discovered electrically conducting polyacetylene in 1977: Alan MacDiarmid, Alan Heeger and Hideki Shirakawa [3].

Since the discovery of polyacetylene there has been much research into conducting polymers and many new conducting polymers have been synthesised. The most important, and common, of these are polypyrrole (PPy), polythiophene (PTh) and polyaniline (PAn). There have been many potential applications suggested for these materials, including sensors, electrochromic devices, corrosion inhibitors, electrochemical actuators, electromagnetic shielding, polymeric batteries, and membrane separations. This wide range of applications is possible in part due to the ability to alter the electrochemical, optical, chemical and mechanical properties of these polymers by changing the monomer and/or dopant incorporated into the polymer.

2.1.2 Synthesis of Conducting Polymers

Conducting polymers such as polypyrrole, polythiophene and polyaniline are generally prepared by oxidation of a suitable monomer (Figure 2.1). In the vast majority of cases the oxidation is either chemical or electrochemical in nature, although limited examples of photochemically and enzymatically-catalysed oxidative polymerizations have been reported [3].

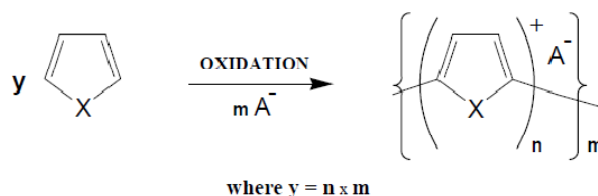


Figure 2.1: Oxidation of pyrrole to form polypyrrole (X = NH) or thiophene to form polythiophene (X = S).

2.1.2.1 Electrochemical Polymerization

Electrochemical polymerization results in a film deposited on the working electrode surface. The electrochemical method is the most useful as it provides greater control over the rate of polymerization and results in a more reproducible product. It also allows the insertion of a much wider range of dopant anions as any anion present in the reaction mixture can be incorporated into the polymer to maintain electrical neutrality.

The polymerization of conducting polymers is classified as a free radical propagation reaction and consists of a number of steps. These steps are clearly seen in the mechanism for electropolymerization of the 5-membered heterocycles thiophene and pyrrole.

The four steps involved in the mechanism of electropolymerization are:

Step 1: Oxidation of the monomer, resulting in formation of a radical cation which exists in three resonance forms.

Step 2: The most stable of these resonance forms (the α -radical) couples with another α -radical producing a dicationic dimer

Step 3: The dicationic dimer undergoes a deprotonation reaction leaving a neutral dimer.

Step 4: The neutral dimer is oxidised to a radical cation. This dimer couples with

other radical cations leading to chain propagation. Upon reaching a certain length, the polypyrrole chain becomes insoluble and precipitates onto the electrode surface [4].

The electropolymerization of aniline occurs in a similar manner. Again, there are four key steps involved in the reaction. These steps are:

Step 1: Oxidation of the monomer, resulting in the formation of a radical cation which exists in three resonance forms.

Step 2: An oxidised aniline species with the radical cation centred on the nitrogen atom couples with an oxidised aniline with an unpaired electron centred in the *para*-position, forming a dicationic species. Deprotonation of this species results in a neutral dimer.

Step 3: The neutral dimer is oxidised forming a radical cation, with the radical cation centred on the nitrogen atom. This couples with an oxidised aniline with an unpaired electron centred in the *para*-position, resulting in chain propagation.

Step 4: The growing polymer chain is oxidised to a radical cation and doped with HA.

2.1.2.2 Chemical Polymerization

Typically, chemical polymerization uses a chemical oxidant such as FeCl_3 or $(\text{NH}_4)_2\text{S}_2\text{O}_8$, which simultaneously oxidises the monomer and provides the dopant anion. This approach to producing conducting polymers is extensively used in industry (e.g. by DSM, Mitsubishi Rayon, Ormecon Chemie), but is limited to the small number of oxidants that can both oxidise the monomer and provide a suitable dopant. Chemical oxidation most often results in the formation of a conducting polymer powder, which generally displays lower conductivity than electrochemically prepared conducting polymer [5]. This is a result of the lack of control over the potential within the reaction mixture, which may rise to a level that over-oxidises the polymer, as well as poor doping control [6].

The chemical polymerization of pyrrole is thought to occur with a mechanism similar to that for electropolymerization. However, for polyaniline the mechanism of chemical polymerization is significantly different from that of the electropolymerization reaction. This difference occurs in the chain propagation and

product formation steps, as the initial product formed is pernigraniline salt. This pernigraniline salt is reduced in a subsequent reaction with free aniline, giving emeraldine salt and a radical cation of aniline [3].

2.1.2.3 Other Polymerization Methods

Other methods of polymerization have been used for the preparation of conducting polymers such as polyaniline and polypyrrole. The enzymatically catalysed synthesis of polyaniline has been achieved with the enzyme horseradish peroxidase (HRP) and H_2O_2 as an oxidant. This procedure was limited, however, by the fact that the products were generally low molecular weight oligomers with extensive branching. Recent studies have overcome these limitations through the use of polyelectrolyte templates, such as poly(styrene sulfonate) PSS or DNA, in the reaction mixture. The template is thought to act by aligning the aniline molecules in such a way as to promote head-to tail coupling while providing the localised low pH environment that is necessary for PAn growth. Polyaniline has also been synthesised photochemically; via electron acceptors; with a plasma polymerization method; and was also found to grow spontaneously by an “electroless polymerization” route on platinum or palladium foil [3]. Polypyrrole has also been prepared via enzymatic catalysis with bilirubin oxidase (BOX) [7]. Pyrrole has also been found to undergo an acid-catalysed polymerization reaction in strong acid solutions (6.0 M HCl). This polymerization occurs via a 2,5-dipyrrol-2-ylpyrrolidine trimer intermediate and results in a brown non-conductive powder. This insulating property is explained by the polymer possessing alternating pyrrole and pyrrolidine units, with varying degrees of ring-opened units and nitrogen loss [8].

2.2 General Properties of Conducting Polymers

Conducting polymers as a class of materials have a number of properties in common, even though their structures can differ greatly. The chief property they have in common is the fact that, unlike traditional polymers, they conduct electricity. These polymers also possess a high degree of conjugation along the polymer chain [9]. This conjugation gives rise to the electrical conductivity as it allows the efficient transfer of electrons (or positive charges) along the polymer backbone. However, this conductivity only exists when the polymer is in an oxidised state [10]. The loss of an

electron from a π -bond results in the formation of a radical cation or polaron charge carrier. Electrical conductivity arises from the delocalisation of these charge carriers, which are capable of both inter- and intra-chain transfer. The positive charge that arises during the formation of the polaron charge carriers necessitates the incorporation of an anion into the polymer to maintain overall charge neutrality in a process known as “doping”. The anions that are incorporated can be anything ranging from small ions such as Cl^- , to more complex ions including proteins [10]. The nature of the dopant has dramatic effects on the electrical, mechanical, physical and morphological properties of the polymer.

Another feature common to all conducting polymers is that they are electroactive and can exist in a number of stable oxidation states. In general, it is possible to reversibly switch the polymer between these different oxidation states, resulting in changes in the electrical, mechanical, physical, chemical and morphological properties of the material [5]. Figure 2.2 shows this redox cycling for polypyrrole.

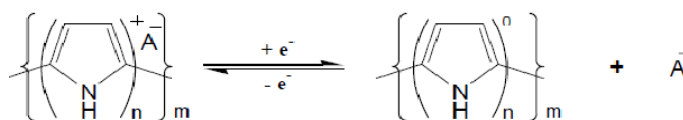


Figure 2.2 : Redox cycling between the oxidised (conducting) and reduced (insulating) forms of polypyrrole (where n is number of monomer units per positive charge, m determines molecular weight and A^- is dopant anion).

2.3 Applications of Conducting Polymers

Conducting polymers have been used in a range of electronic devices. One of the first applications of these materials was in rechargeable batteries. Bridgestone has produced a battery with a polyaniline cathode and a lithium-aluminium alloy anode [11]. A polypyrrole/lithium-aluminium battery was commercialised by Varta and BASF [12]. During cell discharge electrons flow from the anode to the cathode, reducing the polymer to its undoped state. The dopant anions are ejected into the electrolyte phase, while the lithium from the anode dissolves into the electrolyte as lithium ions. During recharging this process is reversed - the dopant anions flow from the electrolyte phase into the polymer, oxidising it, while the lithium ions are deposited at the anode as lithium metal. Poor recycling of the lithium metal is the limiting factor in the lifetime of the batteries [12].

A potential use for conducting polymers such as polyaniline, polyfuran and polythiophene are as gas sensing devices. The conductivity, optical absorption and electrical capacitance of metal-polymer interfaces are strongly affected by the presence of certain gas molecules. Thin-film polyaniline-based gas sensing elements are inexpensive, and have been shown to be sensitive to gases such as CO, NH₃, HCl and HCN. Polyfuran and polythiophene have been considered as humidity sensors, radiation detectors and gas sensors [13].

2.4 Polypyrrole

2.4.1 General Overview

Polypyrrole is one of the most widely studied conducting polymers and has been well characterised. This is in part due to the fact that it is known to exhibit a relatively high conductivity of up to 100 s.cm⁻¹ and good environmental stability [14]. Like most conducting polymers, polypyrrole is electroactive and can act as an anion exchanger. During the synthesis of polypyrrole, dopant anions (A⁻) are incorporated to balance the positive charges that develop on the oxidised polymer. Upon reduction of polypyrrole the positive charges are removed and hence the dopant anions are expelled from the polymer. Upon reoxidation of the polymer, anions from the supporting electrolyte will be incorporated to balance the developing positive charges. However, if large and immobile dopants anions such as polyelectrolytes (PE⁻) are incorporated into the polymer matrix during growth, then they will be almost completely retained upon reduction of the polymer (Figure 2.3). In order to maintain charge neutrality, cations (X⁺) from the surrounding solution are therefore taken up by the polymer. These cations will be expelled from the polymer when it is reoxidised, opening up the possibility of using these polymers as cation-exchangers [15].

Polypyrrole varies in colour from pale yellow for the fully reduced (de-doped) form to black for the fully oxidised (doped) form. The UV-vis spectrum of polypyrrole has been found to be highly dependent upon the doping level of the polymer[3]. Fully doped polypyrrole generally shows three absorption bands: a low wavelength (ca. 350 nm) $\pi - \pi^*$ transition and two bipolaron bands at ca. 475 nm and 1240 nm. However, the position and shape of these bands is highly dependent on the

environment the polymer is in. For example, polypyrrole films on a hydrophilic glass surface have been shown to have a bipolaron absorption band at 1180 nm, while similar films on hydrophobic silanised glass surfaces have an intense free carrier tail that extends well into the near infrared (2600 nm) [3]. This is thought to signify a shift in the conformation of the polymer chains from “compact coil” to “extended coil”.

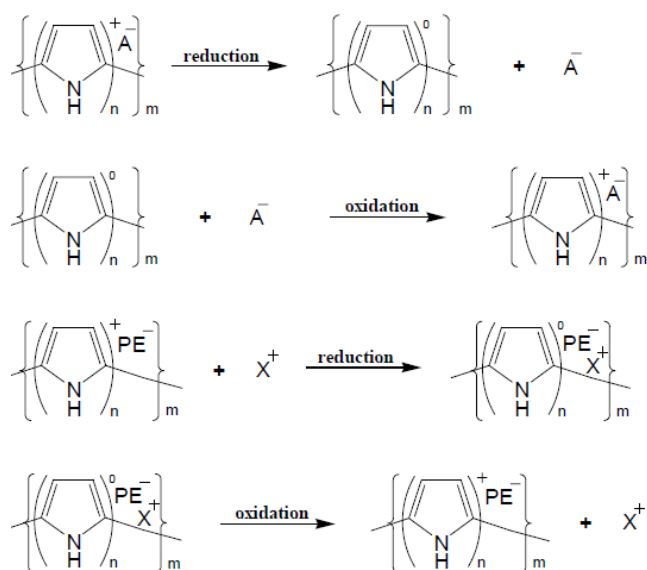
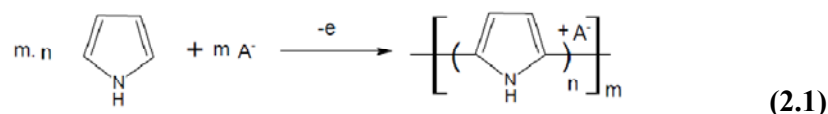


Figure 2.3 Redox cycling of polypyrrole with different ion exchange properties (where n is number of monomer units per positive charge, m determines molecular weight, A^- is a dopant anion, PE^- is a large dopant anion such as a polyelectrolyte, X^+ is a cation).

The rigidity of the polypyrrole backbone means that it is an intractable material in the conducting state [16]. Polypyrrole is generally insoluble in water and common organic solvents, and does not melt upon the application of heat, but instead decomposes. This is due to a high degree of both ionic and covalent cross-linking [3,17]. There are also usually strong inter-chain interactions within polypyrrole that tend to cause aggregation to form non-uniform particles [18]. In many cases this has meant that polypyrrole is yet to come close to realising its potential and therefore there is much interest in preparing more processable polypyrroles [17]. Some progress has been made in this area through counter-ion induced solubility as well as from functional pyrrole monomers [3,18]. The preparation of colloidal dispersions of polypyrrole has also been investigated.

2.4.2 Synthesis of Polypyrroles

Polypyrrole and its derivatives can be easily synthesised either chemically [19] or electrochemically [20]. Chemical polymerization is carried out by reacting pyrrole monomer with an oxidant in a suitable solvent whereas electrochemical polymerization is formed by the oxidation of pyrrole monomer at a suitable anode upon the application of a positive potential. The polymerization process in both cases involves the incorporation of certain charged anionic species into the polymer. A simplistic representation of the polymerization process can be expressed as:



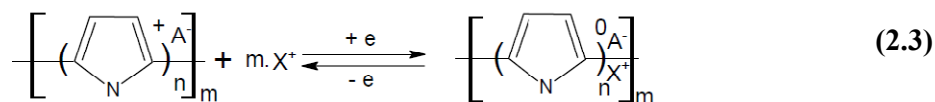
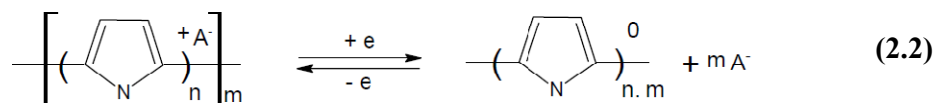
where A^- represents the counterion incorporated into the polymer to balance the charge, n is the number of pyrrole monomers per positive charge (usually 2~3), and m is the number of the counterion incorporated into the polymer.

The overall polymerization process involves several discrete steps as shown in (Equation 2-1) [21]. The first step is the oxidation of the monomer A to form a delocalized radical cation B. This radical cation can possibly exist in resonance forms C, D and E. The next step involves the dimerization of the radical cation, which occurs via radical-radical coupling at the π -position. The coupling is accompanied by the expulsion of two protons to form the neutral dimer F which can be further oxidised to form dimer radical. This can then combine with other monomeric, dimeric, or oligomeric radicals in a similar sequence of events to extend the polymer chains.

It is generally agreed that for preparation of free-standing conducting polymer actuators, electrochemical polymerization is an optimal technique compared to chemical polymerization. The electrochemical method allows the insertion of a wide range of anions into the polymer to form different anion doped polymer species. Also by controlling the electrochemical polymerization parameters, such as applied current, potential, time, electrolytes, temperature and substrates etc, polypyrrole can be varied with different morphology and hence mechanical and electrical properties.

2.4.2.1 Switching Properties of Polypyrrole

After polymerization, polypyrroles exist in their oxidised states. By applying electrochemical stimulation, polypyrroles are capable of switching between their oxidised and reduced states. The switching processes are often described as below:



where A^- represents the counterion incorporated into the polypyrrole, X^+ represents the cation from the electrolyte, n is the number of pyrrole monomers for each A^- incorporated, m is the number of polypyrrole repeat unit to determine molecular weight of polymer.

The changes in polypyrrole redox states are usually accompanied by ion exchange between the polymer and electrolyte. As the polymer is reduced, anions are detached and leave the polymer backbone to maintain the neutral state (Equation 2.2). However, in the case of bulky anions, such as dodecyl benzene sulfonate (DBS^-), which are immobile due to their large size, the charge compensation may be achieved by incorporation of cations from the electrolyte (Equation 2.3). When the polymer is oxidised again, it is possible for the charge to be balanced by either incorporating further anions or releasing newly incorporated cations. In some cases, there is mixture of both cation and anion movement during the redox process [22]. The dominating ion movements at oxidation and reduction are affected by a series of factors, such as counterion size, mobility, charge density, electrolyte and temperature.

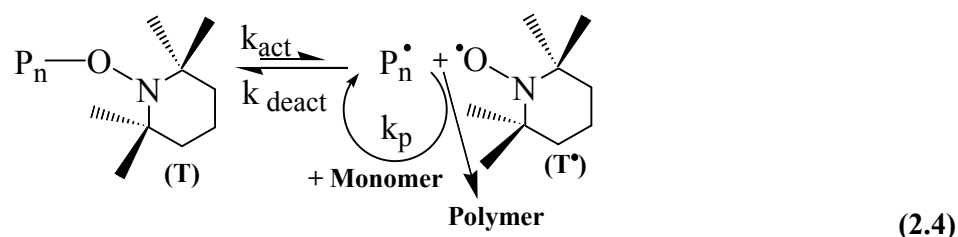
The ion exchange processes occurring during polymer oxidation/reduction causes significant mass and volume changes in the polymer. These polymer volume changes form the basis of conducting polymer electrochemical actuators.

2.5 Controlled Free Radical Polymerization

Many vinyl monomers can be polymerized by a conventional free radical polymerization. However, conventional free radical polymerization does not allow to prepare polymers with well-defined structures. Previously, only ionic methods were used to synthesize such controlled macromolecular structures. However, recent breakthrough in controlled free radical polymerization made it possible to obtain polymers with low-polydispersity and controlled structures. Today, there exist several controlled polymerization methods. In the present study we have utilized Nitroxide Mediated Radical Polymerization (NMP) as the controlled polymerization as it is particularly useful for styrene based monomers. The details of this polymerization will be given below.

2.5.1. Stable Free Radical Polymerization (SFRP)

The first such mechanism, SFRP (Equation 2.4), is a polymerization with reversible termination by coupling with a persistent radical (e.g. nitroxide).



The key reactions in this system have been shown to be the alternating activation–deactivation process, in which the polymer-nitroxide adduct $\text{P}_n\text{-T}$ (dormant species) is reversibly activated by thermal homolysis into the polymer radical ($\text{P}_n\cdot$) and the stable nitroxyl ($\text{T}\cdot$). This dramatically lowered the concentration of active chain species in the polymerization system and, coupled with the inability of the nitroxide radicals to initiate new chains lead to a controlled polymerization [23]. These activation–deactivation cycles allow all the chains to propagate at nearly equal rate, thus controlling the chain length and its distribution. The most commonly used stable radicals have been nitroxides, especially 2,2,6,6-tetramethylpiperidinoxy (TEMPO). TEMPO (2, 2, 6, and 6- tetramethylpiperidiny) is used for the reversible trapping of growing radicals. At a temperature below 100°C the resulting alkoxyamine is stable whereas at higher temperature the C-O bond undergoes homolytic cleavage thus

allowing again the propagation. These systems have been shown to be efficient for controlled polymerization of styrene and substituted styrene.

Although SFRP is one of the simplest methods of controlled free radical polymerization (CRP), it has many disadvantages. Many monomers will not polymerize because of the stability of the dormant alkoxyamine that forms. Also, since the reaction is kinetically slow, high temperatures and bulk solutions are often required. Also, the alkoxyamine end groups are difficult to transform and require radical chemistry.

Recent work in SFRP has revolved around the synthesis and evaluation of new nitroxide radicals, chain end fictionalization, and the exploration of the synthesis of block, random, star, and graft copolymers. A review has recently been published which covers these topics in detail [24].

2.6 Polystyrene

2.6.1 History of Polystyrene

It may well be argued that the history of polystyrene is more closely bound up with the history of the 20th century than is the case with any other plastics material.

In the US semi-plant-scale work at the Dow Chemical Company showed promise of commercial success in 1934. As a consequence there became available shortly before World War II a material of particular interest because of its good electrical insulation characteristics.

In 1942 the US Government initiated a crash programme for the installation of plants for the manufacture of a rubber from butadiene and styrene. This product, then known as GR-S (Government Rubber-Styrene), provided at that time an inferior substitute for natural rubber but, with a renewed availability of natural rubber at the end of the war, the demand for GR-S slumped considerably [25].

After the war, however, there was a large surplus capacity of plant for the manufacture of styrene and polystyrene together with a great deal of knowledge and experience that had been collected over the war years. It was therefore found possible to produce polystyrene, not as an expensive electrical insulator, but as a cheap general purpose thermoplastic.

In the late 1990s a crystalline form of polystyrene, *syndiotactic polystyrene* became commercially available but unless otherwise stated references to polystyrene in this chapter will refer to the traditional amorphous polymer. The rarely used systematic IUPAC name for polystyrene is poly-(1 -phenylethylene).

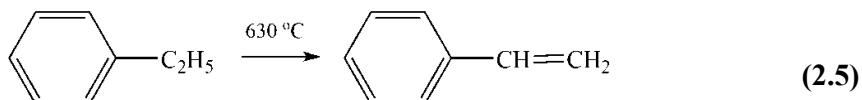
2.6.2 Preparation of Polystyrene

Production of PS is based on polymerization of styrene. This polymer has an enormous industrial importance.

In 1869 Berthflot reported the production of styrene by dehydrogenation of ethylbenzene. This method is the basis of present day commercial methods. Over the year many other methods were developed, such as the decarboxylation of acids, dehydration of alcohols, pyrolysis of acetylene, pyrolysis of hydrocarbons and the chlorination and dehydrogenation of ethylbenzene [25].

2.6.2.1 Dehydrogenation

Styrene is produced from the ethylbenzene by a process of dehydrogenation (Equation 2.5)

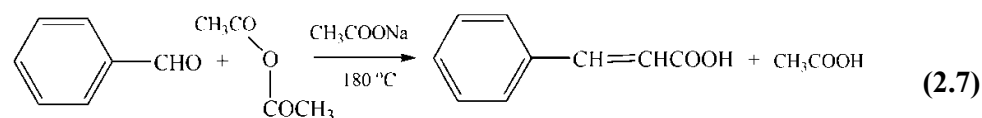
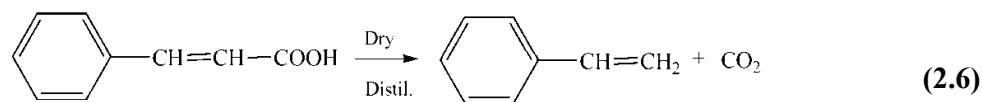


This is an endothermic reaction in which a volume increase accompanies dehydrogenation. The reaction is therefore favoured by operation at reduced pressure. In practice steam is passed through with the ethylbenzene in order to reduce the partial pressure of the latter rather than carrying out a hightemperature reaction under partial vacuum. By the use of selected catalysts such as magnesium oxide and iron oxide a conversion of 35-40% per pass with ultimate yields of 90-92% may be obtained [26].

There are today two methods of interest, (a) the laboratory preparation, and (b) commercial preparation.

Laboratory Preparation

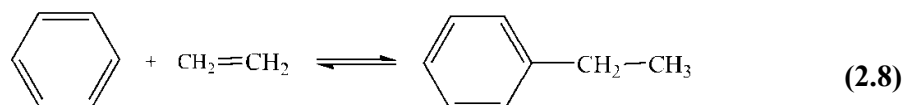
The principal constituent of storax is cinnamic acid and for laboratory purposes styrene is still most easily obtained in high purity but dry distillation of cinnamic acid and its salts under atmospheric pressure (Equation 2.6).



The cinnamic acid is readily prepared by heating benzaldehyde with acetic anhydride and sodium acetate (Equation 2.7).

Commercial Preparation

The bulk of commercial styrene is prepared by the Dow process or some similar system. The method involves the reaction of benzene and ethylene to ethylbenzene, its dehydrogenation to styrene and a final finishing stage. It is therefore useful to consider this process in each of the three stages. Ethylbenzene is prepared by reaction of ethylene and benzene in the presence of a Friedel-Crafts catalyst such as aluminium chloride at about 95°C (Equation 2.8).



To improve the catalyst efficiency some ethyl chloride is added which produces hydrochloric acid at the reaction temperatures.

2.6.3 Polymerization of Polystyrene

Polystyrene was first made by E. Simon in 1839 who at the time believed he had produced an oxidation product, which he called styrol oxide. Since that time the polymerization of styrene has been extensively studied. In fact a great deal of the work which now enables us to understand the fundamentals of polymerization was carried out on styrene.

Styrene can be polymerized by ionic, free-radical or coordination polymerization. Ionic polymerization is used mostly for manufacture-specialty polymers. In industrial manner, free-radical polymerization is preferred more than other types because the yield of the reaction is nearly the same with other methods' yields and during this

reaction, impurity affects the yield less. The rate of free-radical polymerization can be controlled by the choice of initiator and by changing the reaction conditions [25].

Polymerization methods of styrene are mainly; mass (bulk), solution, suspension and emulsion. An industrially important method of production is emulsion polymerization [26]. The key feature of polystyrene is its insolubility in its monomer. Instead of solution, it is negligently swollen by styrene. Also, this is another differing point of polystyrene, neither well swollen nor poorly swollen by its monomer, so its emulsion polymerization is not a regular heterogeneous process [26].

2.6.4 Properties and Structure of Polystyrene

Polystyrene has the simple repeating structure shown in (Figure 2.4) and as might be expected from such a substantially linear polymer it is thermoplastic. As with polypropylene, PVC and other vinyl compounds there is the possibility of various stereo-regular forms. Because of its amorphous nature the commercial polymer has for long been regarded as atactic. As with poly(methyl methacrylate) subsequent work has, however, indicated that the syndiotactic segments are more frequent than atactic segments and it appears that this may be a common feature of most free-radical initiated vinyl polymers. The specific position of the benzene ring is, however, sufficiently random to inhibit crystallization [25].

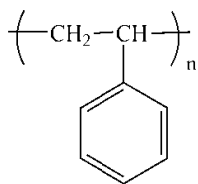


Figure 2.4 Polystyrene

Because of the chain-stiffening effect of the benzene ring the *T_g*s of commercial materials are in the range 90-100°C and isotactic polymers have similar values (approx. 100°C). A consequence of this *T_g* value plus the amorphous nature of the polymer is that we have a material that is hard and transparent at room temperature. Isotactic polystyrenes have been known since 1955 but have not been of commercial importance. Syndiotactic polystyrene using metallocene catalysis has recently become of commercial interest. Both stereoregular polymers are crystalline with *T_g* values of 230°C and 270°C for the isotactic and syndiotactic materials respectively.

The presence of a benzene ring results in polystyrene having greater reactivity than polyethylene. Characteristic reactions of a phenyl group such as chlorination, hydrogenation, nitration and sulphonation can all be performed with polystyrene. Chain rupture and discolouration are frequently additional effects of such reactions. The pure hydrocarbon nature of polystyrene gives it excellent electrical insulation characteristics, as a result of both the fundamentally good characteristics of the material and to the low water absorption of such a hydrocarbon polymer. The insulation characteristics are therefore well maintained in humid conditions [26].

Polystyrene is a hard, rigid transparent thermoplastic which emits a characteristic metallic ring when dropped. It is free from odour and taste, burns with a sooty flame and has a low specific gravity of 1.054. Because of its low cost, good mouldability, low moisture absorption, good dimensional stability, good electric insulation properties, colourability and reasonable chemical resistance it is widely used as an injection moulding and vacuum forming material. Additionally the low thermal conductivity has been made use of in polystyrene foam used for thermal insulation. The principal limitations of the polymer are its brittleness, inability to withstand the temperature of boiling water and its mediocre oil resistance [27].

2.7 Click Chemistry

The reaction that gives opportunity to attach ligands onto polymers for modification is called click reaction and it is also known as Sharpless 'click' reaction [28, 29]. This modification process provides; a) often quantitative yields, b) a high tolerance of functional groups c) an insensitivity of the reaction to solvents and d) reaction at various types of interfaces such as solid/liquid, liquid/liquid, or even solid/solid interfaces [29,30] . Click reactions are preferable reactions for modification because of moderate reaction conditions, high yields, short periods of reaction times and high selectivity [31, 32, 33]. There is a wide range of application field of this reaction, which varies with the sort of polymers [34]. Click reactions enabled the C-C bond formation in a quantitative yield without side reactions and requirement for additional purification steps. Click reactions are particularly important in preparative methods, in which high conversion of functional groups is desirable [35-36]. Numerous applications of click chemistry in polymer science as well as molecular biology and nanoelectronics have recently been reviewed [28, 29, 31].

Click reactions are derivatives of Huisgen 1, 3 dipolar cycloaddition reactions and occurs between terminal acetylenes and azides by metal catalyst at room temperature (Figure 2.5) [28, 37, 38]. Ru, Ni, Pt, Pd and especially Cu (I) species can be used as catalyst for click reactions [32-39]. As stated by several authors, these metals speeds up the reactions [33, 39].

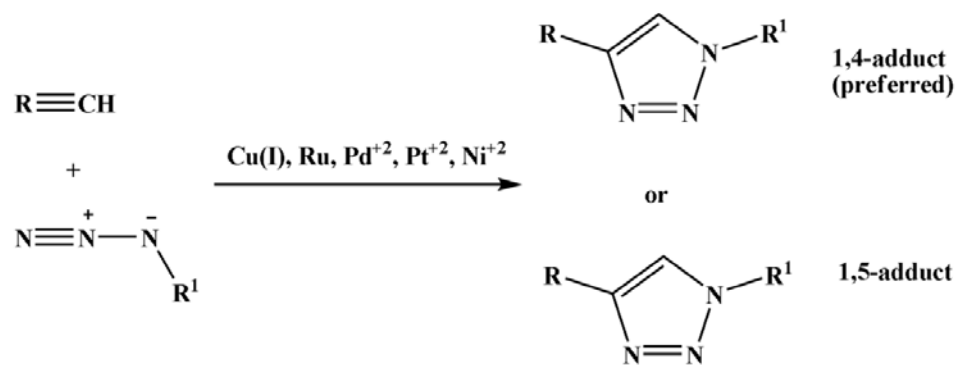


Figure 2. 5 : Azide/alkyne-type click reactions

2.7.1 Suitable Compounds for Click Reactions

Exceptions of self-reactive reagents and materials that can produce stable complexes with Cu (I), all functional groups are suitable for click reactions [40,41]. The figure 2.6 shows the compounds, which are not suitable for, azide/alkyne-type click reactions because of the Huisgen 1, 3 dipolar cycloaddition side reactions [42,43].

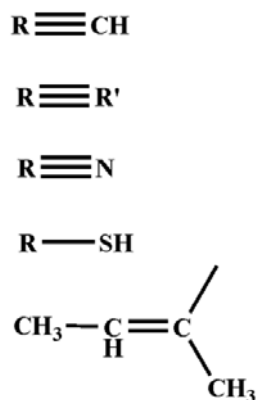


Figure 2. 6 : Suitable compounds for azide/alkyne type click reaction

2.7.2 Mechanism of Click Reactions

As it mentioned before click reactions occurs between terminal acetylenes and azide by metal catalyst. The mechanism of click reactions first explained by Meldal and co-workers and Sharpless and co-workers [40, 44, 45]. Multifarious catalytic systems are present to affect the 1, 3-dipolar cycloaddition process. Cu (I) salts can be directly used or Cu (I) species can be obtained from the reduction of Cu (II) by sodium ascorbate or metallic copper in catalytic systems [40, 45, 46]. The mechanism of click reactions, shown below, depends on the Cu-acetylide formation [40, 45].

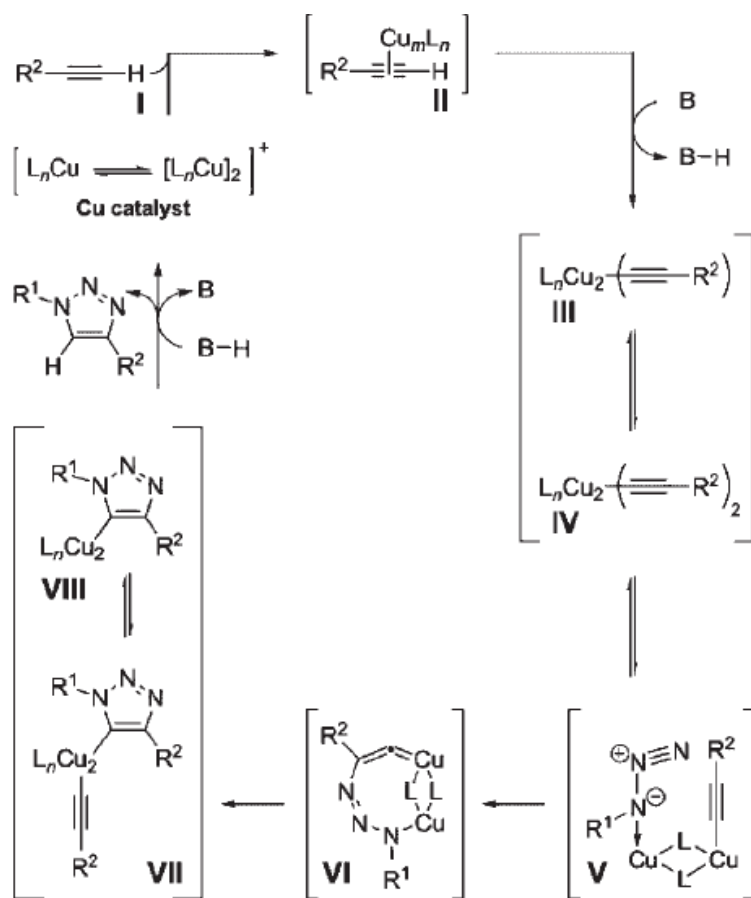


Figure 2.7 : Mechanism of click reaction

Terminal alkynes and Cu (I) particles produce a π -complex (Cu-acetylide) to lower pKa value of the terminal alkynes that allow attack onto C-H bond [32,45]. In addition, 1-5 equivalents of base have positive influences on the formation of the

copper (I)-acetylide. THF, diethyl ether, DMF, DMSO or halogenated solvents are applicable for click reactions. And also, water/alcohol or water/toluene systems can give excellent results [47-48].

3. EXPERIMENTAL

3.1 Materials

Chloroform (99%, Sigma), dimethylformamide (DMF, 99%, Aldrich), ethanol (99.5%, Aldrich), tetrahydrofuran (THF, 99.8%, J.T. Baker), diethylether (98%, Sigma-Aldrich), methanol (99%, Acros Organics), dimethyl sulfoxide (DMSO, 99%, J.T. Baker), anhydrous pyridine (99.5%, Lab-Scan), sodium azide (98.5%, Carlo-Erba Reagent), copper(II) sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) (98%, Fluka), L-ascorbic acid sodium salt (99%, Acros), toluene-4-sulfonic acid monohydrate (PTSA, 99%, Fluka), sodium hydride (98%, Fluka), propargyl bromide (80 vol % in toluene, Fluka), and 1-pyrene methanol (98%, Sigma-Aldrich), dNbipy (Acros Organics %99), were used as received.

3.2 Synthesis of 4-(1*H*-pyrrol-1-yl)phenol

A cooled solution of (6.45 g, 60 mmol) of p-aminophenol in 50 ml glacial acetic acid is placed in a round-bottomed flask equipped with a reflux condenser and a magnetic stirrer. 2,5-dimethoxytetrahydrofuran (7.5 ml, 58 mmol) is added to the cooled solution during 10-15 minutes. The solution refluxed for 1.5 hour, during which time the solution turns deep red to black in color. The heating discontinued and the acetic acid is removed by distillation. The dark residue was dissolved in 20 ml methanol and subsequently poured into water. The precipitate was filtered and washed with water, then dissolved in chloroform and filtered again to remove insoluble products. Chloroform was boiled off, and the remaining residue dissolved in 20 ml methanol to precipitate in water. Precipitates were filtered and washed with water then dried. Beige coloured solid was obtained.

3.3 Synthesis of 1-(4-(prop-2-ynoxy)phenyl)-1*H*-pyrrol

In a flask, (1) (5.5 g, 35 mmol) was dissolved in 100 ml NaOH (0.8 N) solution. The mixture was heated at 60 °C until a clear solution was formed.

Tetrabutylammoniumbromide (1.12 g, 35 mmol) of was added to this solution as a phase transfer catalyst. A solution of propargyl bromide (4.28 g, 35 mmol.) in 50 ml toluene was added portionwise to the solution. The mixture was kept stirring at 60 °C for 24 h. The precipitates were filtered and washed with copious amount of water. Then, the solid was recrystallized from 1:1 MeOH/water.

3.4 General Procedure For Synthesis Of Polystyrene-co-chloromethyl styrene PS-co-PCMS copolymers

PS-co-PCMS copolymers containing various amount of CMS moieties (% 20, 30 and 40) were prepared via nitroxide-mediated radical polymerization (NMP) of st and CMS of 125 °C .

3.5 Synthesis Of (PS-co-PMS-N₃) copolymer

PS-co-PCMS copolymers dissolved in N,N-dimethylformamid (DMF), NaN₃ (2 times excess to the mole of chloro group of each copolymers) was added. The resulting solution was allowed to stir at 25 °C overnight and precipitated into methanol/ water mixture (1/1 by volume).

3.6 Procedure For The “Click “ Coupling Of Azide

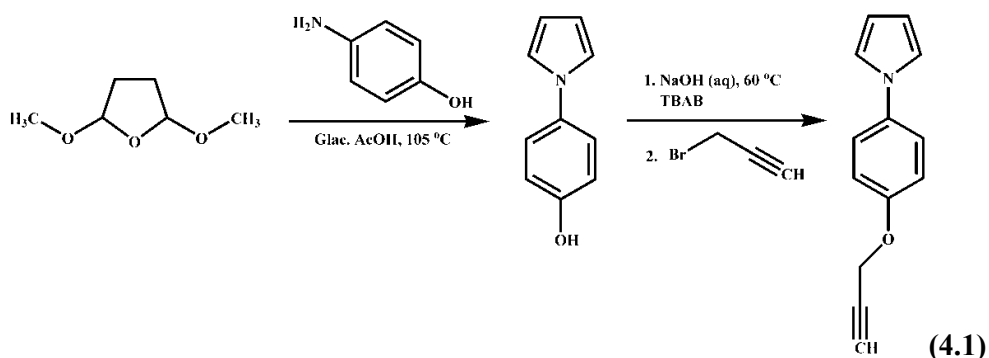
In a flask, PVA-N₃ (0.1 g), propargyl pyrrole (0.04489 g, 0.45 mmol) dissolved in 5 mL of DMF. Freshly prepared aqueous solution of sodium ascorbate (0.06451 g, 0.34 mmol) was added followed by aqueous solution of copper(II) sulfate pentahydrate (0.012186 g, 0.068 mmol), so that the final concentrations of sodium ascorbate and copper(II) sulfate pentahydrate in the mixture 30 and 6 mM, respectively. The ratio of azide and alkyne groups was 1. The mixture stirred for 2 days of ambient temperature. Functionalized polymer precipitated in diethyl ether (10 times excess), filtered and dried under vacuum.

4. CONCLUSION AND RECOMMENDATIONS

Pyrrole side-chain polystyrene was synthesized by using “Click Reaction” concept. This procedure involves the preparation of polymer and pyrrole possessed with the appropriate click components. First, pyrrole monomer with acetylene terminal groups was synthesized. The other component, namely azide group functional polystyrene was synthesized independently. The click reactive molecules were then combined to yield the desired polymers. The details of the procedure will be given below.

4.1 Synthesis and Characterization of 1-(4-(prop-2-ynoxy)phenyl)-1H-pyrrol

In this study, 1-(4-(prop-2-ynoxy)phenyl)-1H-pyrrol (*propargylpyrrole*) was synthesized as electroactive click component. A new procedure for the Clauson-Kaas pyrrole synthesis was used to synthesize *propargylpyrrole* (Equation 4.1). This method was reported by Smith *et al.* [49] and led to the formulation of a new procedure that avoids the contact of pyrroles to heat or strongly acidic conditions that cause decomposition of the desired products. The procedure involves mild hydrolysis of 2,5-dimethoxytetrahydrofuran in water to the activated species 2,5-dihydroxytetrahydrofuran that reacts with primary amines in an acetate buffer at room temperature to give *N*-substituted pyrroles in high yield. In our case, *propargylpyrrole* was obtained in high yield and purity after two stages, and used to synthesize propargyl pyrrole as a readily available monomer for click type reactions.



The chemical structure of synthesis of *propargylpyrrole* was confirmed by both FT-IR and $^1\text{H-NMR}$. The characteristic absorptions of pyrrole structure appeared at 1455 cm^{-1} due to the C=C ring stretching and at 1244 cm^{-1} stretching of C-N proved the presence of pyrrole (Figure 4.1).

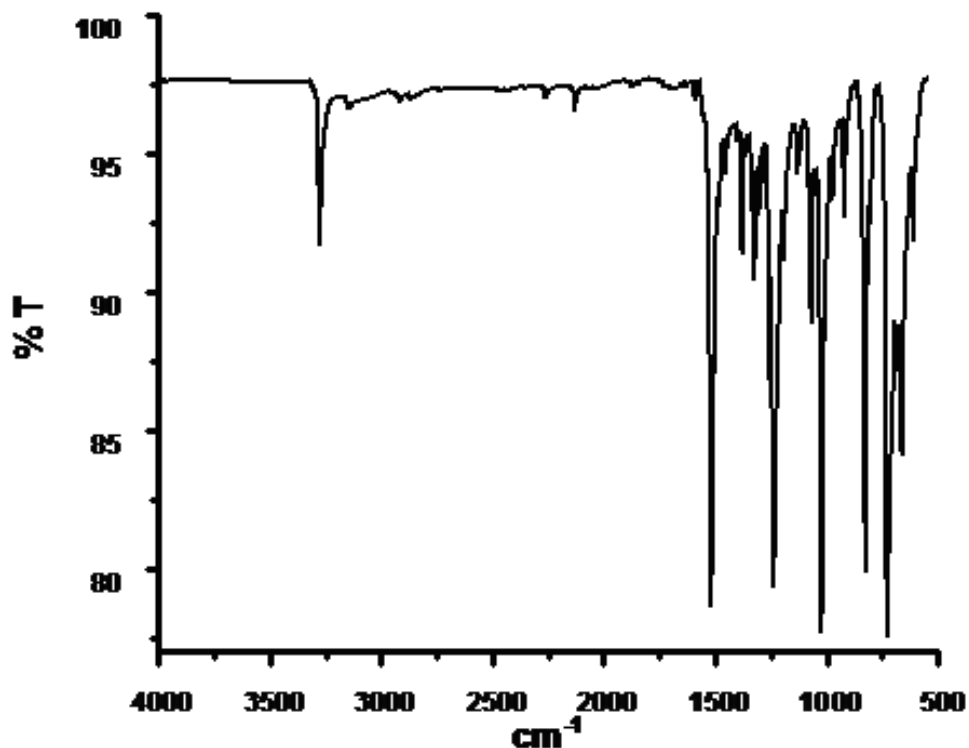


Figure 4. 1 FT-IR spectrum of 1-(4-(prop-2-ynoxy)phenyl)-1H-pyrrol.

The $^1\text{H-NMR}$ spectrum of *propargylpyrrole* gave further support to its chemical structure (Figure 4.2.). The *propargylpyrrole* was characterized with the absorption peaks at 6.25 (-C=CH-C-) and 7.03 ppm (-N-CH=C-). The characteristic absorption peaks belong to phenol was observed at 4.95 ppm (-Ar-OH-). Also, $\text{H-C}\equiv$ and CH_2 (propargyl) protons are detectable at 2.5 ppm and at 4.75 ppm.

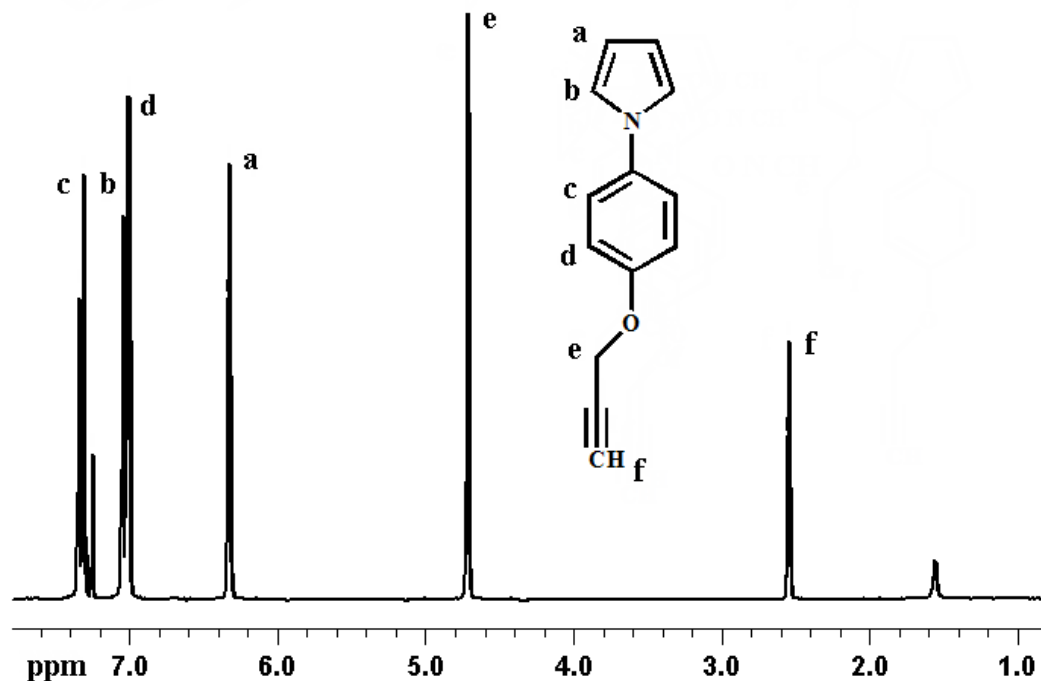


Figure 4. 2 ^1H -NMR spectrum of 1-(4-(prop-2-ynoxy)phenyl)-1H-pyrrol.

4.2 Synthesis and Characterization of Azide Functional PS

For the synthesis of parent azide functionalized polymer, we first prepared poly(styrene-co-chloromethylstyrene), P(S-co- CMS), via nitroxide-mediated radical polymerization (NMP) of styrene (S) and chloromethylstyrene (CMS) at 125 °C. The composition of copolymer was determined using ^1H NMR spectroscopy. The mole fractions of CMS and S were calculated from the ratio of the peak areas around 4.5 ppm, corresponding to two methylene protons of in the side chain of CMS to the total area between 6.3 and 7.4 ppm, which was attributed to the total aromatic protons. (PS-co-CMS) with $M_{n(\text{GPC})} = 6.197$ and 54.10 mol % chloromethyl groups was then quantitatively converted into polystyrene-azide (PS- N_3) in the presence of NaN_3/DMF at room temperature.

From the ^1H NMR spectrum of PS- N_3 shown in Figure 4.3, it was observed that while the signal at 4.5 ppm corresponding to $\text{CH}_2\text{-Cl}$ protons of the precursor (PS-co-CMS) completely disappeared, and a new signal appeared at 4.25 ppm due to CH_2 linked to azide groups.

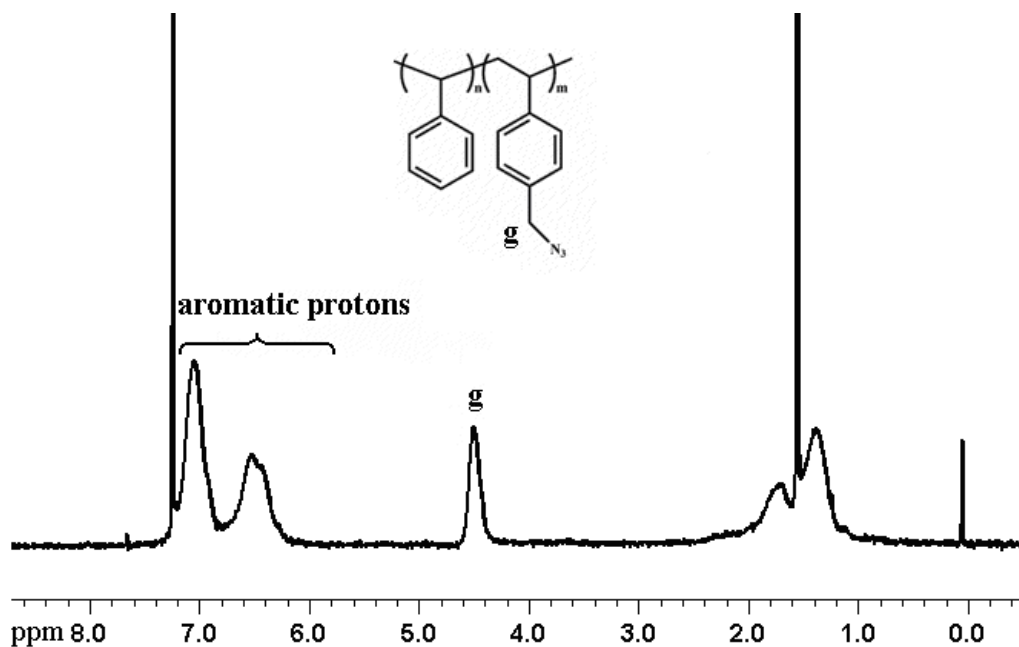
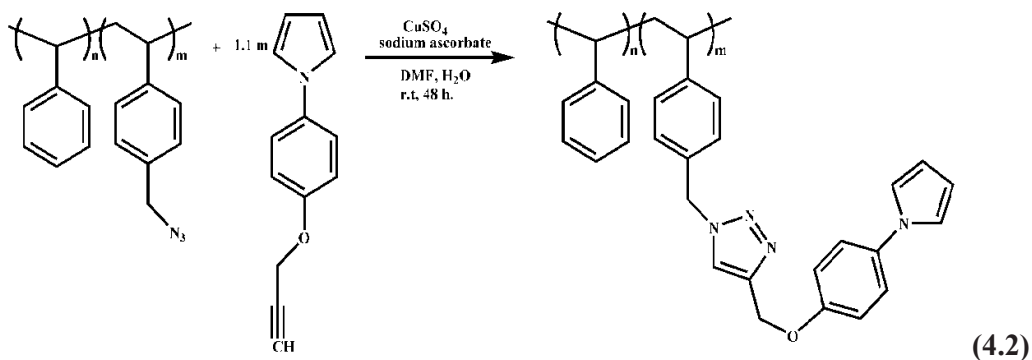


Figure 4.3 $^1\text{H-NMR}$ spectrum of PS-N_3 .

4.3 Synthesis and Characterization of Pyrrole Functional PS

Pyrrole functional polystyrene was synthesized with click chemistry which is modular, wide in scope and also it gives very high yields. For the click reaction, the PS-N_3 was dissolved in dimethyl sulfoxide (DMF) and reacted with *propargyl*pyrrole in the presence of aqueous solution of sodium ascorbate and copper(II) sulfate pentahydrate at room temperature (Equation 4.2). The substituted polymer was precipitated and dried under vacuum.



Evidence for the occurrence of the “click reaction” obtained from ^1H NMR and IR spectroscopy. The extent of conversion of the side azido moieties to triazoles was monitored by spectroscopy by observing the appearance of the new methylene protons adjacent to the triazole and pyrrole ring at 5.10 and 5.31 ppm (triazole- CH_2 -O- CH_2 -Py) and the triazole proton (N-CH=C-) at 7.60 ppm (Figure 4.4). The peaks between 5.10 and 5.20 ppm, characteristic for $-\text{CH}-$ protons of pyrrole ring were also observed.

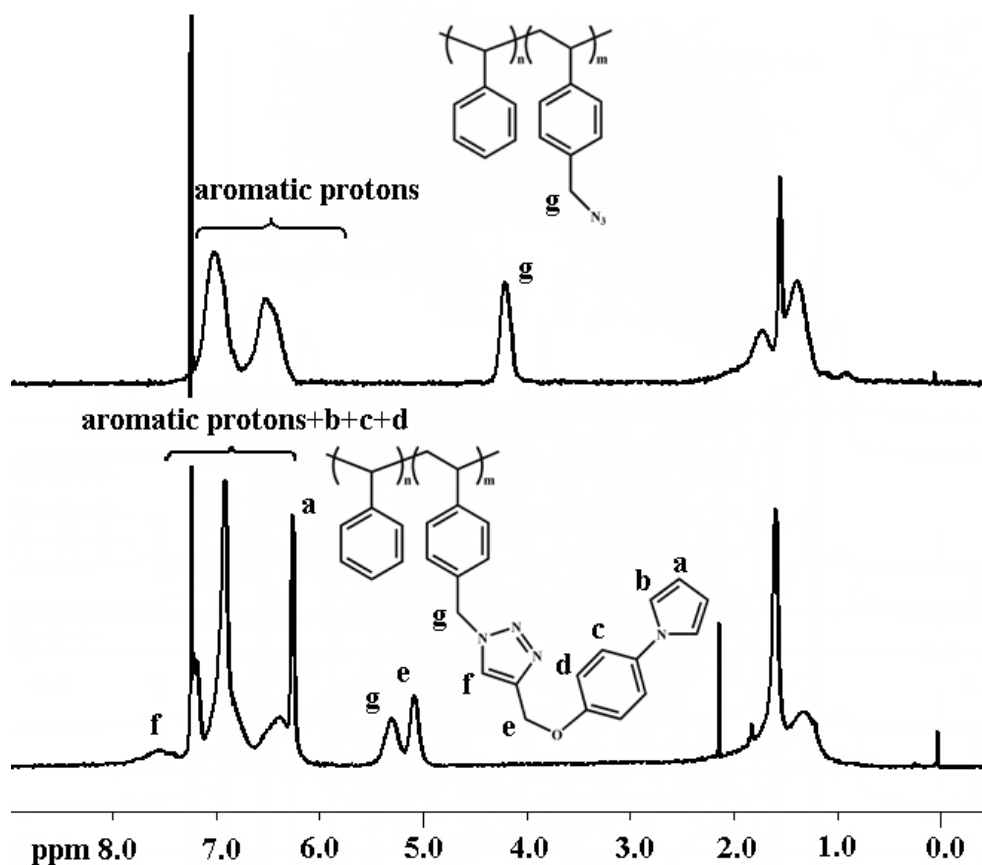


Figure 4.4. ^1H -NMR spectrum of PS- N_3 and PS-pyrrole.

Moreover, the band corresponding to $-\text{N}_3$ group at 2105 cm^{-1} completely disappeared (Figure 4.5). Moreover, C=C ring stretching at 1455 cm^{-1} and C-N stretching at 1244 cm^{-1} proved the presence of pyrrole moieties in the substituted polymer. Thus, the side group click reaction was efficient, as evidenced by near-quantitative functionalization.

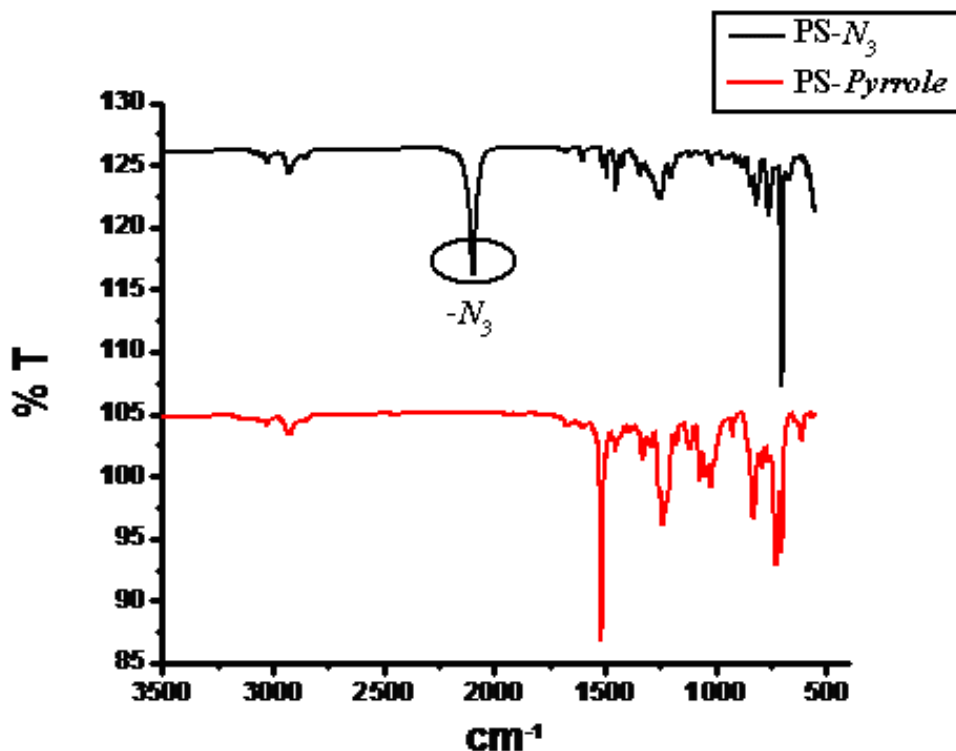


Figure 4.5. FT-IR spectrums of PS- N_3 and PS-pyrrole.

4.4. Conclusion

In summary, we have demonstrated a novel route, for the introduction of pyrrole functional groups to polystyrene via click [3+2] chemistry. The process involves the synthesis of azide functionalized PS and reaction of these functional groups with pyrrole as electroactive molecules also possessing propargyl groups as the components of the click reaction. The spectral analysis confirmed the presence of pyrrole functionality in the resulting polymer. The strategy adopted in this study appears to be entirely satisfactory in terms of efficiency and simplicity. Further work is in progress to expand this approach to other functionalities.

The new polymer is expected to undergo electropolymerization leading to crosslinked polymers having conjugated segments side-chain, so electrochemical properties will be characterized.

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