SYNTHESIS AND APPLICATION OF POLYANILINE SUBSTITUTED AZO-DYES AND THE STUDY OF THEIR ANTIMICROBIAL ACTIVITY AND ELECTRICAL CONDUCTIVITY ON POLYESTER AND NYLON 6, 6 FABRIC

BY

OBADAHUN JOSHUA
P14SCTX8020

SUPERVISORS: PROF K.A. BELLO

Dr.A.A. KOGO, Dr.A.A. ABDELMALIK.

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AHMADU BELLO UNIVERSITY,
ZARIA, NIGERIA
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DECLARATION

I, **OBADAHUN JOSHUA (P14SCTX8020)** hereby declare that this research dissertation titled "**Synthesis and Application of Polyaniline Substituted Azo-Dyes and the Study of their Antimicrobial Activity and Electrical Conductivity on Polyester and Nylon 6,6 Fabric**" was conducted by me and to the best of my knowledge has not been presented anywhere for the award of Bachelor Degree or Master Degree in any institution of learning. All sources of information, materials and quotations used for this study have been duly acknowledged in the bibliography.

_____ _____

OBADAHUN JOSHUA **Date**
(P14SCTX8020)

CERTIFICATION

This is to certify that this research dissertation "**Synthesis and Application of Polyaniline Substituted Azo-Dyes and the Study of their Antimicrobial Activity and Electrical Conductivity on Polyester and Nylon 6,6 Fabric**" conducted by Obadahun Joshua meets the requirements for the award of a Master Degree in Colour Chemistry and Technology by the School of Postgraduate Studies, Ahmadu Bello University, Zaria. The dissertation work is this day approved for its contribution to knowledge and literally presentation.

_____ _____

Prof K.A Bello **Date**
Chairman, Supervisory Committee

_____ _____

Dr. A.A Kogo **Date**
Member, Supervisory Committee

_____ _____

Dr. A.A Abdelmalik **Date**
Member, Supervisory Committee

_____ _____

Professor Abu Lawal **Date**
Head of Department

_____ _____

Professor Kabiru Bala **Date**
Dean, School of Postgraduate Studies

DEDICATION

This dissertation is dedicated to the Almighty God, ever merciful and convenant keeping God and to my parent Mr. and Mrs. Obadahun

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ABSTRACT

Polyaniline substituted azo dyes were synthesized from polyaniline obtained by oxidative polymerization of aniline and different azo dyes obtained from 2-aminothiophene intermediates. Four different polyaniline substituted dyes were synthesized and there melting points were found to be from 286°C- 319°C and spectroscopic assessment such as Visible spectroscopy, Fourier Transform-Infra Red (FT-IR) spectroscopy and Gas chromatography-mass spectroscopy (GC-MS) were carried out to elucidate the structures of the synthesized polyaniline substituted azo dyes. The maximum absorption wavelenght (λmax) of the polyaniline substituted azo dyes ranges from 518-587nm in DMSO and 511-553nm in acetone. The FT-IR spectra of the polyaniline substituted azo dyes showed absorption peaks in the range 3213.0- 3242.8cm^{-1} due to the presence of an amino group. The benzenoid and quinoid rings for all the polyaniline substituted azo dyes appeared in the range 1461-1487cm^{-1} and 1543-1595cm^{-1} respectively while the carbon nitrogen single bond (C-N) absorption were found in the range 1263.6-1285cm^{-1}. For the assessment of the antimicrobial properties of the synthesized dyes, different microorganisms such as Staphylococcus aureus, Salmonella typhi, Bacillus subtilis, Escherichia coli, Candida albican, Aspergillus niger were selected based on their pharmacological incidence and Agar well diffusion method was used. The result of the antimicrobial studies showed zones of inhibition ranging from 14-34mm. The strong activity of the synthesized polyaniline substituted azo dyes against Staphylococcus aureus, Salmonella typhi, Escherichia coli and Candida albican showed that it may be effective against infectious diseases which these microorganisms causes. The MIC and MBC/MBF value of 12.5mg/ml of the synthesized polyaniline substituted Dye A had activities against Staphylococcus aureus and Escherichia coli. The electrical conductivity measurement were obtained by employing a standard process of using a programmable inductance capacitor resistance (LCR) meter. The electrical conductivity value of polyaniline substituted azo dyes was found to be in the range of $10^{-2} – 10^{-4}$ S .m^{-1} and moreso, the dyes synthesized from the 2-aminothiophene and sulphanilic acid were successfully applied to polyester and nylon 6,6 fabric and the light and washing fastness properties were evaluated. The dyes gave mostly purple, deep pink, deep purple and yellow shades on the fabric and exhibited good to excellent wash fastness and moderate to very good light fastness properties on the substrates.

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CHAPTER ONE

1.0 Introduction

Synthetic dyes and especially polymer linked dyes are of growing interest for technical and medical application due to their versatile properties and increasing environmental consciousness (Carolin *et al*., 2015). The advantages over low molecular compounds seem to be not only the reduced toxicity or the possibility of better recovery and reusability but also improved quality characteristics such as high colour fastness in textile dyeing (Warner *et al*., 2004). The applications of dye-containing polymers are not limited to colour impression in paintings or textile dyeing. Conducting polymers (CPs) such as polyanilines, polyacetylenes, polythiophenes, and polypyrroles, are promising materials for potential industrial applications such as electrorheology (ER), electronics, and optics due to their high electrical conductivity and good environmental stability (Yılmaz *et al*., 2011). The conductivities of these conjugated polymers are achieved through chemical oxidation or reduction reactions using a series of simple anionic or cationic species called dopants (Chandrasekhar, 1999). The earliest reported application of conducting polymers (CPs) has been used in the free-standing polymers as sensor devices. Chemical sensors are analytical devices that convert the chemical potential energy of a targeted analyte into a proportionate measurable signal, usually electrical or optical. In this conducting polymers, polyaniline is a typical phenylene-based polymer having a chemically flexible –NH– group in the polymer chain flanked on either side by a phenylene ring. The protonation, deprotonation, and various other physicochemical properties of polyaniline are due to the presence of the –NH– group.

There have been a number of reviews on conducting polymers with regard to biomedical applications. The commercially available soluble Conducting polymers e.g polyaniline (PANI) grafted to lignin, poly (aniline sulfonic acid), and polypyrrole (PPy) are effective scavengers of

the stable 1, 1-diphenyl-2-picrylhydrazyl (DPPH) free radical. This property may be particularly beneficial in tissues suffering from oxidative stress, where the ability to lower the excessive levels of reactive radical species is desirable. This free radical reducing ability of conducting polymers is revealed by efficient scavenging of DPPH radicals, with two and four radicals scavenged per aniline or pyrrole monomer unit during the 30-min test period of the DPPH assay, indicating the potential for CPs to be effective antioxidants when present in biological medium. The various vitamins and polyphenol free radical scavenging antioxidants present in beverages, fruits, and vegetables are currently of great interest, as these antioxidants may offer protection against various diseases, such as cardiovascular diseases and cancer (Gizdavio-Nikolaidis *et al*., 2004).

It appears that the presence of an acidic functional group (–COOH) in the polymer chain improves the antibacterial efficacy of the copolymer. Without being bound by theory, the acidic dopants on the molecular chains of copolymers may react with the bacteria (or other relevant microbial organism) which result in their death. Alternatively, due to electrostatic adherence between copolymer molecules and the bacteria, which carry charges of different polarity, the walls of the bacteria may break and the contents of the bacteria become exposed or leak out, which cause the bacteria to die (Allan *et al*., 2009).

Marija *et al*., (2011) has investigated the antimicrobial properties of conductive functionalized polyanilines by exploring their interaction with bacterial cells. It has been observed that lower concentrations of PANI strongly inhibited the growth of wild-type *Escherichia coli*, *Pseudomonas aeruginosa*, and *Staphylococcus aureus* as well as several other antibiotic resistant clinical pathogens. Nanofibre of polyaniline combined with fluconazole have been prepared by simple and cost-effective sol–gel method using d-10-camphorsulfonic acid (d-

CSA) as a dopant and as a surfactant, and ammonium persulfate as the oxidant. The synthesized nano-structured material was dissolved in dimethylsulfoxide at different concentrations and tested for its antifungal properties against *Candida albicans* , *Candida tropicalis* , and *Candida krusei*. The results showed that, compared to nanofiber-structured conducting PANI, polyaniline doped with fluconazole showed higher antifungal activity on all the species tested. It is very much evident that PANI-doped fluconazole has a considerably enhanced antifungal activity. *Candida tropicalis* is more susceptible than *Candida albicans* and *Candida krusei* (Yehgambaram *et al*., 2013).

Azo dyes are known for their medicinal importance and are well recognized for their use as antineoplastics, antidiabetics , antiseptics antibacterial, and antitumor agents. They are known to be involved in a number of biological reactions such as inhibition of DNA, RNA, and protein synthesis, carcinogenesis, and nitrogen fixation. Azo dyes are important structures in the medicinal and pharmaceutical fields (Chandravadivelu and Senniappan, 2011) and it has been suggested that the azoimine linkage might be responsible for the biological activities displayed by some Schiff bases. In addition, Evans Blue and Congo Red azo dyes have been studied as HIV inhibitors of viral replications. This effect is believed to be caused by the binding of azo dyes to both protease and reverse transcriptase of this virus (Swati, 2011). The existence of an azo moiety in different types of compounds has caused them to show antibacterial and antifungal activities (Adegoke *et al.*, 2008). In recent times, exploration of azo dyes as antimicrobial agents has received considerable attention. In the present study, polyanilines substituted azo dyes were synthesized by oxidative polymerization of aniline which was characterized by FT-IR and GC-MS spectrum. This was then followed by the subsequent antimicrobial and electrical conductivity assessment of the respective dyes.

1.1 Statement of the Problem

The growth of micro-organism on fibre materials inflicts a range of negative effects not only on the textile itself but also on the wearer. These include the generation of unpleasant smell, stains, discoloration in the fabric, a reduction in fabric strength and an increased likelihood of contamination (Ramachandran *et al*., 2004). Micro-organisms are found almost everywhere in the environment and can multiply quickly when basic requirements such as moisture, nutrients and temperature are met (Gupta *et al*., 2005). Recent research groups have explored the integration of flexible device such as solar cell, field effect transistor (FETs), light emitting diodes (OLEDs) and photovoltaic devices into textiles, however these component cannot operate without sufficient electrical energy, making the development of energy harvesting and storage harvesting essential (Shridhar *et al*., 2012). To survive bacterial developed antibiotics mechanism and to have a textile material with high efficiency, large capacity, easy fabrication and flexibility there is a great demand for a new polyaniline substituted dyes with improved antimicrobial property and enhanced electrical conductivity.

1.2 Justification

The traditional applications of dyes are well known since they represent high volume uses (Klause, 2009). However, the last 20years and particularly the last decade, has witnessed a phenomenal rise in the growth of dyes for high technology (hi-tech) applications (Christie, 2000). The advent of new imaging technologies, such as electrophotography, optical data storage, and displays such as liquid crystal displays and the newer emissive display such as organic light emitting devices; electronic materials such as organic semiconductors and biomedical applications such as fluorescent sensors and anti-cancer treatment such as photodynamic therapy, created the need for novel dyes to meet these new and demanding criteria

(Klause, 2009). Azo dyes are known for their medicinal importance and are well recognized for their use as antineoplastics, antidiabetics , antiseptics antibacterial, and antitumor agents. They are known to be involved in a number of biological reactions such as inhibition of DNA, RNA, and protein synthesis, carcinogenesis, and nitrogen fixation. Azo dyes are important structures in the medicinal and pharmaceutical fields (Chandravadivelu and Senniappan, 2011) and it has been suggested that the azoimine linkage might be responsible for the biological activities displayed by some Schiff bases. A promising approach to fulfilling these requirements is the combination of dyes and polymeric materials (Carolin *et al.*, 2015).

1.3 Aim and Objectives

1.3.1 Aim

The aim of this research work is synthesis and application of polyaniline substituted azo-dyes and the study of their antimicrobial activities and electrical conductivity on polyester and nylon 6, 6 fabric

1.3.2 Objectives

i. To synthesize different polyaniline substituted azo dyes

ii. To elucidate the structure of the polyaniline substituted azo dyes using Uv-visible Spectroscopy, Fourier Transform-Infra Red spectroscopy (FT-IR), and Gas chromatography-mass spectroscopy (GC-MS).

iii. To evaluate the antimicrobial activities of the synthesized polyaniline substituted azo dyes.

iv. To assess the electrical conductivity of the synthesized polyaniline substituted azo dyes.

v. To apply the dyes on textile fabric (Nylon 6,6 and polyester) and assess their fastness properties (light and washing fastness).

1.4 Scope of the Study

These include synthesis of polyaniline via oxidative polymerization and 2-aminothiophene intermediate derived from o-acetoacetanilide and N-(2,4-dimethylphenyl)-3-oxobutyramide which serves as diazo components with N,N-dimethylaniline, p-N,N-dimethylaminobenzaldehyde serving as the coupling components. The synthesized dyes, and intermediates were purified and characterized using visible spectroscopy, FT-IR spectroscopy, and GC-MS. The antimicrobial and electrical conductivity of the polyaniline, dyes and polyaniline substituted azo dyes were assessed.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Dyes and their Required Properties

Dyes are water soluble organic coloured substance, that have affinity to the substrate to which it is applied and anchored on the substrate by adsorption. Some are only useful as indicators in chemical titration (e.g.methyl orange), while some are used as stains or solvent dyes for colouring solvent such as petrol, etc. (Nkeonye, 1993). For a dye to be useful as a textile dye, it must have the following properties:

(a) Intense colour-arising mainly from charge transfer.

(b) Attraction or affinity for the fibre.

(c) Substantivity; capable of being absorbed and retained by the fibre after application and/or fixation, and reactivity, -ability to be chemically combined with the fibre.

(d) Sufficient degree of resistance (fastness) to common agencies encountered during use of the coloured materials e.g. light, water, rubbing, etc.

(e) Solubility in aqueous solution either permanently or during the dyeing operation. This is because the dyes are usually in form of salts. In addition to colouring textiles, some textile dyes can be used to colour substances such as paper, leather, fur, etc.

2.2 Azo Dyes

Nitrous acid (HONO) was one of the reagents tried in the early experiments with aniline, and in 1858 the German chemist Johann Peter Griess obtained a yellow compound with dye properties. Although used only briefly commercially, this dye sparked interest in the reaction that became the most important process in the synthetic dye industry. The reaction between nitrous acid and an arylamine yields a highly reactive intermediate; the reaction of this intermediate with phenols and aryl amines is the key step in the synthesis of more than 50 percent of the commercial dyes produced today (Stothers, 2016). The chemistry involved in these reactions was

unclear until 1866, when Kekulé proposed correctly that the products have aryl rings linked through a −N=N− unit, called an azo group; hence, the dyes containing this functional group are termed the azo dyes. The reaction of nitrous acid with $Ar-NH_2$ (where Ar represents an aryl group) gives an aryl diazonium ion, which readily couples with anilines or phenols to furnish azo compounds. An early commercial success was chrysoidine, which had been synthesized by coupling aniline to *m*-phenylenediamine; it was the first azo dye for wool and has been in use since 1875. (Booth, 2000).

Diazotization of both amino groups of *m*-phenylenediamine followed by coupling with more of the di -amine gives Bismark brown, a major component in the first successful disazo dye i.e., a dye with two azo groups. In 1884 a conjugated disazo dye, Congo red, made by coupling 4-sulfo-1-naphthylamine with bisdiazotized benzidine, was found to dye cotton by simple immersion of the fabric in a hot aqueous bath of the dye. Congo red was the first dye to be known as a direct dye; today it is used as a pH indicator. Until the 1970s derivatives from methyl- or methoxyl-substituted benzidines constituted the major group of disazo dyes, but they are no longer produced in many countries because they are carcinogens.



fig. 2.1

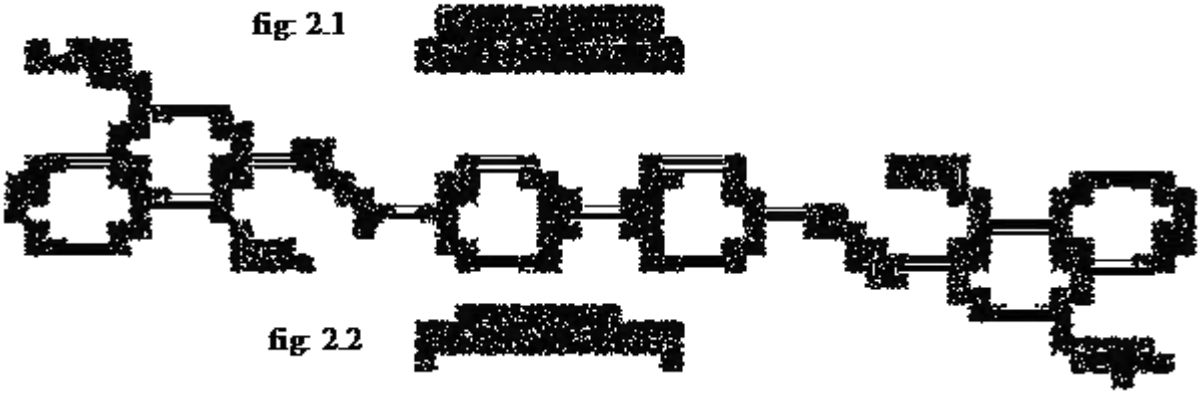


fig. 2.2

The discovery of the azo dyes led to the development of ingrain dyeing, whereby the dye is synthesized within the fabric. Since the process was done at ice temperature, some dyes were called ice colours. In 1912 it was found that 2-hydroxy-3-naphthanilide (Naphtol AS, from the German *Naphtol Anilid Säure*) forms a water-soluble anion with affinity for cotton, a major step in the development of the ingrain dyes. Its reaction with unsulfonated azoic diazo components on the fabric gives insoluble dyes with good wetfastness with Diazo Component and Fast Scarlet R is formed with member of the Naphtol AS series.

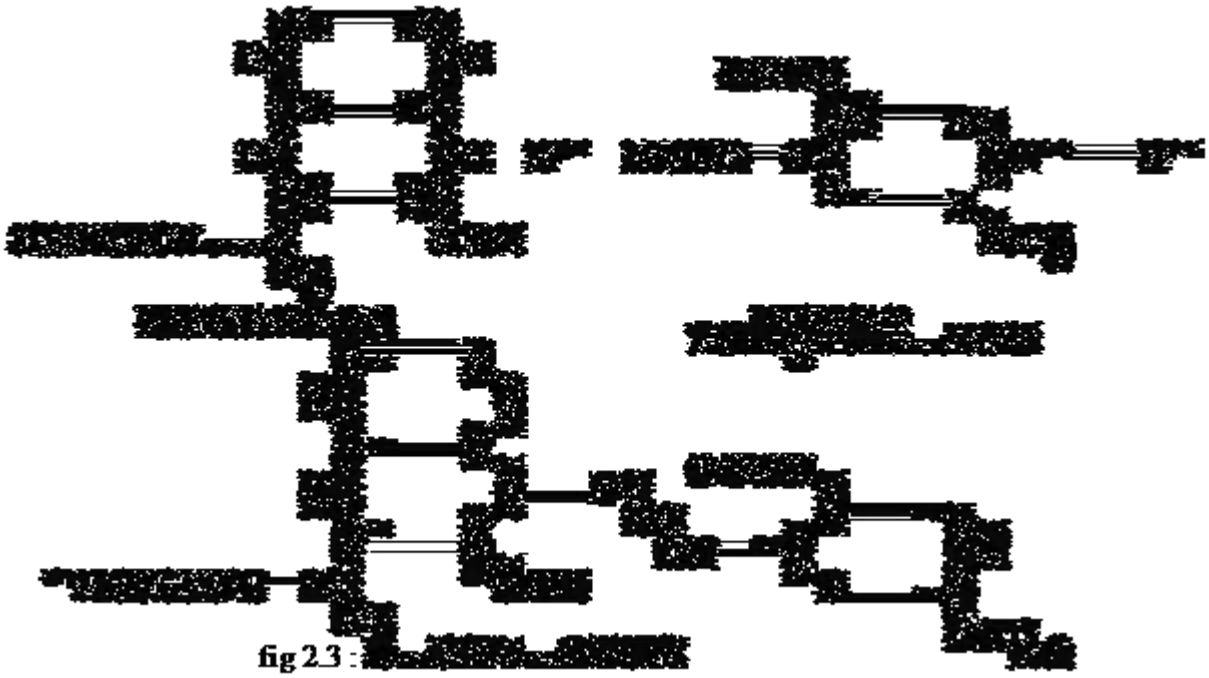


fig 2.3 :

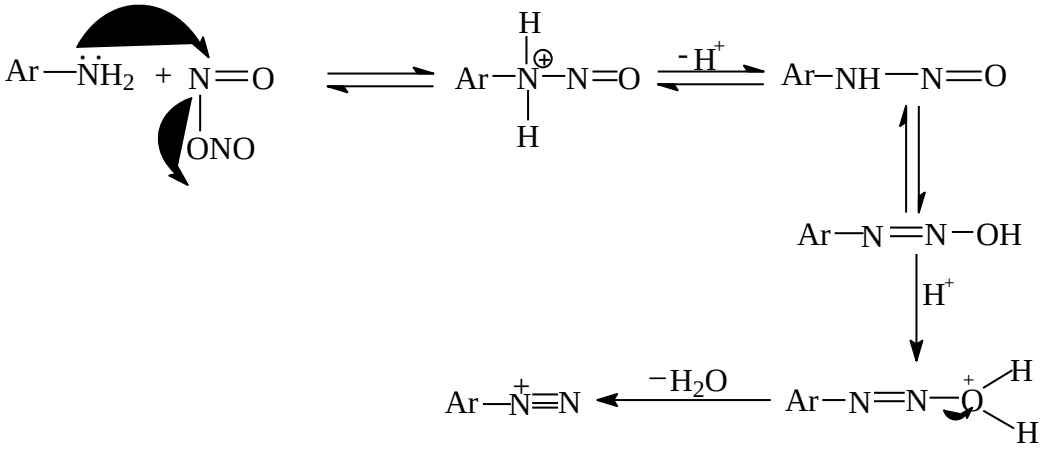
Many arylamides have been employed as coupling components, but Naphtol AS is the most important. However, Over the years, azo compounds constitute one of the largest classes of industrially synthesized organic compounds, potent in drug and cosmetics (Rathod and Thakre, 2013). Thus,of all classes of dyestuffs, azo dyes have attained the widest range of usage because variations in chemical structures are readily achievable and methods of application are generally not complex (Chudgar and Oakes, 2003). In fact, 60-70% of all dyes stuff in use and production fall in this group (Carliel *et el*., 1995). According to a statistical data survey, one million tons of such dyes are produced annually worldwide (Pandey *et al*., 2007). In 1876, Witt introduced the concept of the chromophore, chromogen and auxochrome. The chromophore is defined as a group of atoms in a molecule which is responsible for the colour, such as NO, NO_2, -N=N-, -C=C- and C=O. Compound containing chromophore are referred to as chromogens. Although some chromogens such as azobenzene are themselves coloured, a chromophoric group does not necessarily confer colour on a molecule, but rather gives it a potentiality for colour. An

auxochrome however is best regarded as an electron donor group, and includes any substituent which possesses lone pair electrons in conjugation with a π-electron system, exemplified by – NH_2, NHR, COOH, SO_3H and NR_2. Whilst being incapable of conferring colour on a substrate by itself, the introduction of an auxochromic group into a chromogen develops the colouring power of the latter and in general shift its absorption to longer wavelength and intensity. The presence of an electron donor is an essential pre-requisite for the chromogen to exhibit dyeing properties (Al-Rubaie and Mhessn, 2012). Synthesis of most azo dyes involves diazotization of a primary aromatic amine, followed by coupling with one or more nucleophiles. Amino-and hydroxy-groups are commonly used coupling components. The traditional application field of the synthetic azo dyes still remains the textile industry, and the finishing of fibrous materials (Heinrich, 1991). The emergence of diverse classes of synthetic dyes including azo dyes occurred due to constant effort to find specific dye for application in diverse materials of industrial importance which include, LCD, color filters, chromophoric substrates for redox enzymes, optical switches, lasers, optical data storage, non- linear optics ,chemical sensor, also they have advance application in organic synthesis (Olayinka *et al*., 2013). Azo compound are among the compounds which are suitable for biocidal treatment of textile materials due to the fact that some of them exhibit biological activity, as a result of the presence of some bioactive templates that form a definite type of bonding with the molecules of the fibrous material (Simu *et al*., 2010). Azo compounds are known for their medicinal importance and are well recognized for their use as antineoplastics, antidiabetics , antiseptics, antibacterial, antitumor. They are known to be involved in a number of biological reactions such as inhibition of DNA, RNA and protein synthesis, carcinogenesis and nitrogen fixation (Shridhar *et al*., 2012). Furthermore, azo dye compounds also have a lot of applications in industry and photodynamic therapy as well as

photosensitive species in photographic or electrophotographic systems and are dominant organic photoconductive materials (Thoraya and Farghay, 2008). Azo compounds are important structures in the medicinal and pharmaceutical fields and it has been suggested that the azoimine linkage might be responsible for the biological activities displayed by some reported Schiff bases. In addition, Evans blue and Congo Red are azo dyes being studied as HIV inhibitors of viral replications. This effect is believed to be caused by binding of azo dyes to both protease and reverse transcriptase of this virus (Chandravadivelu *et al*., 2011). The existence of an azo moiety in different types of compounds has caused them to show antibacterial and pesticidal activities. In the recent times, exploration of azo dye as antimicrobial agents has received considerable attention (Gopalakrishnan *et al*., 2011).

2.2.1 Azo dye synthesis

Azo dyes are synthesized by a two stage process (diazotization and coupling) which has remained almost unchanged since its discovery by Greiss in 1861. Diazotization, typically involves the treatment of a primary aromatic amine ($ArNH_2$) with nitrous acid. Stage 1 involves a nitrosation reaction and the exact nature of the nitrosating species varies with the reaction conditions used. Thus in the aqueous process, a solution of the sodium nitrite is added to a solution or suspension of the amine in hydrochloric acid ,and it has been suggested that the nitrosating species is dinitrogen trioxide (N_2O_3) as shown below (Zollinger, 2003).



Scheme 2.1 :Reaction mechanism for diazotization of aromatic amine

Weakly basic amines (e.g 2,4-dinitroaniline) require sulfuric acid for diazotization, and this involves the formation of nitrosyl sulfuric acid ($NO^+HSO_4^-$) obtained by adding concentrated sulfuric acid to solid sodium nitrite , when the nitrosating species may be NO^+ or $HOSO_2ONO$.Aminophenols and aminonaphthol on the other hand require mild diazotizing conditions due to the risk of the formation of quinines under the oxidizing conditions of this process. Commercially important diazo components include chloroanilines, nitroanilines, 2-aminophenols and aminonaphthols, the last two being used to build metalizable groups into azo dyes for cotton and wool , and heterocycles such as 2-aminothiophene and 2-aminothiazoles which are used in azo disperse dye for polyester. The diazonium used in azo dye synthesis is a weak electrophile and will undergo an electrophilic substitution reaction with suitably activated coupling components.These component are typically:

(a) Substituted amines- as in the production of disperse dyes for polyester and basic dyes for acrylics

(b) Substituted naphthols-as in the synthesis of acid and mordant dyes for wool and direct and reactive dyes for cotton

(c) Enolizable ketones – used especially for yellow –orange pigment.

The coupling reaction between diazonium ions and amines take place under slightly acidic conditions. This sequence is particularly important in the manufacture of aminobenzene disperse dyes for polyester. Typically, the diazo component contains electron donors (NO_2, CN) and the amine coupling component contains electron donor (NR_2,OCH_3,$NHCOCH_3$). Increasing degrees of substitution extends the colour range from orange through red to blue as shown below. (David and Geoffery, 1994)

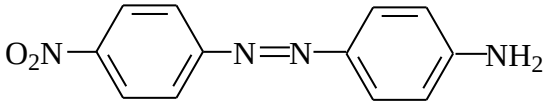


fig 2.4: Disperse Orange 1

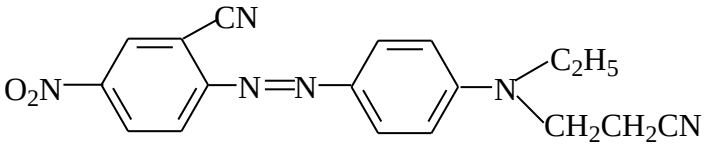


fig 2.5: Disperse Red 72

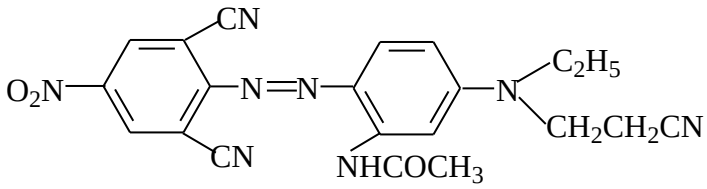


fig 2.6: Disperse dye Blue 14

The use of heterocyclic diazo components is now becoming a prime area of research by dye chemist and remarkable successes have been recorded. The colour range of these dyes extends to blue and blue green, hitherto the exclusive domain of the anthraquinones.

Figure 2.6 shows the structure of a blue disperse dye prepared using 2-amino-3,5-dinitrothiophene as the diazo component.

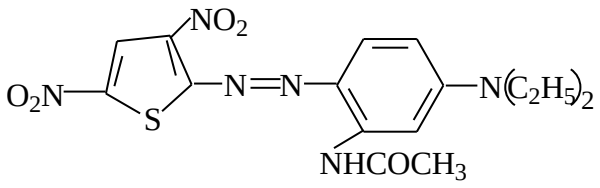


fig 2.7: Heterocyclic blue disperse dye 32

Although hydroxyl groups are known to be electron donors, they are less efficient in arylazo phenol versus aryazo naphthol structure. This is because the naphthol system does not lose full aromatization when electron delocalization occurs. Therefore, Naphthol couplers generally give dyes that are more bathochromic than phenol-based dyes.

2.3 Heterocyclic Dyes

The two main thrusts of dyestuffs research have been improved technical excellence and greater cost effectiveness. One long-term aim had been to combine the brightness and high fastness properties of anthraquinone dyes with the strength and economy of azo dyes, (Maradiya and Patel, 2002a). Heterocyclic azo dyes fall rather conveniently into two main groups: those derived from heterocyclic coupling components and those derived from heterocyclic diazo components. All the heterocyclic coupling components that provide commercially important azo dyes contain only nitrogen as the heteroatom. They are indoles, pyrazolones and pyridines shown below as figures 2.8, 2.9, 2.10:

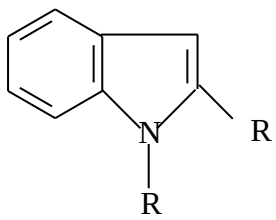


fig 2.8: Indole

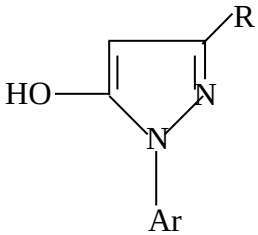


fig 2.9: Pyrazolone

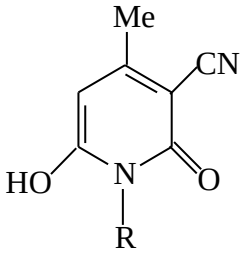


fig 2.10: Pyridones

Until recently, many yellow dyes were of the azopyrazolones type. Nowadays, these have been largely superseded by the azopyridones dyes. Azo pyridones yellow dyes are brighter, stronger and generally have better fastness properties than azopyrazolones dyes. These dyes according to (Gregory *et al.,* 1990) exist in the hydrazone tautomeric form. It should be noted that the concept of azo/hydrazone tautomerism is not interesting but also extremely important as far as commercial azo dyes are concerned. This because the tautomers have different colours, different properties e,g light fastness, different toxicological properties and most importantly different tinctorial strengths. Since the tinctorial strength of a dye primarily determines its cost effectiveness, it is desirable that commercial azo dyes should exist in the strongest tautomeric form, namely the hydrazone form. Heterocyclic compounds have been utilized as coupling components in preparing azo dyes for polyester, in addition to diazonium components, but, according to the volume of patent literature, less emphasis seems to have been expended towards their use as a couplers. However, one series of heterocyclic couplers which has achieved spectacular success consists of the so called pyridine couplers. Azo dyes from these couplers on polyester produce bright yellow dyeing with particularly high light fastness, excellent dyeing and other fastness properties. One important feature of these dyes is their particularly high extinction coefficients, which together with the ready availability of raw materials for the coupler and the dye's ease of synthesis, make for an economic combination of properties.

In contrast to the heterocyclic coupling component, all the heterocyclic diazo components that provide important azo dyes contain sulfur, either alone or in combination with nitrogen. These heterocyclic azo dyes provide bright, strong shades that range from red to blue and therefore, compliment the yellow/orange colours of the nitrogen heterocyclic azo dyes in providing a

complete coverage of the entire shade. Representative dyes are the thiadiazole red, the nitrothiazole reddish blue and the thiophene greenish-blue as shown in figures below:

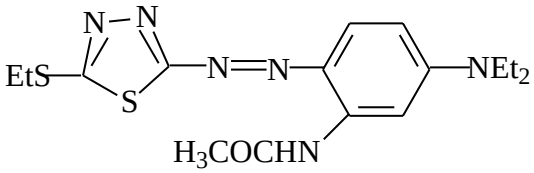


fig 2.11: Thiadiazole red disperse dye

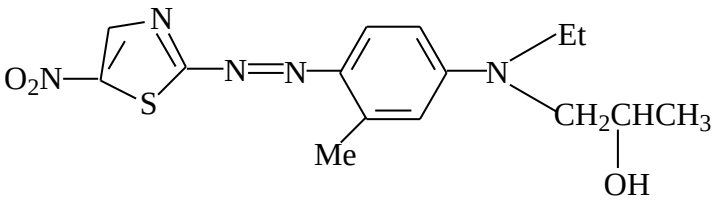


fig 2.12: Nitrothiazole blue disperse dye

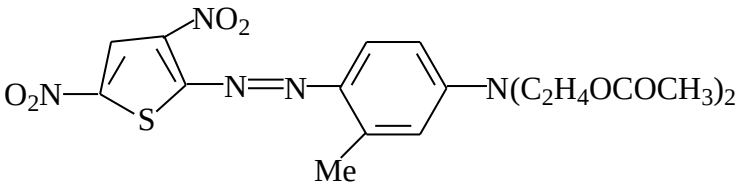


fig 2.13: Thiophene greenish-blue disperse dye

2.4 Antimicrobial Dyes

Antibacterial and antifungi qualities of incorporated dyes in food, beverages, cosmetics and fabrics become desirable as that prolong the utility of such products by inhibiting bacterial and fungal growth. (Dixit *et al*., 2007) worked on the antimicrobial and fabric-protective activities of naphthol- based azo dyes using 2,4-dihydroxybenzophenone, an aromatic ketone (diphenylketone), as an important starting material in organic synthesis of dyes. They observed

that the antimicrobial properties of these azo dyes reduced and prevent damages made to the mechanical strength of materials, colour changes, stains and stale odour. Azo dyes produced from naphthols and phenol has wide applications as polymer additives (Yurteri *et al*., 2012). Their hydroxyl groups are good UV light absorbers which prevent photo degradation of most vinyl polymers. (Baskar *et al*., 2006) found out that various naphthol dyes e.g naphthoxazole and nerolins possess outstanding biological activities like anti-amnesic, anti inflammatory, analgesic as well as antibacterial and antifungal properties, by using Agar diffusion method against *S. aureus, B. subtilis P. aeruginosa, E. coli* and *A.niger*. Zone of inhibition recorded compared with standard antimicrobial agents such as ciprofloxacin,chloramphenicol and clotrimazole. Naphathoxazole showed the best activity against all strains including fungi, while others showed comparative and moderate activities against all bacteria strains. (Abedi *et al*., 2008) found out that acrylic fabric treated with direct dye (CI direct blue 168) using $CuSO_4$ as mordanting agent showed considerable antimicrobial properties against common pathogenic bacteria. Activities increased with increase in temperature and using 2% CuSO4 in pre- and post-mordanting scenarios. Also, bactericidal triazine dyestuffs impart the ability to inhibit growth of bacterial, *S.aureus* while azo dyestuffs was developed to impart fungicidal properties to protein fibrous materials, especially under tropical climate, that is, at increased humidity and elevated temperature. Untreated azo dyes from industrial water waste was found to have a high toxic effect on soil bacterium, *P. aeruginosa*, while treated dyes (Decolourised) has reduced toxicity because of decrease in concentration,while high concentration of azo dyes eliminated microbial colonies due to high frequency of mutation. This last two reports show that the higher the concentration of azo dyes, the higher would be the toxic or antimicrobial effect. Indole and its azo dye derivatives under aerobic condition exhibit toxic activity on both pathogenic and non

pathogenic micro organisms; *B. thuringiensis, B. subtilis, B. megaterium, P. aeruginosa, S. aureus, E. coli and S. cerevisiae* (Oztuurk and Abdullah, 2006). Some azo dyes have been found to have antimicrobial properties due to the presence of active functional groups. This biological activity of some azo dyes has increased their usage in textile, foods, and pharmaceutical industries, since they have this vital ability to inhibit microorganisms which cause degradation to textile materials, degradation to food materials, skin diseases produced from bacteria which live inside clothing and textile fabrics and other ailments that affect human health. A search for azo dyes with potent antimicrobial properties is still on-going. 4-carboxy-2, 6-dinitrophenylazohyroxynaphthalenes series are therefore being investigated as potential antimicrobial agents due to the presence of phenolic functional group in these dyes. These dyes were synthesized from various naphthol derivatives (Adegoke *et al*., 2008). Further attempts at some physicochemical characterizations were carried out using various hydrophobicity parameters and subtle differences were discovered in their migration patterns on thin layer chromatography (Idowu *et al*., 2007). The solvatochromic behaviours and structure-spectra properties of the dyes have also been recently reported (Adegoke *et al*., 2010).

2.5 Polymeric Dyes

Polymeric dyes are composed of optically chromophoric groups bound to or into polymers which offer the advantage of allowing a range of physical properties, such as solubility, absorption, migration, and viscosity, that are tunable. They do not sublime, are nonabrasive, and generally have low toxicity. The range of products possible offered by the joining of the fields of polymer chemistry and color chemistry is virtually inexhaustible. They have been widely applied on the fiber because of certain essential dye properties such as fast leveling, fastness to light and wet treatment, low sublimation rate, and very good thermal and chemical resistance. Polymeric

dyes used in textile fields can be classified as crosslinking polymeric dyes, disperse polymeric dyes, “fiber-reactive” polymeric dyes and acidic polymeric dyes according to the methods of dyeing fibers. (Maradiya *et al*., 2002b), synthesized a novel yellow polymeric dye by the reaction of 2,4-dinitrochloro benzene with polyallylamine prepared from the homopolymerization of monoallylammonium chloride. (Alemdaroglu *et al*., 2009) disclosed protein polymeric dyes prepared by the reaction of protein macromolecule with reactive dyes, which were specially used in dyeing protein materials and fixed by use of crosslinking agent.

2.6 Electrical Conductivity:

Electrical conductivity is a function of a material's ability to carry an electrical current. The conductivity (σ) of a material is determined by taking the reciprocal of the measured electrical resistance (R) to the flow of electricity in a length (L) of material divided by the cross-sectional area (A).

$$\sigma = \frac{1}{R} * \frac{L}{A}$$

Conductivity is temperature dependent. The conductivity of pure semiconductors and insulators increases as the temperature increases. Controlling and change in conductivity of materials is one of the challenges facing materials scientists. Any material can, in principle, be classified as an insulator, semiconductor or metal, frequently based on its electrical resistivity. Insulators have high resistivities ($>10^{10}$ ohm.cm); metals have low resistivities ($<10^{-3}$ ohm.cm); semiconductors have intermediate resistivities. The range of resistivities from insulators to metals is enormous as shown in Figure 2. A good insulator such as quartz can have a resistivity as high as 10^{18} ohm.cm; a good metal such as copper can havea resistivity as low as 10^{-6} ohm.cm. It should be noted that, at a certain critical temperature, pressure and magnetic field, either insulators or semiconductors or metals can become superconductors with resistivities as

low as 10^{-25} ohm.cm. Electrical conduction occurs by the long range migration of either electrons or ions. Migration of ions does not occur to any appreciable extent in most ionic and covalent solids such as oxides and halides (Fariz, 2007). Rather, the atoms tend to be essentially fixed on their lattice sites and can only move via crystal defects. Only at high temperatures, where the defects concentrations become quite large and the atoms have a lot of thermal energy, does the ionic conductivity become appreciable, e.g. the conductivity of NaCl at approximately 800°*C*, just below its melting point, is 10^{-3} S/cm whereas at room temperature, pure NaCl is an insulator. Usually, the ionic conductivity of electrolytes is in the range of 10^{-3} to 10 S/cm. resistivity (ohm centimeter). (West, 1987).

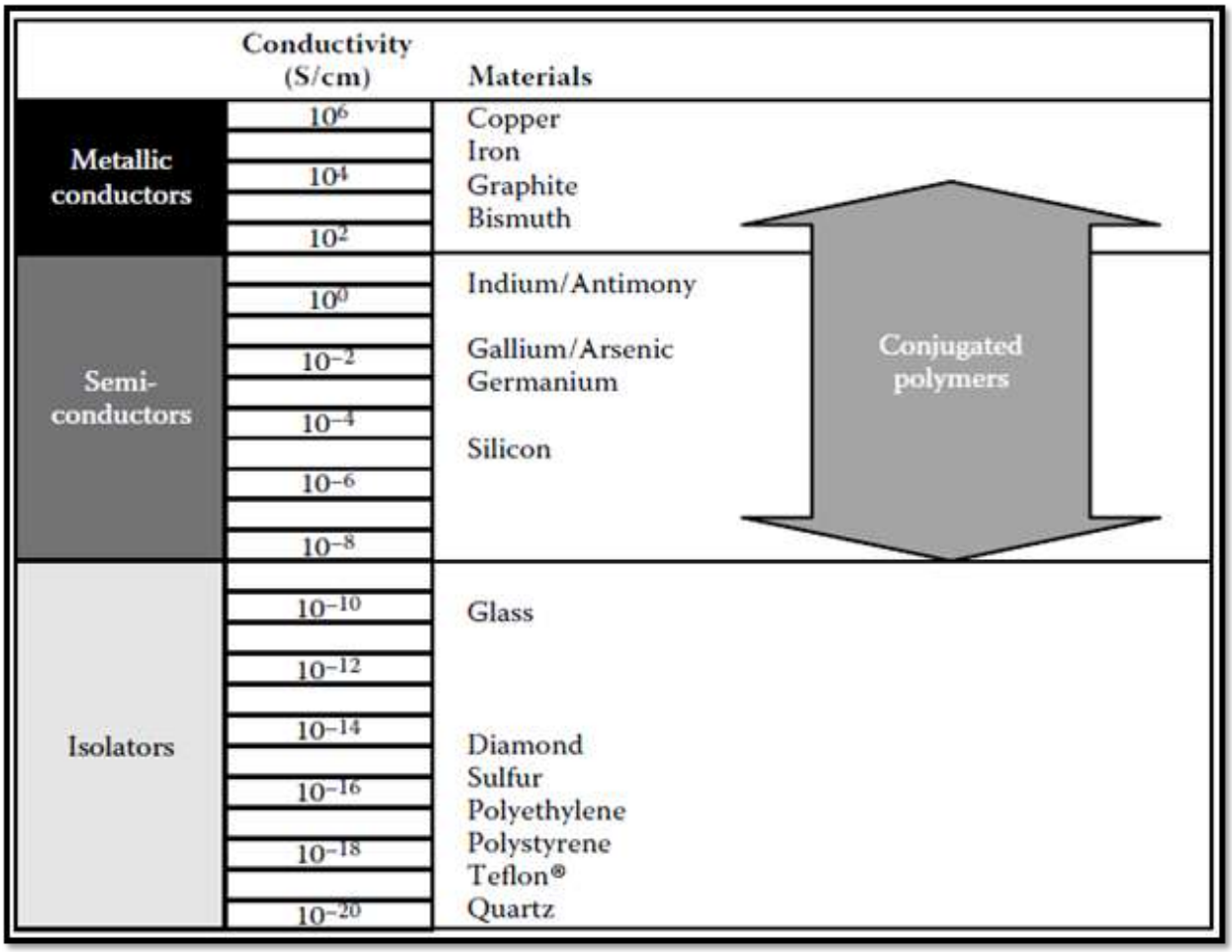


Figure 2.14 : Electrical conductivities of some common materials.

Range of resistivity for various materials, including metals, semiconductors and insulators. The electronic conductivity is dependent on the migration of electrons or their counterpart holes. The conductivity σ is given by the equation: $\sigma = n.e.u$ where n is the number of charge, e the charge and u *is* the mobility of the charge carriers. For metals, n is large and essentially unchanged with temperature. The only variable in σ is u and since u decreases slightly with increase of temperature due to collisions between the moving electrons and lattice atoms, σ also decreases with increase of temperature. For semiconductors and insulators, n usually increases exponentially with temperature. The effect of this dramatic increase in n more than outweighs the effect of the small decrease in u. Hence, σ increases rapidly with temperature (Jiles, 1994). When an electric field is applied, electrons may flow through a material if there are empty states in the outer (valence) shells of the atoms that make up the material. An electron will not easily transfer between atoms if there is not a vacant state of similar energy in the receiving atom for it to occupy. A single atom has electrons localized about itself. An atomic orbital of one atom may overlap with an atomic orbital of another atom forming two molecular orbitals. One, called the bonding molecular orbital, is of low energy and the other with higher energy is called the anti-bonding molecular orbital. As more and more atoms assemble to form a solid, the number of bonding and anti-bonding orbitals of about the same energy increases, and they begin to take on the characteristics of an energy band. The energy differences between orbitals within a band is slight. Electrons can move freely among these orbitals within an energy band as long as the orbitals are not completely occupied. The highest occupied energy band is called the valence band. But, there is a region that separates the valence band from the conduction band where there are no orbitals. Electrons are not allowed to have these energies. In insulators, this energy gap is relatively large and in semiconductors, the energy gap is intermediate.

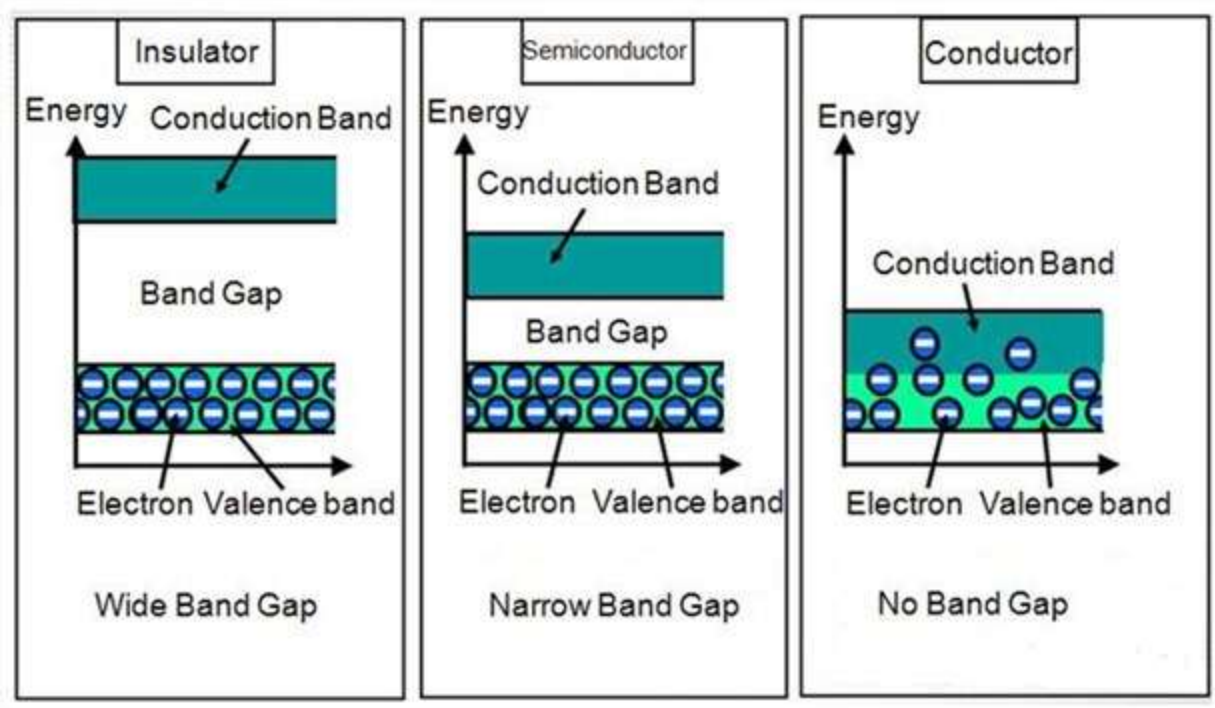


Figure 2.15: The energy bands of metals, semiconductors and insulators. For the insulators and semiconductors, the lower band is called the valence band and the higher band is called the conduction band. The lower energy band in metals is partially filled with electrons (Fariz, 2007).

Atoms that form metallic conductors have many partially and fully unoccupied levels with similar energies: a large number of mobile charge carriers are able to move across the material when an electrical potential (voltage) is applied. In a semiconductor or an insulator, the valence band is completely filled with electrons in bonding states so that conduction cannot occur. There are no vacant levels of similar energy on neighboring atoms. At absolute zero, its anti-bonding states (the conduction band) are completely empty. There are no electrons there to conduct electricity. This is why insulators cannot conduct. In the case of semiconductors, as temperature increases, electrons in the valence band acquire sufficient energy to be promoted across the "energy gap" into the conduction band. When this occurs, these promoted electrons can move and conduct electricity. The smaller the band gap, the easier it is for electrons to move to the

conduction band. conduction in pure (intrinsic) semiconductors in which the charge carriers come from the chemical bonds in the substance itself. Heat energy in a semiconductor increases the number of electrons promoted into the otherwise empty conduction band; the vacancies (or holes) created in this process allow mobility of electrons in the valence band through the material. At high temperatures these semiconductors are relatively good conductors because there are a larger number of electrons in the conduction band and holes in the valence band available for electron movement. But at low temperatures, intrinsic semiconductors are insulators since the number of electrons and holes is diminished. At absolute zero, an intrinsic semiconductor would have no electrons in the conduction band. However, the most important semiconductors are of the extrinsic type, where some impurity (another element) has been intentionally added in the solid to increase the conductivity. The properties of an extrinsic semiconductor are governed by the presence of these impurities.

2.6.1 Doping:

Doping can produce two types of semiconductors depending upon the element added. If the element used for doping has at least one more valence electron than the host semiconductor, then an n-type (negative type) semiconductor is created. For example, if arsenic is added to a silicon crystal, the arsenic has one more valence electron than silicon. That extra electron is available to carry a current. If the semiconductor is doped with an element having at least one less electron than the host material, then a p-type (positive type) semiconductor is formed. As an example, if silicon is doped with aluminum (three valence electrons), a hole will be formed in the valence band. Again any member of Group III could dope a host semiconductor from Group IV and show the same effect. The solid would have a "positive" hole in its electronic structure that would move in the opposite direction of the electron flow. Thus a p-type semiconductor would

be formed. Doping cannot be done to the point where it disturbs the crystalline structure of the host semiconductor. Doping is done in the range of parts per million concentrations, but may be up to a few parts per thousand.

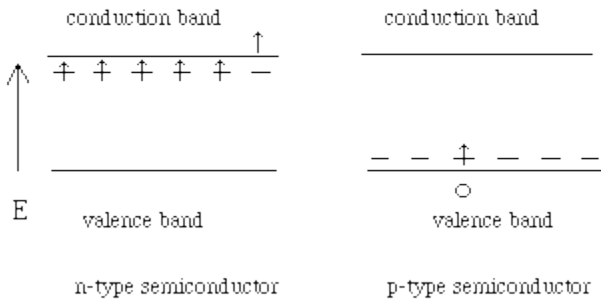


Figure 2.16: A p-type and n-type semiconductor. The fifth valence electron of the n-type dopant can easily jump to the conduction band and carry current. In the p-type semiconductor, electrons are easily promoted to the vacant level in the dopant. This creates a hole in the valence band which can carry current by traveling in the opposite direction of electron flow.

2.7 Conducting Polymer

Electrically conducting polymers are designated as the fourth generation of polymeric materials. Electrically conducting polymers are extensively conjugated in nature and therefore, it is believed that they possess a spatially delocalized band-like electronic structure . These bands stem from the splitting of interacting molecular orbitals of the constituent monomer units in a manner reminiscent of the band structure of solid-state semiconductors. It is generally agreed that the mechanism of conductivity in these polymers is based on the motion of charged defects within the conjugated framework .The charge carriers, either positive p-type or negative n-type, are the products of oxidizing or reducing the polymer respectively (Nirmala *et al*., 2014). The simplest possible form of conducting polymer is of course the arche type polyacetylene (CH)x. Polyacetylene itself is too unstable to be of any practical value, its structure constitutes the core

of all conjugated polymers.(Nirmala *et al*., 2014), had proposed that properly substituted polyacetylene molecule would exhibit superconductivity at room temperature. The electrical conductivity of the order of 10-5 S/cm for trans polyacetylene sample has been reported. Polyacetylene could attain high levels of electronic conductivity when oxidized by suitable reagents. Since late seventies, a large number of polymers have been added to the list of conducting polymers such as polypyrrole, polythiophene, polyparaphenylene, polyphenylene sulphide, polyaniline, polyphenylene vinylene etc. Doping the polymers creates new states (donor or acceptor states), which exist within the band gap and are energetically accessible to the pi electrons, resulting in significant increase in conductivity (Skotheim *et al*., 1998). In fact, the conductivity of doped polymers may be up to ten orders of magnitude greater than that of the neutral (undoped) polymers. The concept of conductivity of conjugated polymers was quickly broadened from polyacetylene to include a conjugated hydrocarbon and aromatic heterocyclic polymers, such as poly (p-phenylene) and polythiophene . The conductivity of various doped and undoped polymers, some common semiconductors and metals are shown in Table 2.1
(Nirmala *et al*., 2014).

Materials	Conductivity (s/cm)
Gold, Silver and Copper	10^{6}
Doped trans polyacetylene	10^{5}
Doped polyaniline	10^{1}
Germanium	10^{-2}
Silicon	10^{-6}
Undoped trans polyacetylene	10^{-6}
Undoped polyaniline	10^{-10}
Glass	10^{-10}
Quartz	10^{-12}
H_2SO_4 doped polyaniline	10^{-8}

As the conducting polymers may be doped to various degrees, there is an element of control in doping level, hence the conductivity. This ability to tailor the polymer's electrical properties exemplifies the versatility of conducting polymers. Conductivity of conductive polymers compared to those of other materials, from quartz (insulator) to copper (conductor).

2.7.1 Factors affecting conductivity of polymers

It is only the doping which makes most of the conjugated polymers conducting from their insulating state to semiconducting or conducting. Although the charged species are incorporated by doping, the electrical conductivity is not ionic but electronic. Electronic conductivity of conducting polymers depend upon numerous factors. Significant among these are:

i. Nature or chemical reactivity of the dopant

ii. Process of doping

iii. Doping level

iv. Method and condition of polymer synthesis

Chemical reactivity of the dopant is of prime importance to obtain a conducting polymer. Not all dopants are equally capable of oxidizing a polymer chain. Iodine is a dopant for increasing the electrical conductivity of polyacetylene by thirteen orders of magnitude but is too weak to oxidize polypyrrole or polyaniline where as HCl is used to oxidize polyaniline. The electrical conductivity of polyaniline hydrochloride was observed is 4.4 + 1.7 S cm–1. Doping conditions also play an important role. Electrical conductivity usually increases with the doping level due to increase in charge carriers concentration. Rapid increase in mobility of the charge carriers may be responsible for this high rate of increase in conductivity. Development of quantitative model for conduction is hampered by the fact that there are at least three elements contributing to the carrier mobility:

i. Single chain or intramolecular transport

ii. Interchain transport

iii. Interparticle contact

Electrical conductivity is very much dependent on the method of polymer synthesis, purification of the polymer, physical treatment of the polymer etc. in addition to the nature of the dopants and the process of doping.The electronic properties of conjugated polymers are due to the presence of electrons. (Wallace, 2002)

2.7.2 Different Conducting Polymers

Polyacetylene, polythiophene, polypyrrole, poly (p- phenylene vinylene) are commonly used conducting polymers. These polymers are costly, less stable mechanically after doping and difficult in processing. Therefore, here polyaniline (PANI) is selected for study because polyaniline owing to its ease of synthesis, remarkable environmental stability and high conductivity in the doped form, has remained one of the most thoroughly studied conducting polymers.Some examples of conjugated polymers are shown figures below: (Heeger, 1997).

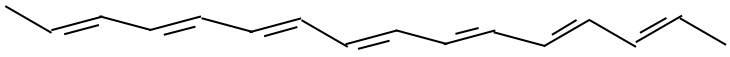


Fig 2.31: Polyacetylene

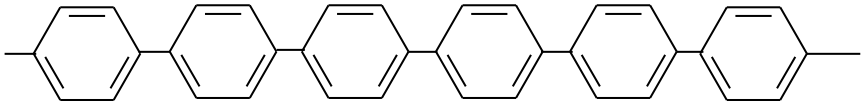


fig 2.17: Polyphenylene

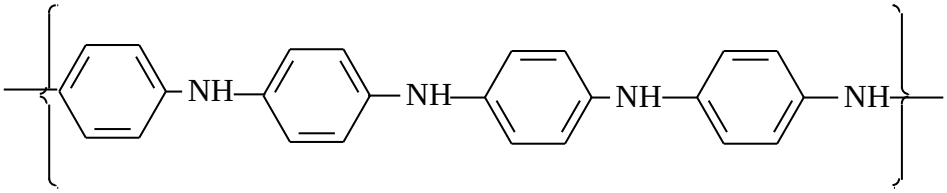


fig 2.18: Polyaniline

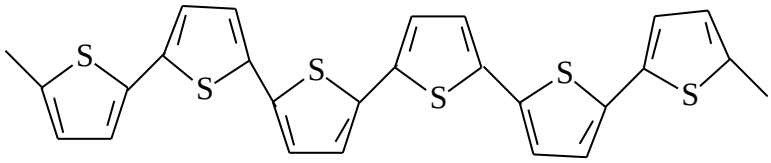


fig 2.19: Polythiophene

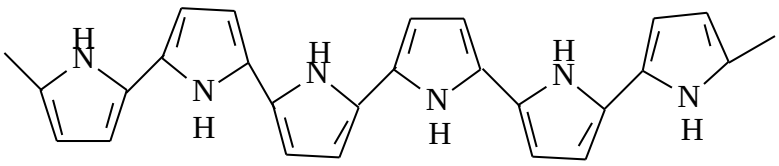


fig 2.20: Polypyrrole

2.8 Polyaniline (PANI)

Polyaniline (PANI) has been known from the beginning of XIX century as “aniline black”. It was used as a dye to blacken cotton fabrics. At the beginning of the XX century number of works were realised with aim to resolve PANI structure. Initially, aniline black was considered as an aniline octamer in different oxidation states. Lately, it was shown that oxidation

of aniline under certain conditions gives a polymer. It was Woodhead and Green who named three basic polyaniline forms (described below),these names are commonly used till today.An important breakthrough in the polyaniline research took place in early 1980s, when polyaniline has been discovered as a member of a novel group of macromolecular compounds; namely conductive polymers. Since then, it has become the most extensively studied polymer in this group. In reality, "polyaniline" is a name for a whole family of polymers, which can be described by the structure presented below: (Krzysztof, 2006).

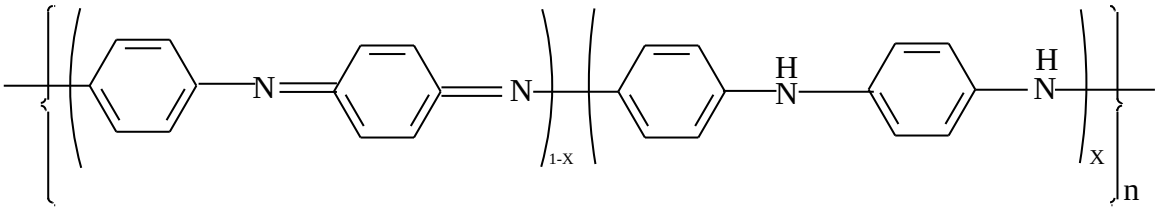
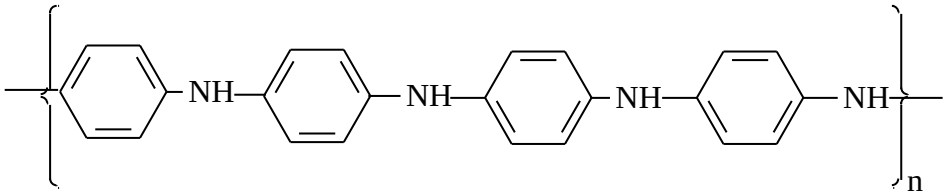


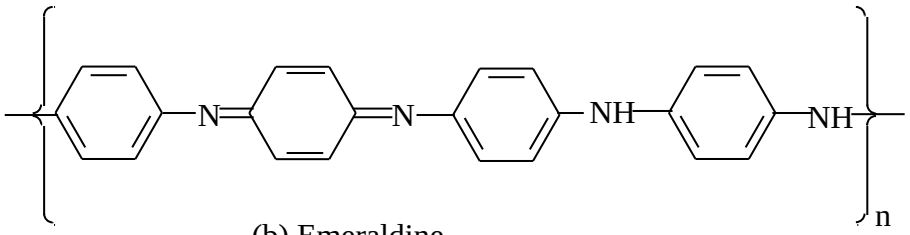
fig 2.21: General formula for different forms of polyaniline base

Correctness of the formula presented above was proved, among others, by spectroscopic studies of Wudl and co-workers. As already mentioned, three principal forms of polyaniline can be distinguished. All these forms exhibit interesting spectroscopic properties, but two of them – fully reduced (a) and fully oxidised (c) are environmentally instable.

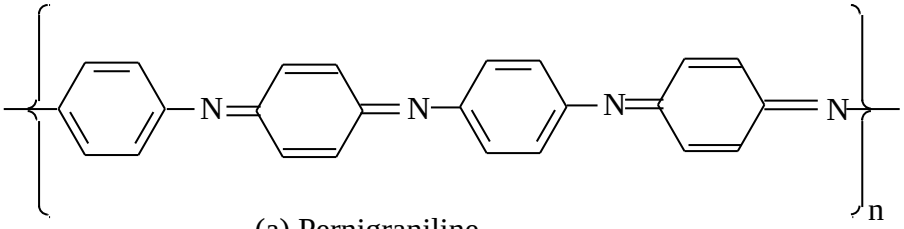
Leucoemeraldine (a) (white powder) is a strong reducing agent that easily reacts with air oxygen giving emeraldine (b) as the product. Pernigraniline (c) (red-purple, partially crystalline powder) composed of oxidised units, easily undergoes hydrolytic type degradation via chain scission. Emeraldine base (dark blue powder with metallic gloss) – semi-oxidized form of PANI - is stable in air and can be stored for long time without chemical changes. Emeraldine is the most extensively studied form of polyaniline. (Nirmala *et al*., 2014). Thus, in the majority of publications, names "polyaniline" and "emeraldine" are used interchangeably.



(a) Leucoemeraldine



(b) Emeraldine



(a) Pernigraniline

fig 2.22: Principal form of polyaniline base (Krzysztof, 2006).

The color change associated with polyaniline in different oxidation states can be used in sensors and electrochromic devices. Though color is useful, the best method for making a polyaniline sensor is arguably to take advantage of the dramatic conductivity changes between the different oxidation states or doping levels . The most common synthesis of polyaniline is by oxidative polymerization of aniline. Aniline has been dissolved in HCl or other acids (dopant) and ammonium persulphate (oxidant) has been added drop – wise and reaction has been continued for few hours. Using special polymerization procedures and dopants, the polyaniline powder can be recovered after polymerization and can be made dispersible and hence useful for practical applications. A three stage model for the formation of emeraldine base has been proposed. In the first stage of the reaction the pernigraniline salt (PS) oxidation state is formed. In the second stage pernigraniline is

reduced to the emeraldine salt as aniline monomer gets oxidized to the radical cation. In the third stage this radical cation couples with ES salt. (Irena Kulszewicz, 2006). In the doped emeraldine salt form, polyaniline is electrically conductive, which makes it suitable for e.g. manufacture of electrically conducting yarns, antistatic coatings, electromagnetic shielding and flexible electrodes. (Nirmala *et al*., 2014). Polyaniline is more noble than copper and slightly less noble than silver which is the basis for its broad use in printed circuit board manufacturing (as a final finish) and in corrosion protection. Polyaniline is typically produced in the form of long chain polymer aggregates, surfactant (or dopant) stabilized nanoparticle dispersions, or stabilizer-free nanofiber dispersions depending on the synthetic route.

Polyaniline Zr (IV) sulfosalicylate been tested against various bacterial (*E. coli*, *Bacillus thuringiensis*, and *P. aeruginosa*) and fungal strains (*A. nigrus*, *Fusarium oxysporum*, and *Penicillium chrysogenum*). Relatively higher activities have been observed than the known antibiotics. Polyaniline-grafted chitosan (Chit-*g*-PANI) has been screened for its antimicrobial activity against *Staphylococcus epidermidis, S. aureus*, *Staphylococcus pyogenes, E. coli*, *C. albicans*, *C. tropicalis*, *and C. krusei*. The results of antimicrobial activity of PANI and Chit-*g*-PANI were assessed based on the average diameter of zones of inhibition. The results confirm that Chit-*g*-PANI has an enhanced antimicrobial activity compared to PANI (Karunanithy *et al*., 2013).

Functionalized polyaniline dispersions have been available for commercial sale since the late 1990s. The continuously growing interest in the study of PANI over the years is mainly because of its diverse, but unique properties of PANI, allowing its potential applications in various fields. It is an environmentally stable and highly tunable

conducting polymer, which can be produced as bulk powder, cast films, or fibers. Due to its low- cost and large- scale production, it has various applications. Much of the structural characterization of polyaniline has taken place in the last 20 years or so, and is fairly well established, although the large number of papers published in the last five years would indicate that polyaniline is still under much scrutiny.(Yilmaz, 2011).

Polyaniline is a typical phenylene based polymer having a chemically flexible –NH group in a polymer chain flanked on either side by a phenylene ring. It can also be defined as the simple 1, 4- coupling product of monomeric aniline molecule. The protonation and deprotonation and various other physico-chemical properties of polyaniline is due to the presence of the –NH- group. Polyaniline is the oxidative polymeric product of aniline under acidic conditions. There are several reports of polyaniline found in the literature over the decades about the structure and constitutional aspect of aniline polymerization reported the proton exchange and redox properties with the influence of water on the conductivity of polyaniline. Polyaniline can be synthesized by both chemical and electrochemical oxidative polymerization. Structure of the polymer was described in terms of degree of order, for example crystalline, semicrystalline, or amorphous. Bulk synthesis of polyaniline nanofibers has led to a highly scalable and commercially applicable form of polyaniline that has been researched extensively since their discovery in 2002. As synthesis of polyaniline nanostructures is facile and they have been prepared by various methods, polyaniline is an important nanomaterial. (Fariz, 2007).

2.8.1 Properties of polyaniline

(i) Polyanilines electrical properties can be reversibly controlled by charge-transfer doping and protonation.

(ii) Polyaniline is environmentally stable and inert (noble) where stainless steel is corroded.

(iii) Polyaniline is applicable to electrical, electrochemical, and optical applications.

(iv) Polyaniline is currently used in cell phones and calculators, and other LCD technology etc.

2.8.2 Synthetic routes of polyaniline

Polymerisation process of aniline and its derivatives has been investigated for more than one century and several synthetic routes have been proposed. Due to the fact that only emeraldine base is stable in ambient conditions, the most popular polymerization procedures are aimed on the preparation of this form. When pernigraniline or leucoemeraldine are required, the oxidation or the reduction of emeraldine usually obtains them.

2.8.3 Chemical oxidative polymerisation

The most common synthesis of polyaniline involves oxidative polymerization, in which the polymerization and doping occurs concurrently, and may be accomplished either electrochemically or chemically. Electrochemical methods tend to have lower yields than that obtained by chemical methods. Synthesis of polyaniline by chemical oxidative route involves the use of either hydrochloric or sulfuric acid in the presence of ammonium persulphate as the oxidizing agent in the aqueous medium. The principal function of the oxidant is to withdraw a proton from an aniline molecule, without forming a strong co-ordination bond either with the substrate / intermediate or with the final product. However, smaller quantity of oxidant is used to avoid oxidative degradation of the polymer formed. (Krzysztof, 2006).

2.8.4 Electrochemical polymerisation

Oxidative polymerisation of aniline can also be performed using the electrochemical route. First papers describing successful electrochemical polymerisation of aniline were published in early 1960. Polyaniline can be synthezised potentiostatically, galvanostatically or by potential scanning (cyclic-voltammetry polymerisation). Well-controlled conditions of the

electrochemical polymerisation cause good reproducibility of the product. Moreover, the oxidation state of the polymer can easily be modified when changing the potential of the working electrode. Unfortunately, small quantities of obtained PANI (comparing to chemical polymerisation) eliminate this method when bigger polyaniline quantities are required.(Nirmala *et al*., 2015).

2.9. Dye Containing Polymer

Natural and synthetic dyes are compounds of great interest since they play an important role in our everyday life. The broad variety of technical and industrial applications, which includes "classical" utilizations like dyeing of textiles and other consumer goods as well as rather new usages such as laser dyes and dyes for organic light emitting diodes (OLEDs), liquid crystal (LC) displays, optical data storage and fluorescent labeling, has produced a great deal of research in this field. The main driving force is the constant demand for improved dyeing efficiency or photochemical/photophysical properties while also focusing on eco-friendly procedures reduced toxicity, and decreased production costs. A promising approach to fulfilling these requirements is the combination of dyes and polymeric materials. The great advantage of such systems is the controllability of many features like solubility, stability, and toxicity through appropriate choice of polymeric material (Carolin *et al*., 2015).

(Hetzer *et al*., 2013), investigated the attachment of polymer on phenolphthalein which was obtained through reaction of phenolphthalein with N-(hydroxymethyl) acrylamide. The latter compound possesses a relatively high reactivity towards nucleophilic attacks, which enables condensation with electron-rich aromatic substances under Friedel-Crafts-like conditions. The versatility of the reaction products, namely a monofunctional monomer as well as a bifunctional cross-linker, was demonstrated in several publications.. As a first step, the

compounds were reacted with a hydroxy-functionalized amine in a nucleophilic aromatic substitution reaction. The free aliphatic hydroxy groups were then methacrylated by treatment with methacryloyl chloride or methacrylic anhydride, respectively. The bifunctional cross-linkers and the monofunctional monomer obtained were polymerized with different methacrylate-based comonomers and the resulting polymers were found to be stable against UV radiation.

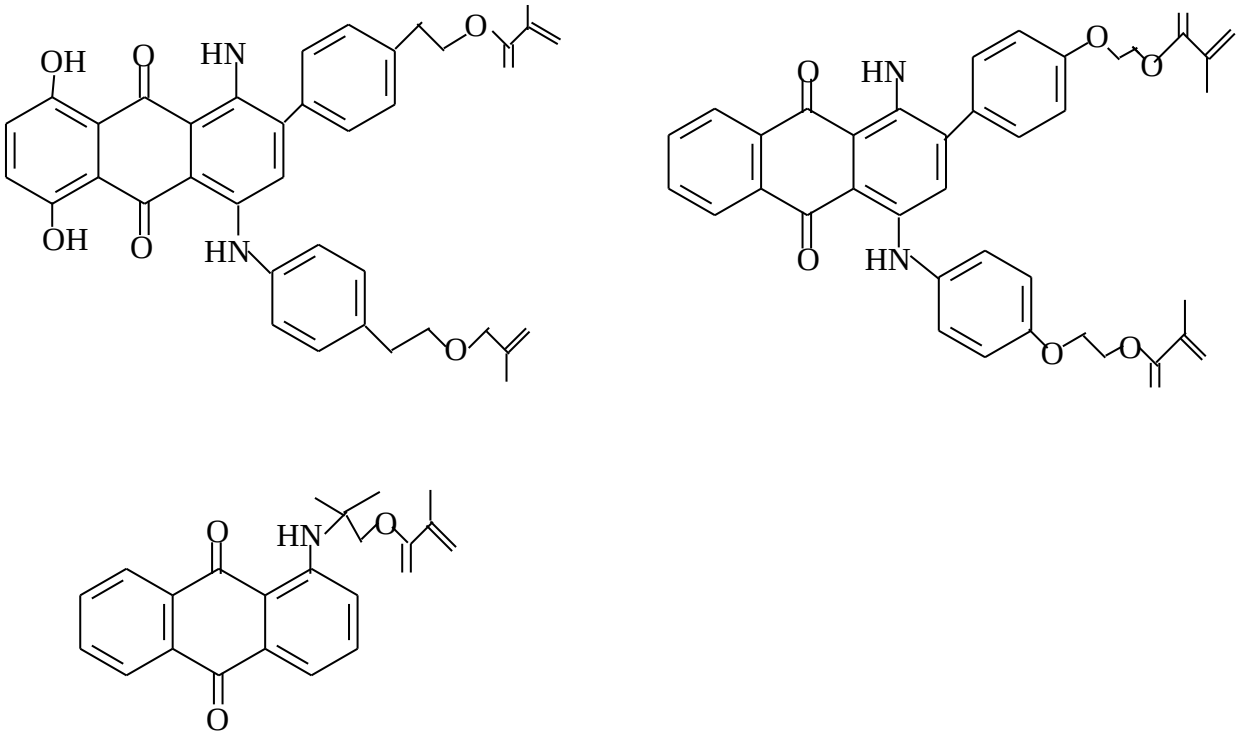


Fig 2.23: Chemical structures of several polymerizable anthraquinone derivatives

Several further examples of polymerizable dye derivatives belonging to different classes of dyes were described. For instance, the covalent emplacement of laser dyes into polymeric materials offers a variety of advantages such as improved handling and increased lasing efficiency. This was shown for 2-(2'-hydroxyphenyl) benzimidazole derivatives bearing allyloxycarbonyl groups that allow for radical polymerization (Donati *et al.*, 2008). Methyl methacrylate was found to be the best co-monomer for the preparation of such solid dye materials due to the excellent transparency of the resulting polymers in the spectral range of

interest (Serin *et al*., 2002). Another common way of introducing perylene dyes to polymeric materials is the coupling of dihalogenated derivatives with adequate comonomers that results in the formation of copolymer. For instance, the emplacement of perylene dyes into the polymer backbone in a statistical fashion was achieved via Yamamoto polymerization of bis-brominated perylene derivatives and dibromodioctylfluorene. A useful route for the polymer analogous attachment of azo dyes to soluble catalyst carrying polymers was developed. The polymeric backbone was synthesized from copolymerization of NIPAM and *N*-acryloxysuccinimide, which yielded linear polymers bearing active ester side groups. These were reacted with a catalyst derivative and amino-terminated methyl orange resulting in the formation of polymeric catalysts, including a colored "phase tag". A variety of examples describing the attachment of azo dyes to preformed polymers have been published. (Ego *et al*., 2003).

2.9.1 Application of dye containing polymer

i. **Waste Water Treatment:** Polymers are not only used for waste water purification processes with dye pollutants. Due to the dyes' affinity to polymers and several low-molecular compounds, or rather metal ions, dye-containing polymers can be used for the detection and determination of metal pollutants in industrial waste waters. The increasing use of lead in industry causes a high contamination of effluent and therefore produces hazards to human health. Early studies revealed the high selectivity of specific anthraquinone derivatives to lead ions. Correspondingly, anthraquinone based poly(vinyl chloride) (PVC) membranes in which the anthraquinone is covalently attached to the polymer are of great value for lead determination in waste water.

ii. **Paintings and Textiles*:*** The best-known applications of dyes for hundreds of years are painting and colorization of textiles. These applications refer more to the color

impression of the compounds than the chemical characteristics, whereby every dye class like azo, anthraquinone, indigo and triphenylmethane is represented. Most dyeing processes are restricted to non-covalent attachment to textile fibers like nylon, wool, silk and cotton. Covalent dye-polymer systems are also known, often offering even better characteristics. The most important dye-polymer systems in textile industry and paintings are described below. Indigo is known as one of the oldest natural dyes in the world, having been used for more than 5000 years in the painting and textile industry. Due to its low solubility in most solvents, the applications are limited in terms of use as a vat dye and pigment. Regardless, polymeric indigo derivatives are known that show a high resistance towards heat and solvents due to their low solubility and stability. Therefore, they can be used as high quality fibers and films. Nowadays, indigo is still used for blue jeans but has been gradually replaced by different dye classes with diversified colors A much higher fastness to light, washing and solvents can be achieved by using polymer-linked dyes. Anthraquinone can be modified to enable the synthesis of dye-containing polyamides, polyesters, polyureas or poly (acrylonitrile). These polymers can show both a certain color impression and improved properties such as enhanced thermal stability

iii. **Medicine**: Dyes play an important role in medical applications because of both their physicochemical properties and color impression. Since this often involves applications inside the human body, it is quite important to use non-toxic derivatives. To skirt that problem, polymers are a good alternative to low-molecular dyes for *in vivo* applications like polymer-linked water-soluble rylene dyes for staining. Perylene-dicarboxmonoimide, perylene-tetracarboxdiimide and benzoylterrylen-3,4-dicarboximid were modified with a single poly(ethylene oxide) chain to obtain polymeric rylene dyes which are suitable for

staining cellular membranes (Chinese hamster ovarian cell line, bronchial carcinoma cell line and ovarian carcinoma cell line). The special feature of these polymeric materials is their ability to indicate the polarity of their environment due to their high fluorescence in nonpolar solvents and a much lower fluorescence in polar medium caused by aggregation (Xie *et al*., 1993). Another can be found in *in vivo* application of polymer-attached dyes in medicine whivh could be the therapy of rheumatoid arthritis. In this case the dye is instead needed for polymer tracking in the body, as it is used as a fluorescence dye.

iv. **Photochemistry**: Azo dyes are one of the most important dye classes in the world since many of them exhibit nonlinear optical characteristics, liquid crystallinity, light-induced dichroism, and birefringence . These properties are complemented by their ability to switch from the more stable *trans*-configuration into the *cis*-configuration upon exposure to UV-radiation or visible light. Therefore, they find various applications in photochemistry such as optical storage devices. The azo dye was functionalized with a polymerizable maleimide group and copolymerized with styrene to yield an active layer with rewritable flash memory performance (Liu et al., 2011). Additional, cross-linked azo-polymers are known; however, cross-linking seems to depress the azo groups' isomerization ability. Azo dye doped polymers like poly(methyl methacrylate) can also be used as optical data storage media. Another advantage of azo polymers is their nonlinear optical behavior. Therefore, they can be used as modulators or optical frequency doublers and switches while showing good mechanical characteristics and processability. Polymers used for the preparation of nonlinear optical azopolymers are amongst others—polyacrylates, polyesters and polysilanes.

v. **Optical Sensors*:*** Besides medicine, paintings, waste water treatment, and photochemistry, polymer-attached dyes have various other applications, for instance in electrochemistry or chemical research. One example of polymer-attached dyes, which refer to the optical characteristics of the dye, is polymer-attached phenolphthalein that can be used as pH-sensitive material for analytical purposes. The triphenylmethane-based indicator dye phenolphthalein is colorless within a pH range of 0–8.2 and turns violet at higher pH values.

vi. **Electrochemical and Optoelectronic Applications*:*** Another application of dye-containing polymers in electrochemistry is the coating of electrodes with polypyrrole films and use of indigo carmine as the counter ion. Polypyrrole is a conducting polymer with the advantages of good stability and simple preparation. Therefore, it can be used as a modified electrode for a biosensor, electrocatalyst or electrochemically controlled release device. Incorporating indigo-carmine as a counter ion is advantageous due to its good electroactivity and optical properties, as it is a redox indicator, which shows a color change in redox reactions (Natansohn *et al.,* 2002). A quite new field of interest in polymers combined with dyes is organic light-emitting diodes (OLEDs) or rather polymer light-emitting diodes (PLEDs), which can be used as a full-color, high-efficiency and low-drive voltage material for flat-panel displays. These polymers are required to be uniform and smooth amorphous films without exhibiting pinholes and to be thermally stable without crystallizing. These diodes use two electrodes between which one or more semiconducting organic layers with either fluorescence or phosphorescence capability are placed. The advantages of using, for example, polymer-attached dyes instead of inorganic LEDs are the low costs of production, their good processability and

their high chemical and electrical stability. Furthermore, the optical and electrical properties can be changed easily by modifying the polymer structure. For example, perylene-containing polyfluorenes can be obtained through copolymerization and the emission color can be tuned over the whole visible region by synthesizing either main-chain copolymers or attaching the perylene dye to the polymer backbone as a side-chain or endcapping group. (Song *et al*., 2009).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Chemicals and Reagent

Analytical grade reagents and chemicals from Sigma Aldrich were used for this research work, These include; o-Acetoacetanilide, N-(2,4-dimethylphenyl)-3-oxobutyramide, N,N-dimethylaniline, p-N,N-dimethylaminobenzaldehyde, malononitrile, morpholine, propionic acid, acetic acid, dimethylformamide (DMF), dimethylsulfoxide (DMSO), sodium nitrite, concentrated sulphuric acid, concentrated hydrochloric acid, ammonium persulfate, ammonium hydroxide, absolute ethanol, sulphanilic acid, aniline, urea, sodium hydroxide, sodium carbonate, tetrahydrofuran, butyl lithium, n-hexane, ethylacetate and ethanol, mueller hinton agar, potato dextrose agar, nutrient agar. These chemicals and reagents were used without further purification.

3.1.1 Materials and Equipment

Magnetic stirrer, oven, reflux condenser, melting point apparatus, Agilent Uv-visible spectrophotometer, Agilent Fourier transform infra-red spectrophotometer, Agilent GC-MS, conductivity meter set up, autoclave, incubator, compound microscope, culture media, starch indicator, inductance capacitor resistance (LCR meter), micrometer screw guage

3.2 Synthesis of Aminothiophene Intermediates

3.2.1 Aminothiophene Intermediate 1.

Acetoacetanilide (21.16 g, 0.1 mol), malononitrile (6.96 g, 0.1 mol) and sulphur (3.37 g, 0.1 mol) in ethanol were stirred in the presence of morpholine (8.97 g, 0.1 mol) at 60-70 °C for 3 hrs. The resulting thick dark solution was then cooled and stored overnight in a refrigerator,

followed by filtration, washing with ethanol and then ethanol/water (1:1) solution and was dried. The light brown powder obtained was recrystallized from ethanol.

3.2.2 Aminothiophene Intermediate 2

N-(2,4-dimethylphenyl)-3-oxo-butyramide (20.72 g, 0.1 mol), malononitrile (6.96 g, 0.1 mol) and sulphur (3.37 g, 0.1 mol) in ethanol were stirred in the presence of morpholine (8.7 g, 0.1 mol) at 60-70 °C for 3 hrs. The resulting thick dark solution was then cooled and stored overnight in a refrigerator, followed by filtration, washing with ethanol and then ethanol/water solution and dried. The dark brown obtained powder was recrystallized from ethanol.

3.2.3 Purification of the Intermediate

All the aminothiophene intermediates were purified by three to four recrystallization from ethanol. A known weight of the intermediate was dissolved in small quantity of ethanol and heated up. It was then filtered off while hot using in buchner funnel with a suction pump. The crystals were collected, washed several times with water and dried**.**

3.3 Procedure for Diazotization

Sodium nitrite (1.38 g, 0.02 mol) was added in portions to 10ml of concentrated sulphuric acid at 10 °C with stirring for 15 min. The solution was then cooled to 5 °C and 20 ml mixture of acetic acid and propionic acid (17:3) was then added to the mixture. The aminothiophene intermediate 1 (5.14 g, 0.02 mol) was added within 30 min below 5 °C and the whole mixture was stirred at 0-5 °C for 3 hrs. This was repeated for intermediate 2 with (5.70 g, 0.02 mol).

3.3.1 Diazotization of Sulfanilic Acid Intermediate

Sulphanilic acid (3.5 g, 0.02 mol) was dissolved in aqueous NaOH (30 ml, 0.02 mol). The solution was then cooled in an ice bath. A solution of sodium nitrite (50 ml, 0.02 mol) and

10 ml concentrated HCl was then added drop- wise on an ice-bath with continuous stiring for 30 min to form the diazonium salt.

3.3.2 Coupling Reaction

The coupling components, N,N-dimethylaniline and p-N,N-dimethylaminobenzaldehyde were dissolved separately in acetic acid and cooled to 0 °C by adding ice. The diazonium solutions of the intermediate 1 and 2 were then added separately for 30-40 min with vigorous stirring (Maradiya and Patel, 2010). The mixture was stirred further for 3 hrs, under 5 °C and the pH of the solution was adjusted to 4-5 using 5 ml of 10 % NaOH. The resulting product was filtered, washed with water and dried. The crude product was purified by recrystallizing it from ethanol and DMF of ratio 9:1 .

3.3.3 Purification of the Dyes

A known weight of the dyes were dissolved in small quantity of ethanol and heated up. It was then filtered off while hot using buchner funnel with a suction pump. However, dyes from intermediate 1 and 2 required the mixed solvent of ethanol/DMF (9:1 solvent mixture) according to procedure suggested by Alaa and Tarek, (2006).

3.4 Synthesis of Polyaniline

Polyaniline was synthesized according to the method of (Krzysztof, 2006). Ammonium persulfate (22.8g, 1mol) was dissolved in 100 ml of 1 M HCl acid in a 500 ml beaker and kept at room temperature. Aniline (9 ml) was dissolved in 100 ml of 1 M HCl acid solution in another 500 ml beaker and also kept at room temperature. The polymerization was initiated by dropwise addition of ammonium persulfate as an oxidizing agent to the acidified solution containing the aniline monomer under an ice-bath at constant stiring for 2 hrs. Thus, after completion of the polymerization reaction the blue-coloured polyaniline was isolated by filtration and was washed

with distilled water and acetone until the filtrate becomes colourless to ensure the complete removal of unreacted reagent. The pure polyaniline synthesized by this method was found to be dark green in colour after washing. The precipitate was then allowed to equilibrate with 20 ml of ammonia solution overnight to convert the polyaniline to its emeraldine base (EB) and was dried in the oven at 90 °C for 24 hrs.

3.4.1 Synthesis of Polyaniline Substituted Azo Dyes

The emeraldine base of hydrochloric acid doped polyaniline (1.0 g) was dissolved in 30 ml tetrahydrofuran (THF). The solution was allowed to cool to 0 °C and 2 ml of BuLi was added with stirring. The colour of the solution changed from dark green to green black due to the formation of lithium salt of polyaniline. In a dry conical flask Dye A (0.025 g) was dissolved in 10 ml THF. The solution of the dye was then added to the solution of the lithium salt of polyaniline which was then stirred at room temperature for 24 hrs. This procedure was then repeated with dyes A1, B and dye C solution. The colour of the solution turned black due to the formation of black precipitate. The precipitate was filtered and washed with acetone and ethanol to remove residual amount of unreacted dye.

3.5 Determination of percentage Yield of the Intermediates and Dyes

The percentage yield of the dyes and intermediates were determined using the formula shown below:

$$\%\, Yield = \frac{MP}{MMP} \div \frac{MR}{MMR} \times 100$$

MP is the mass of the product

MMP is the molar mass of the product

MR is the mass of the reactant

MMR is the molar mass of the reactant.

3.6 Characterization of the Intermediates and Polyaniline Substituted Dyes

The intermediates, synthesized dyes and polyaniline substituted dyes were characterized using UV-visible spectrophotometer, Fourier transform-infra red spectrophotometer and Gas chromatography- mass spectrophotometer . Other tests carried out on the intermediates and dyes were the melting point determination.

3.6.1 Melting Point Determination

The melting points were determined by the open capillary method and are expressed in °C. All the intermediates and the polyaniline substituted dyes were determined using Gallenkamp melting point apparatus. The values obtained are shown in Table 4.1, 4.2 and 4.3

3.6.2 Determination of Visible Absorption Spectroscopy.

Visible absorption spectra were recorded on Agilent UV-visible spectrophotometer. 0.01 g of the dyes was dissolved separately in DMSO and acetone in a cuvete and the wavelength of maximum absorption were taken as described by (Dudley and Lan, 1980). The results are presented in Table 4.4.

3.6.3 Fourier Transform Infrared Spectroscopy

Each of the dyes were thoroughly mixed with KBr, the dried mixture was pressed which resulted into a homogeneous sample disk. The measurement was carried out over the frequency range of 400-4,000 cm^{-1} using the Agilent fourier transform infra-red spectrophotometer to determine the functional groups present (Kassai, 2009). The results are summarized in Table 4.5 and 4.6.

3.6.4 Gas Chromatography-Mass Spectroscopy (GC-MS) of the Synthesized Dyes and Intermediate.

The fragmentation pattern and the relative mass to charge ratio (m/z) of the synthesized dyes and intermediate were determined using Agilent Gas chromatography-mass spectrometer to confirm their relative molecular weight, the result is showed in Table 4.7.

3.7 The Antimicrobial Screening

3.7.1 Test Microorganisms:

The test microorganisms used for this analysis were pure cultures of bacteria and fungi obtained from Department of Microbiology, Ahmadu Bello University, Samaru. Zaria. The isolates were: *Bacillus subtilis, Staphylococcus aureus, Escherichia coli, Salmonella typhi, Candida albicans and Aspergellus niger*.

3.7.2 Culture Media

The culture media used for the analysis includes Mueller hinton agar (MHA), Mueller hinton broth (MHB), Potato dextrose agar (PDA) and Nutrient agar (NA). These media were used for sensitivity test, determination of minimum inhibitory concentration (MIC), and minimum bactericidal/fungicidal concentration (MBC/MFC). All media were prepared according to manufacturer's instructions and sterilized by autoclaving at 121 °C for 15 minutes.

3.7.3 Determination of Inhibitory Activity (Sensitivity Test) of the Synthesized Samples Using Agar Well Diffusion Method

The standardized inucula of both the bacterial and fungal isolates were streaked on sterilized Mueller hinton and potato dextrose agar plates respectively with the aid of a sterile swab sticks. Four wells were punched on each inoculated agar plate with a sterile cork borer. The wells were properly labeled according to different concentrations of the synthesized samples

which were 100, 50, 25 and 12.5 mg/ml respectively. Each well was filled up with 0.2 ml of the sample. The inoculated plates with the sample were allowed to stay on the bench for about 1hour, this is to enable the extract to diffuse on the agar. The plates were then incubated at 37 °C for 24 hour (plates of Mueller hinton agar) while the plates of potato dextrose agar were incubated at room temperature for about 3-5 days. At the end of the incubation period, the plates were observed for any evidence of inhibition which will appear as a clear zone that was completely devoid of growth around the wells (Zone of inhibition). The diameter of the zones was measured using a transparent ruler calibrated in millimeter and the results were recorded.

3.7.4 Determination of Minimum Inhibitory Concentration (MIC).

The minimum inhibitory concentration of the synthesized samples was determined using tube dilution method with the Mueller hinton broth used as diluents (Adeniyi *et al*., 2000). The lowest concentration of the synthesized samples showing inhibition for each organism when the sample was tested during sensitivity test which was serially diluted in the test tubes containing Mueller hinton broth. The organisms were inoculated into each tube containing the broth and the synthesized samples. The inoculated tubes were then incubated at 37 °C for 24 hours. At the end of the incubation period, the tubes were examined/observed for the presence or absence of growth using turbidity as a criterion, the lowest concentration in the series without visible sign of growth (turbidity) was considered to be the minimum inhibitory concentration (MIC). The results are shown in Table 4.7 .

3.7.5 Determination of Minimum Bactericidal/Fungicidal Concentration (MBC/MFC):

The result from the minimum inhibitory concentration (MIC) was used to determine the minimum bactericidal/fungicidal concentration (MBC/MFC) of the synthesized sample. A sterilized wire loop was dipped into the test tubes that did not show turbidity (Clear) in the MIC

test and a loopful was taken and streaked on a sterile nutrient agar plates. The plates were incubated at 37 °C for 18-24 hours. At the end of incubation period , the plates were examined for the presence or absence of growth. This is to determine whether the antimicrobial effects of the synthesized samples is bacteriostatic or bactericidal. (Adeniyi *et al., 2000*). `

3.8 Electrical Conductivity of the Polyaniline substituted dyes

The electrical conductivity measurements were obtained by employing a standard process of (Bekkali, *et al*., 2004). A known amount of sample was pressed into pellets using a Carver Laboratory press. These pellets were then utilized for the measurement of the conductivity of the materials. The thickness and diameter of the sample pallet were measured using a micrometer screw guage. The pellet thickness of about 2.45 mm and the sample cell diameter of about 3.89 cm were held constant for the electrical resistance measurement at a frequency range of 20-100,000 Hz using a programmable LCR meter and the result obtained was used to calculate the electrical conductivity of the samples using the relation below:

$\sigma = l/RA$. Where σ is the electrical conductivity, l is the thickness of the dye pellet (l = 2.45 mm), R is the electrical resistance of the dye pallet and A is the cross-sectional area of the dyes.

But $A = \pi r^2$ where r is the radius of sample pellet obtained from the diameter of the sample pellet

(i.e r = d/2) but d = 3.89 cm hence r = 1.945 cm.Hence :

$A = 3.142 \times (1.945 \times 10^{-2})^2$

$A = 1.1886 \times 10^{-3}\ m^2$

Therefore: $\sigma = 2.45 \times 10^{-3}/R\ (1.1886 \times 10^{-3})$, where R is the resistance value of the synthesized compound measured at different frequency using LCR-meter

3.9 Dyeing the Fabric with Synthesized Dyes

Polyester and Nylon 6,6 fabrics were dyed using the synthesized dyes. The fastness properties of the dyes were examined using standard method.

3.9.1 Application of Dyes

1 % stock solution of each dye was prepared, a aliquot ratio of 50:1 was used, 2 % shade on weight of fabric (o.w.f) and 1 g of fabric each of nylon and polyester. The volume required from each stock solution was calculated based on the formula

$$V = \frac{P \times W}{C}$$

Where:

P = percentage shade

W = weight of fabric

C = percentage concentration of stock solution.

For the polyester a carrier (phenol) and dispersing agent (anionic detergent) was used to facilitate the dyeing process. The fabric was wetted and thoroughly squeezed to remove excess water. It was then immersed into the bath at 40 °C and allowed to reach the boil within 15 minutes. Dyeing was carried out for one hour at a temperature of 100 °C with agitation. At the end of the dyeing process the substrate was removed, squeezed and rinsed thoroughly under running tap and allowed to dry at room temperature (Giles and Rahman, 1992; Nkeoye, 1987; Burkinshaw, 1994).

3.9.2 Measurement of Dye Exhaustion

Dye uptake was determined by measuring the absorbance of diluted dyebath samples at the wavelength of maximum absorption of each dye. The bath was sampled before and after dyeing. A 1ml aliquote was taken from the bath and diluted in 20 ml acetone. This is to ensure

that the absorbance falls within the readable range of 1.5. The percentage of dyebath exhaustion (%E) was calculated using the equation below, (Jae-Hong Choi *et.al*., 2008; Ozan *et.al*., 2006).

$$\%E = \frac{A_{\circ} - Ai}{A_{\circ}} \times 100$$

where A_o and A_i are the absorbance at ʎmax of the dyebath prior to dyeing and after dyeing respectively.

3.10 Measurement of Fastness Properties

3.10.1 Wash Fastness Test

The dyed samples were subjected to I.S.O.2 wash fastness test by the following procedures: The specimens were prepared by cutting the dyed fabrics into 5cm x 2cm dimensions; they were then made into composites by stitching the test specimen made of the dyed sample place in between white cotton of dimensions 10cmx4cm. The composite was agitated in solution made up of the following:

Soap solution 5 g/l

Liquor ratio 50:1

The washing was maintained at 50 °C for 45 minutes with continuous agitation in the automated test machine. At the end of the washing test the composite specimen was rinsed in cold water, squeezed to remove excess water and dried. The change in colour of the dyed samples and the staining of adjacent undyed cloths were assessed using the standard grey scale and the results are shown in Table 4.12 and 4.13. (SDC, 1965).

3.10.2 Light Fastness Test (Nunn, 1979)

The dyed samples and blue wool standard were exposed facing due south and inclined at an angle to the horizontal approximately equal to the latitude of the place where the exposure is being made. Adequate ventilation of the samples during exposure was ensured. The partly

covered samples were exposed to Ultra-violet radiation. As exposure proceeded for 3days , the samples under test and the blue wool standard were examined at interval and the change in colour of the samples compared visually with the changes that occur in the standards. The light fastness of the sample is the number of the standard that shows a similar visual contrast between the exposed and unexposed part of the samples. The exposure was terminated when the blue wool standard seven fades or when fully exposed and non-exposed test samples is equivalent to grade 3 on the grey scale. The result are shown in Table 4.12 and 4.13

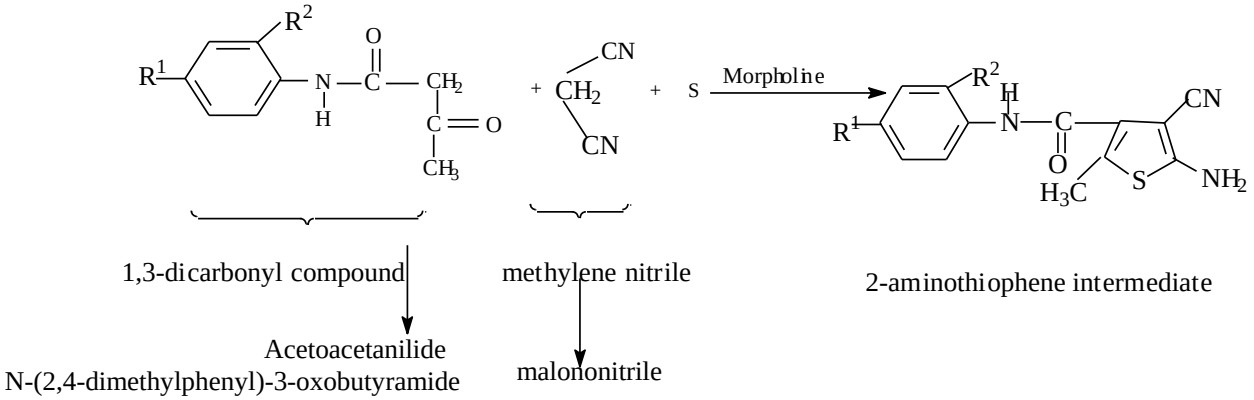
CHAPTER FOUR

4.0 RESULTS

4.1 Physicochemical Properties of the Synthesized Intermediate and Polyaniline Substituted Dyes

4.1.1 Synthesis of the Aminothiophene Intermediates

The aminothiophene intermediate 1 and 2 was synthesized by following the methods reported in the literature by (Alaa and Tarek, 2006). In these study, aminothiophene intermediate 1 and 2 were prepared using the Gewald's methodology. This convenient methodology includes the condensation of the 1,3-dicarbonyl compound such as acetoacetanilide and N-(2,4-dimethylphenyl)-3-oxobutyramide with an α-methylene nitriles which is malononitrile in the presence of sulphur in ethanol. As shown in the equation below:



Equation 4.1:Synthesis of aminothiophene intermediate

3.3.1 Structures of Synthesized Intermediate

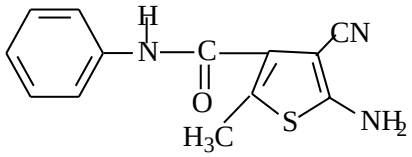


Fig 4.1: Intermediate 1

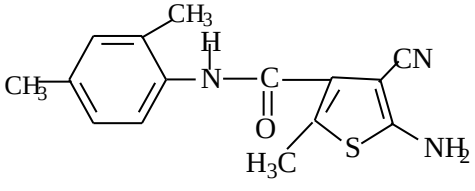


Fig 4.2: Intermediate 2

4.1.2 Physical Properties of the Synthesized Intermediates

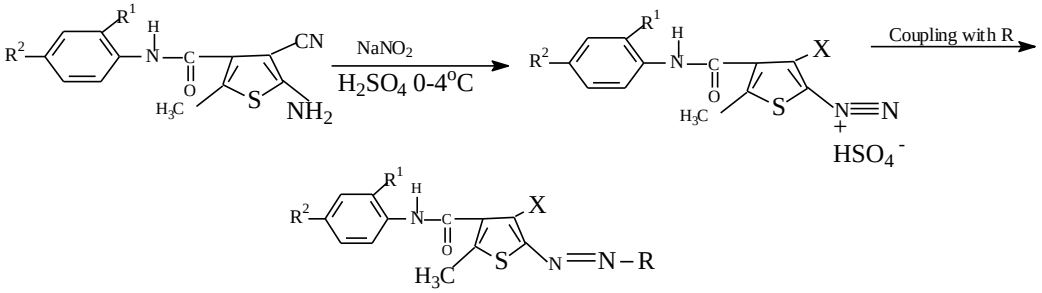
The result from Table 4.1 shows the colour of the diazo compounds ranges from brown to dark brown for the intermediate 1 and 2 respectively. The theoretical molecular mass of the intermediates were calculated to span from 257-285 g/mol while the melting point were 168-204 °C.

Table 4.1: Physical Properties of Aminothiophene Intermediates

Intermediate	Molecular formular	Molecular weight g/mol	Melting point °C	% Yield	Colour of the crystal
1	$C_{13}H_{11}N_3OS$	257	199-204	47	Brown
2	$C_{15}H_{15}N_3OS$	285	168-171	51	Dark brown

4.1.3 Synthetic Routes of the Azo Dyes

The azo dyes were synthesized by diazotization of the intermediates 1 and 2 with nitrosyl sulphuric acid generated in-situ by the reaction of sodium nitrite and conc sulphuric acid in an ice-bath and was coupled with N,N- dimethylaniline and p-N,N-dimethylaminobenzaldehyde as shown in the scheme below:



Scheme 4.1: Diazotization and Coupling of 2-aminothiophene.

where R^1 and R^2 are H for the intermediate 1, CH_3 for the intermediate 2 and R is the coupling component shown below:

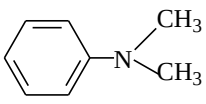


Fig 4.3:N,N-dimethylaniline

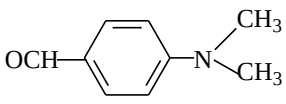


Fig 4.4: P-N,N-dimethylaminobenzaldehyde

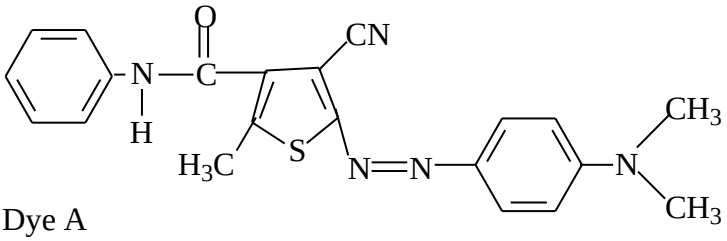
However, sulphanilic acid was diazotized via a direct method of diazotization with nitrosonium ion generated in-situ by reacting sodium nitrite and concentrated hydrochloric acid in an ice-bath as shown in the equation below:



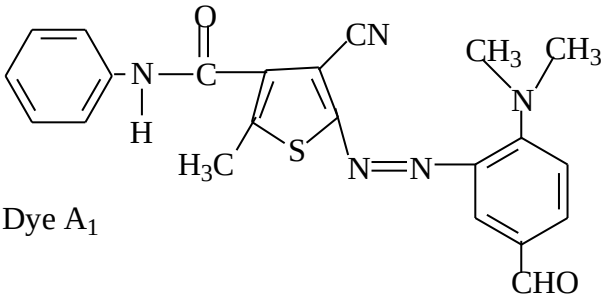
Sulphanilic acid Diazonium salt of sulphanilic acid

Equation 4.2 : Diazotization of sulphanilic amine

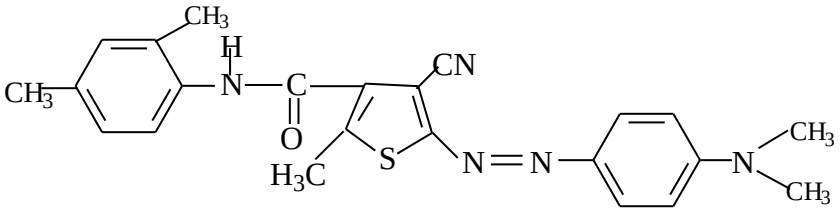
4.1.4 Structures of the Synthesized Dyes



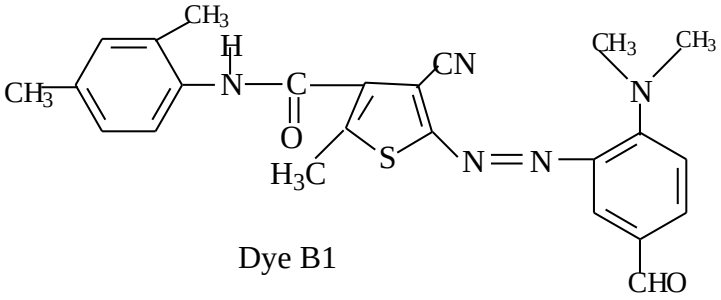
Dye A



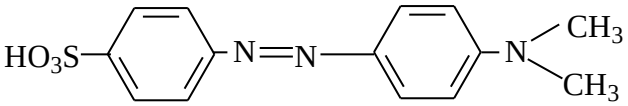
Dye A_1



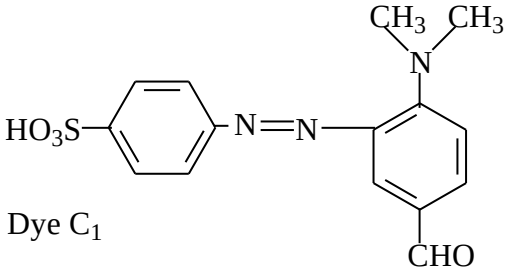
Dye B



Dye B1



Dye C



Dye C_1

Figure 4.5: Structures of the synthesized dyes

4.1.5 Physical Properties of the Synthesized Dyes

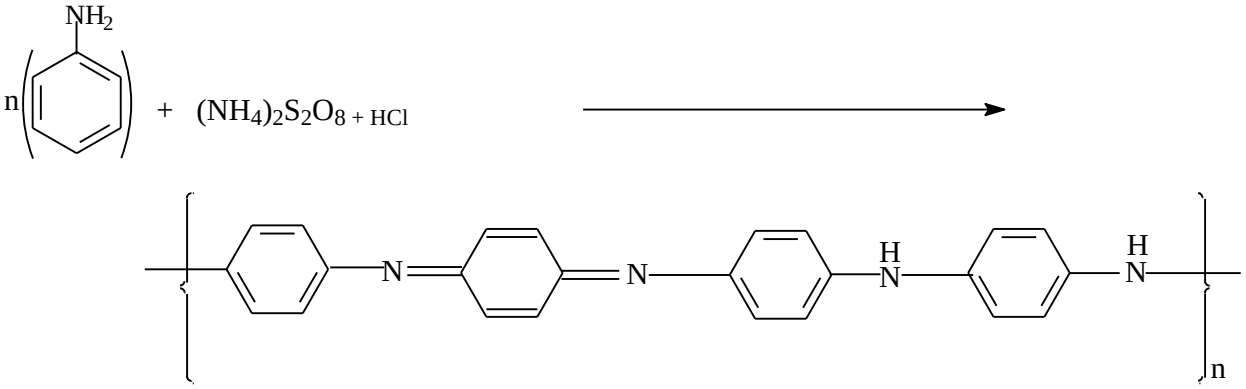
The result from Table 4.2 shows the physical properties of the dyes with the colour of the dyes crystals ranging from red to dark magenta, percentage yield ranging from 31.50-74.63 %, the molar mass for the dyes was also calculated to span from 305-445 g/mol and there melting point were also determined to span from 167-209 °C.

Table 4.2: Physical Properties of the Synthesized Dyes

Dyes	Molecular formular	Molecular weight (g/mol)	Melting point(°C)	%Yield	Colour of the dyes
A	$C_{21}H_{19}N_5OS$	389	204-209	58	Dark magenta
A1	$C_{22}H_{19}N_5O_2S$	417	201--205	41	Margenta
B	$C_{23}H_{23}N_5OS$	417	174-178	42	Maroon
B1	$C_{24}H_{23}N_5O_2S$	445	167-170	31.5	Dark purple
C	$C_{14}H_{15}N_3O_3S$	305	180-183	74.63	Deep red
C1	$C_{15}H_{14}N_3O_4S$	332	187-191	62	Red

4.1.6 Synthesis of Polyaniline

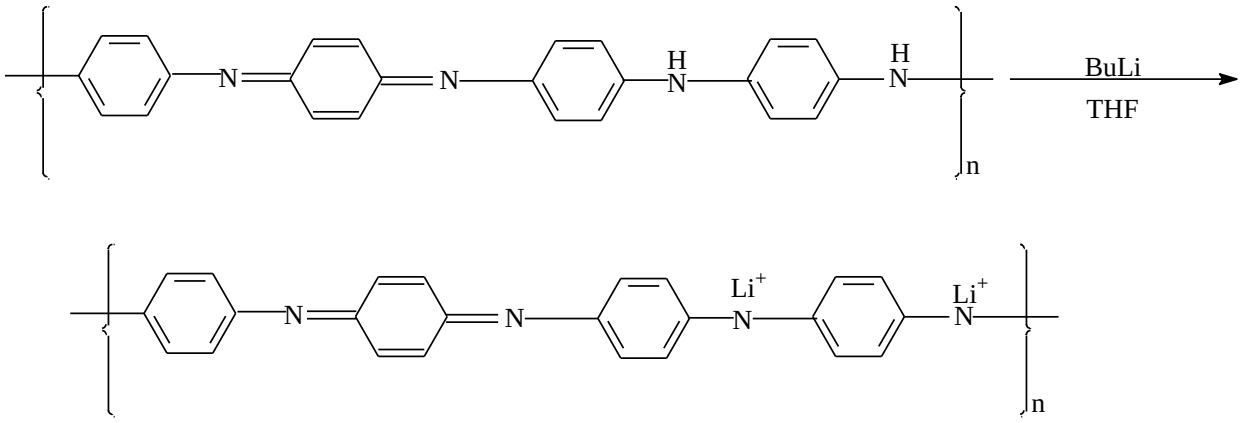
The polyaniline was synthesized by oxidative polymerization of aniline in the presence of ammonium persulfate acting as the oxidant and hydrochloric acid which served as the dopant, as shown in the equation below:



Equation 4.3: Synthesis of polyaniline (PANI-HCl) using HCl as the dopant

4.1.7 Synthesis of Lithium Salt of Polyaniline

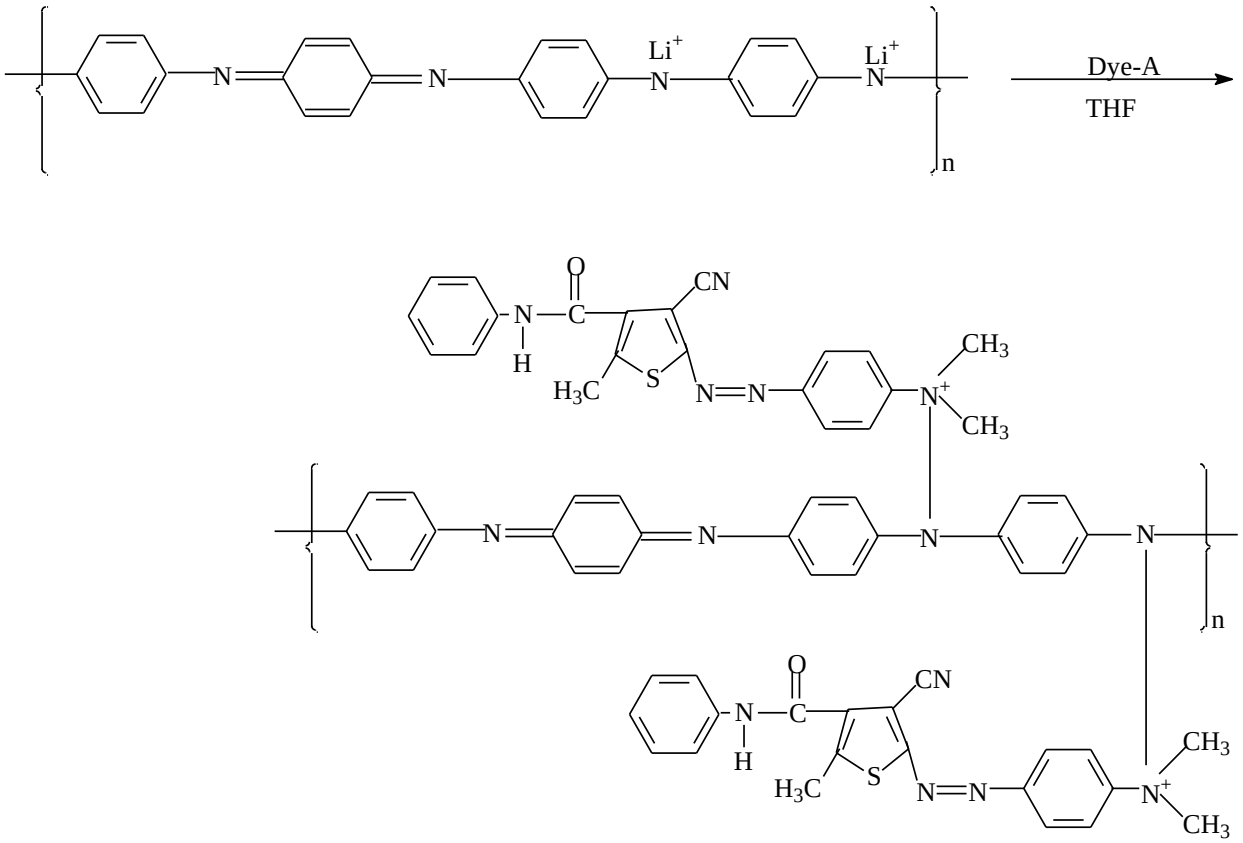
Lithium salt of polyaniline was synthesized in order to convert the polyaniline to its salt form and was obtained by dissolving polyaniline in tetrahydrofuran and reacting it with butyl lithium, as shown in the equation below:



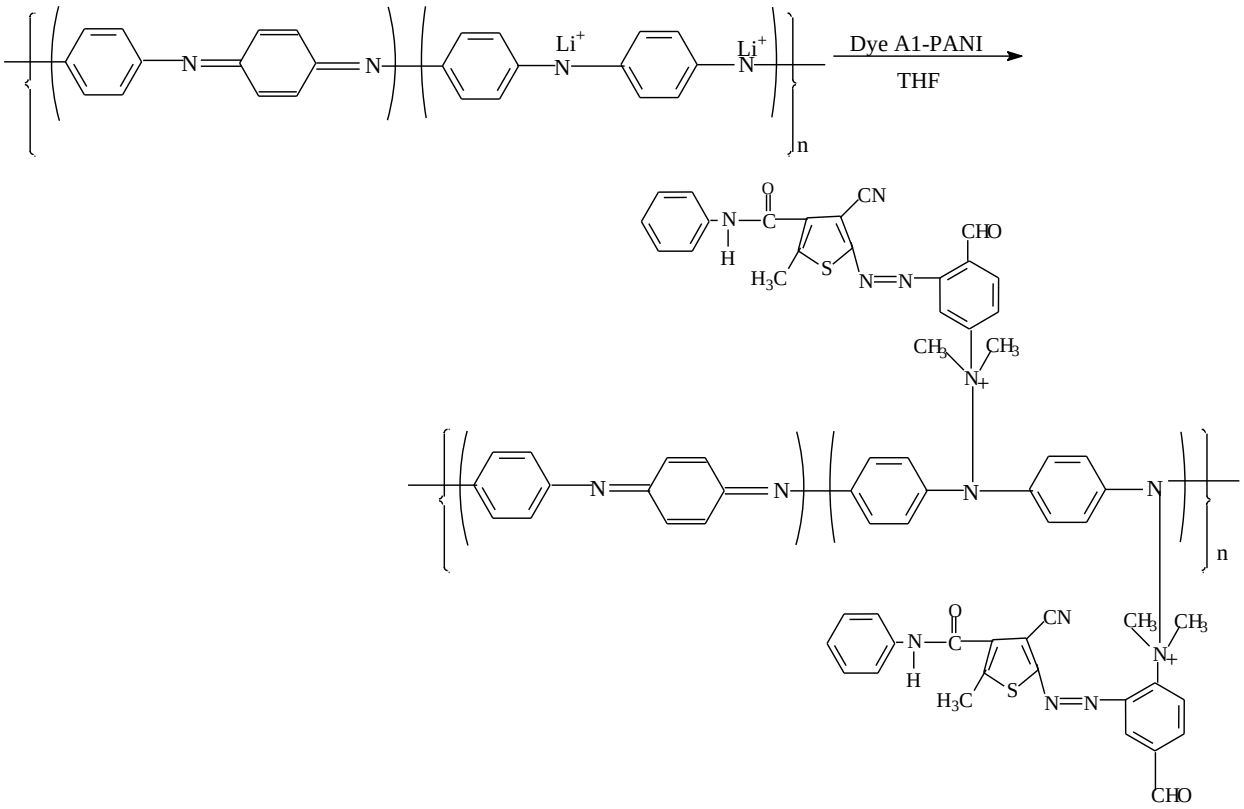
Equation 4.4: Synthesis of lithium salt of polyaniline

4.1.8 Synthesis of Polyaniline Substituted Dyes

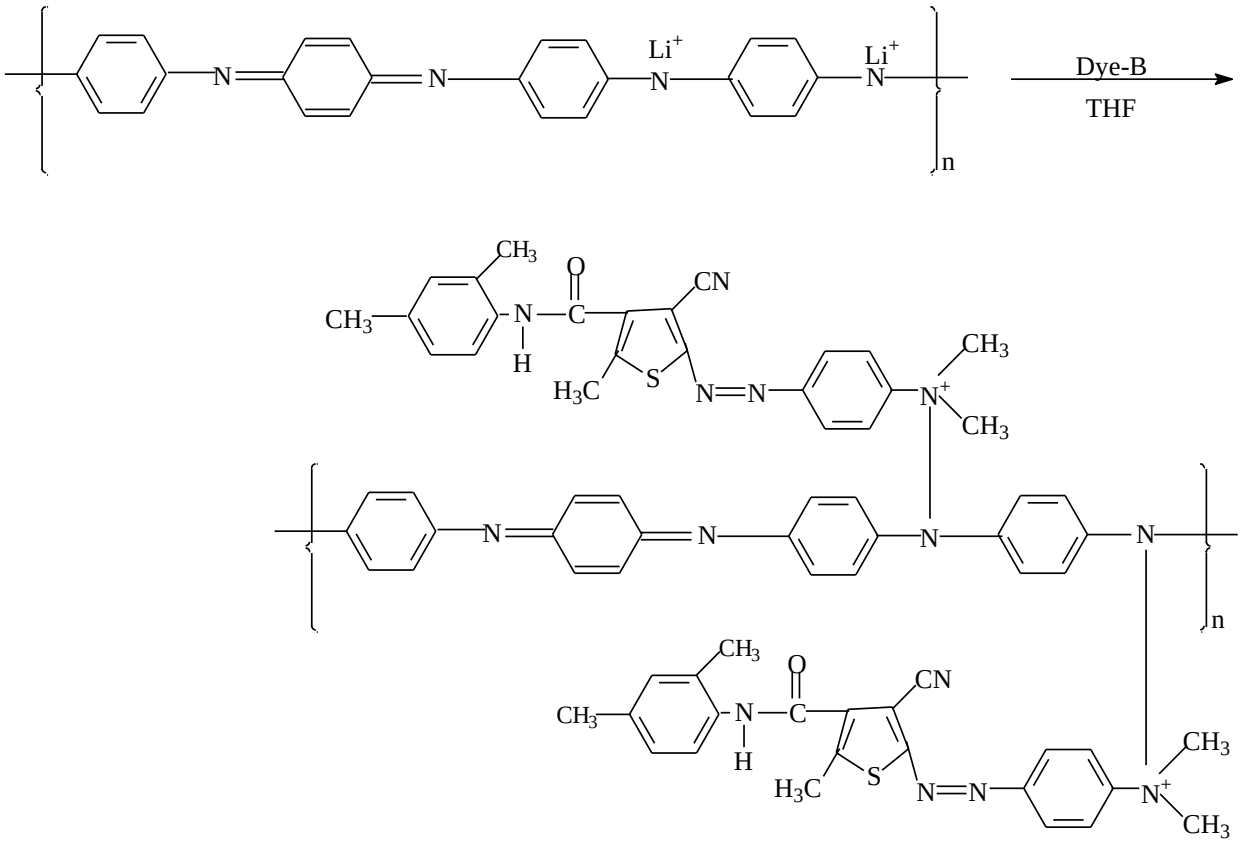
Polyaniline substituted dyes were synthesized by cross-linking the lithium salt of the polyaniline with the dyes at room temperature for 24 hrs and the result obtained shows the emplacement of the dyes moiety on the polyaniline backbones, as shown in the equations below:



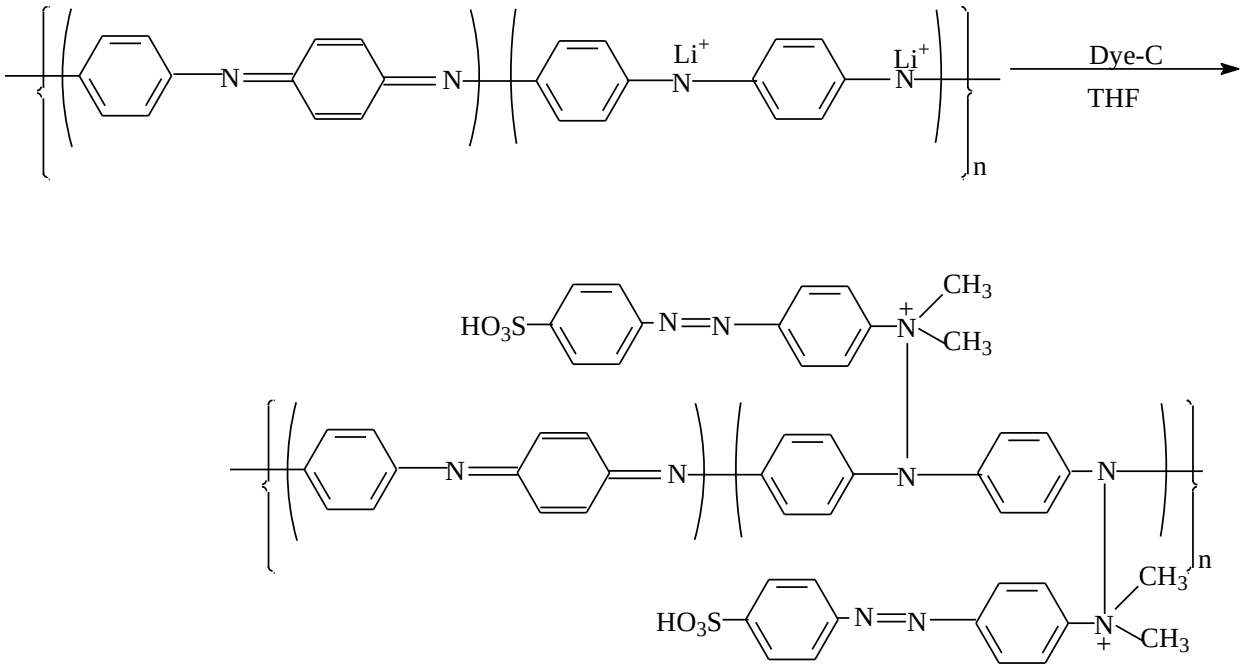
Equation 4.5: Synthesis of polyaniline substituted dye A (Dye A-PANI)



Equation 4.6: Synthesis of polyaniline substituted dye A1 (Dye A1-PANI)



Equation 4.7: Synthesis of polyaniline substituted dye B (Dye B-PANI)



Equation 4.8: Synthesis of polyaniline substituted dye C (Dye C-PANI)

4.1.9 Physical Properties of the Synthesized Polyaniline Substituted Dyes

The melting point, percentage yield, and colour of the synthesized polyaniline substituted dyes are shown in Table 4.3 and from the results the melting point of polyaniline, Dye A-PANI, and Dye C-PANI span from 280-293 °C while the decomposition temperature for Dye A1 and Dye-B-PANI are in the range of 306-319d °C. Also, the percentage yield are the range of 63.16-87 %

.

Table 4.3: Physical Properties of the Synthesized Polyaniline Substituted Dyes

Dye-PANI	Molecular formula	Melting point(°C)	% Yield	Colour of the crystals
PANI	$(C_{24}H_{18}N_4)_n$	290-293	80.12	Black
A	$(C_{24}H_{18}N_4)_n$. $C_{42}H_{38}N_{10}O_2S_2$	286-290	87	Dark purple
A1	$(C_{24}H_{18}N_4)_n$. $C_{44}H_{38}N_{10}O_2S_2$	306-310d	75.08	Black
B	$(C_{24}H_{18}N_4)_n$. $C_{46}H_{46}N_{10}O_2S_2$	314-319d	63.16	Dark purple
C	$(C_{24}H_{18}N_4)_n$. $C_{28}H_{30}N_6O_6S_2$	280-284	70	Black

4.2 Visible Absorption of the Synthesized Polyaniline Substituted Dyes

The result of wavelength of maximum absorption (ʎmax) of the synthesized polyaniline substituted dyes in acetone and dimethylsulfoxide (DMSO) solvent are shown in Table 4.4 and from the results the wavelength of maximum absorption of the dyes ranges from 429-560 nm in DMSO and 416-542 nm in acetone while the wavelength of maximum absorption of the polyaniline substituted dyes range from 518-587 nm in DMSO and 511-553 nm in acetone.

Table 4.4 :Visible Absorption Spectral of the Synthesized Polyaniline Substituted Dyes

	λmax in Acetone and Dimethylsulfoxide (DMSO) Solvent (nm)		
Dyes	**Acetone**	**DMSO**	**Molar Extinction Coeficient ($lmol^{-1}$ cm^{-1})**
A	536	540	248,000
A1	536	553	192,434
B	542	560	148,521
B1	520	553	134,374
C	416	429	26,183
C1	421	429	27,139
Dye A-PANI	537	559	
Dye A1-PANI	553	587	
Dye B-PANI	552	576	
Dye C-PANI	511	518	

4.3 The Infra-Red Absorption of the Synthesized Intermediate and Dyes

Table 4.5 shows the IR-vibrational frequencies of the synthesized dyes and its intermediates and the result obtained indicates that aminothiophene intermediate 1 and 2 show absorption peaks in the range 2199-2206 cm^{-1} due to the presence of cyano group .The amino group absorption for the two intermediate appeared in the range 3198-3421.7cm^{-1} while the carbonyl absorption showed up in the range 1602-1695 cm^{-1}. However, the vibrational frequency obtained for the synthesized dyes shows the characteristics absorption peaks due to stretching frequency of the NH-group in the region 3097-3365 cm^{-1}. An absorption peak in the region 2217.8, 2221.5, 2214.0, 2206.6 cm^{-1} was observed for dye A, A1, B and B1 due to the presence

of cyano group. The IR spectra of the prepared azo dye also showed an absorption peak in the region 1438.8-1599 cm^{-1} attributed to $V_{N=N,}$ while the observed peak in the region 1602.8-1736.9 was due to $V_{C=O.}$

Table 4.5: IR-Vibrational Frequecies of the Synthesized Dyes and Intermediates

Intermediate and Dyes	IR Vmax (cm^{-1})
Intermediate 1	3421.7,3276.3(NH), 2199(CN), 1625,1662,1695(C=O)
Intermediates 2	3354,3317,3198(NH), 2206(CN), 1647,1631,1602(C=O)
Dye A	3309(NH), 2217.8(CN), 1666.1,1695.9(C=O), 1528(N=N)
Dye A1	3328(NH), 2221.5(CN), 1736.9,1602.8,1662(C=O), 1528.2(N=N)
Dye B	3369.5(NH), 2214.0(CN), 1651.2(C=O), 1498,1438.8(N=N)
Dye B1	3313.6,3354.6(NH),CN(2206.6),1651.2(C=O),1599.0,1520.8(N=N)
Dye C	3220,3097(NH), 2803.0(CH), 1599,1543(N=N)
Dye C1	3365(NH),1654.9(C=O), 1513.3(N=N

4.3.1 The Infra-Red Absorption of the Synthesized Polyaniline Substituted Dyes

The band 1479 and 1584 cm^{-1} are related to the stretching of the C-N bonds of the benzenoid and quinoid rings, respectively, while the broad band 3220.4 cm^{-1} is assigned to the N-H stretching vibration of amine group and the peak C-H-stretching vibration is 2922.2 and 2780 cm^{-1}. However, the IR-vibrational frequencies of the polyaniline substituted dyes shows an absorption peaks due to stretching frequency of the NH group in the region 3213-3242.8cm^{-1}. An absorption peak in the region 1461-1487 due to the presence of C-C stretch of the benzeniod ring while 1580-1595 cm^{-1} was due to the presence of C=C stretch of the quinoid rings and the absorption peak in the region 1263-1285 cm^{-1} which is attributed to V_{C-N} stretching. Comparing

to polyaniline some shifted band in the spectra of polyaniline substituted dyes were observed as shown in Table 4.6 below:

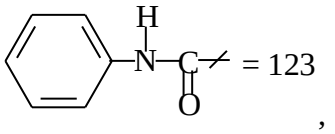
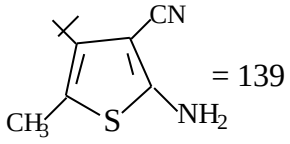
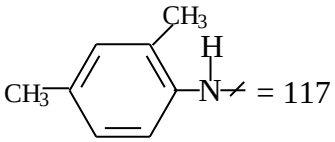
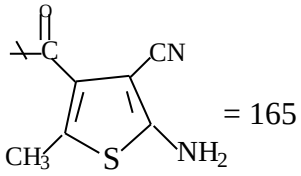
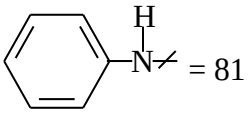
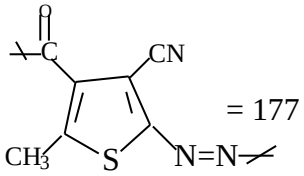
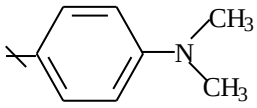
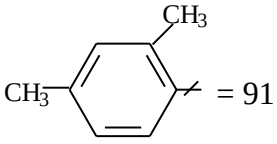
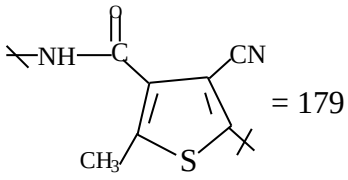
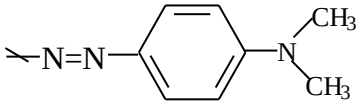
Table 4.6: IR-Vibrational Frequencies of Synthesized Polyaniline Substituted Dyes

	Observed Frequencies of Synthesized Polyaniline Substituted Dyes (cm^{-1})				
Vibrational Mode	**PANI**	**Dye A-PANI**	**Dye A1-PANI**	**Dye B-PANI**	**Dye C-PANI**
Para-substituted	797, 764	790	764	790	797, 765
Benzenoid ring	1479	1461.1	1487	1461.1	1479
Quinoid ring	1584	1580.4	1595, 1543	1580.4	1580
C-H- Stretching	2922.2, 2780	2877.5	2922.2	2877.5	2952.1
N-H- Stretching	3220.4	3213.0, 3056.4	3220.4	3220.4, 3052.7	3242.8
C-N- Stretching	1289, 1118.2	1282.2	1263.6, 1230	1282.2	1285, 1140

4.4 GC-MS Spectra of the synthesized intermediates and Dyes

The result from Table 4.7 showed the fragmentation of the intermediates and dyes and their respective mass (m/z), thus intermediate 1 and 2 showed intense molecular ion peaks at 259 ± 2 and 282 ± 3. The molecular ion of the intermediates 1 underwent fragmentations to produce peaks at m/z 140 and 123 while intermediates 2 produce peakes at m/z 117 and 165 respectively. However, dye A and B showed intense molecular ion peaks at m/z 394.2 ± 5 and 414.6 ± 3. Thus, dye A produces fragments with peaks at m/z 81.1, 177 and 129 respectively while dye B produces fragment with peaks at m/z 91, 179 and 149 respectively.

Table 4.7: GC-MS Spectra of the synthesized intermediates and Dyes

Intermediate/Dyes	Mass (m/z)
Intermediate 1	 = 123,  = 139
Intermediate 2	 = 117,  = 165
Dye A	 = 81,  = 177,  = 129
Dye B	 = 91,  = 179,  = 149

4.5 Antimicrobial Screening of the Synthesized Polyaniline Substituted Dyes

The results from Table 4.8 shows that all the synthesized polyaniline substituted dyes have various inhibitory effect against test microorganism as compared to with zone of inhibition ranging from 10-34 mm. From the result above the best activity was shown by the dye A-PANI against Staphylococcus aureus and Escherichia coli with zone of inhibition of 32 and 34 mm respectively, followed by dye A1-PANI, dye B-PANI and dye C-PANI with maximum zone of inhibition of 31, 29, and 26 mm respectively. Thus, as low as MIC value 12.5mg/ml and MBC/MFC value of 12.5mg/ml of the polyaniline substituted dye A had biostitic and biocidal effect against Staphylococcus aureus and Escherichia coli as shown in Table 4.9 and 4.10 respectively.

Table 4.8: Zone of Inhibition (Diameter) of the Synthesized Polyaniline Substituted Dyes Against Test Microorganism (mm)

Test Organism	PANI	Dye A	Dye A1	Dye B	Dye C	Dye A-PANI	Dye A1-PANI	Dye B-PANI	Dye C-PANI	Cipro	Fluco
Staphylococcus aureus	14	18	20	16	14	32	25	29	26	35	0
Salmonella typhi	17	20	15	20	16	30	31	26	23	38	0
Bacillus subtilis	0	14	11	10	13	24	27	18	14	32	0
Escherichia coli	20	20	15	21	20	34	31	26	25	37	0
Candida albican	0	9	6	7	3	23	25	18	14	0	30
Aspergillus niger	10	7	9	10	0	17	19	20	0	0	32

Key: Cipro = Ciprofloxacin

Fluco = Fluconazole

Table 4.9: Minimum Inhibition Concentration of the Synthesized Polyaniline Substituted Dyes Against Test Microorganism (mg/ml)

Test Organism	PANI	DYE A	DYE A1	DYE B	DYE C	DYE A-PANI	DYE A1-PANI	DYE B-PANI	DYE C-PANI
Staphylococcus aureus	25	25	25	25	25	12.5	12.5	25	50
Salmonella typhi	50	25	25	25	25	25	25	12.5	25
Bacillus subtilis	ND	50	50	25	50	25	25	25	25
Escherichia coli	50	25	50	25	25	12.5	25	25	25
Candida albican	50	50	25	50	50	25	25	25	50
Aspergillus niger	50	50	25	50	ND	50	50	50	ND

Table 4.10: Minimum Bactericidal/Fungicidal Concentration of the Synthesized Polyaniline Substituted Dyes Against Test Microorganism (mg/ml)

Test Organism	PANI	DYE A	DYE A1	DYE B	DYE C	DYE A-PANI	DYE A1-PANI	DYE B-PANI	DYE C-PANI
Staphylococcus aureus	50	25	50	50	-	12.5	25	50	-
Salmonella typhi	50	50	25	25	-	50	50	50	50
Bacillus subtilis	ND	50	50	25	50	25	-	-	50
Escherichia coli	50	25	25	50	50	25	12.5	25	25
Candida albican	50	50	25	50	-	50	50	25	-
Aspergillus niger	-	50	50	-	ND	50	50	12.5	ND

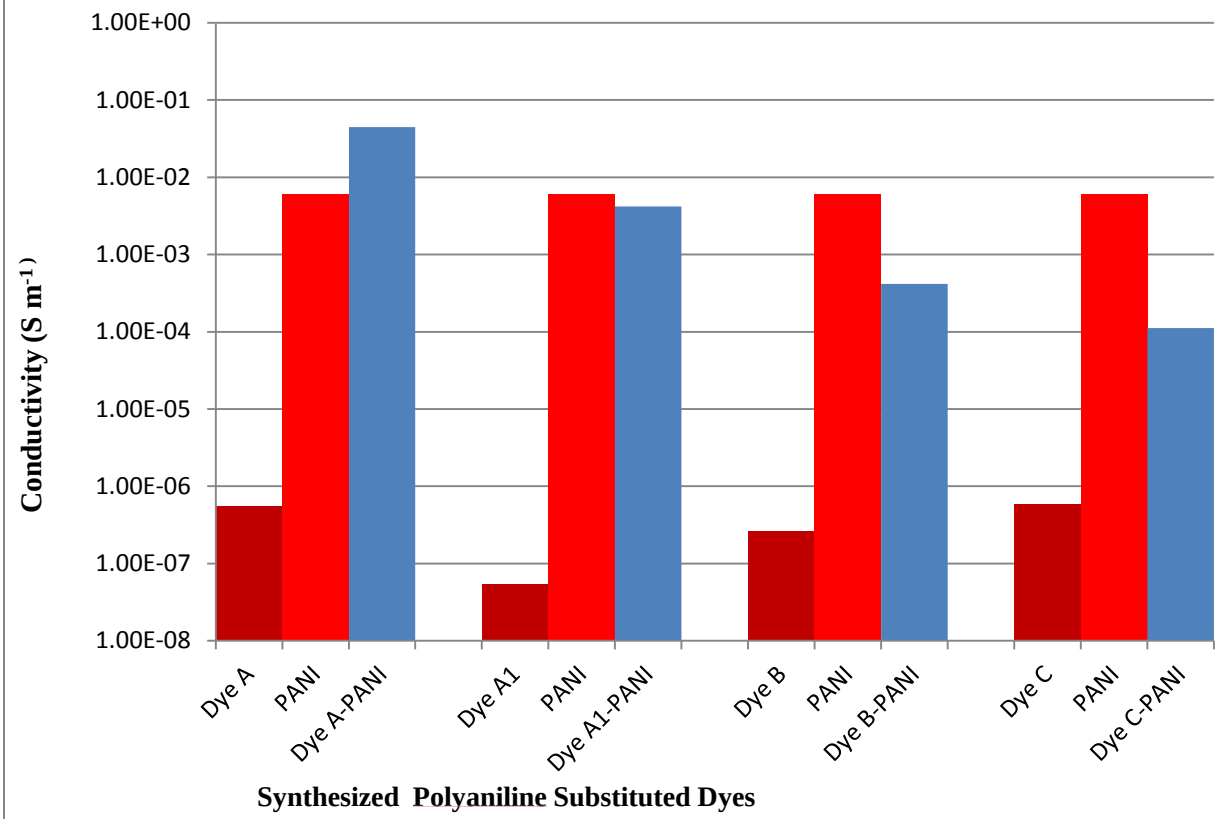
4.6 Electrical Conductivity of the Synthesized Polyaniline Substituted Dyes

Fig 4.1 shows the variation of electrical conductivity of the polyaniline substituted dyes with change in frequency and the result obtained shows that polyaniline, dye A, dye A1 and dye C have relatively stable electrical conductivity with frequency change but decreases at a higher frequency of 20,000- 10,000 Hz. Thus, the electrical conductivity of the polyaniline substituted dyes at 60 Hz power frequency ranges from $10^{-2} – 10^{-4}$ $S.m^{-1}$ while for the dyes moieties span from $10^{-7} – 10^{-8}$ $S.m^{-1}$ as shown in Table 4.11.

Table 4.11: Electrical Conductivity of the Synthesized Polyaniline Substituted Dyes at 60 Hz.

Samples	Electrical Conductivity (S/m)
PANI	5.96E-03
Dye A	5.53E-07
Dye A1	5.42E-08
Dye B	2.61E-07
Dye C	5.85E-07
Dye A-PANI	4.46E-02
Dye A1-PANI	4.17E-03
Dye B-PANI	5.13E-04
Dye C-PANI	1.12E-04

Fig 4.1: Electrical Conductivity of the Synthesized Polyaniline Substituted Dyes at 60 Hz



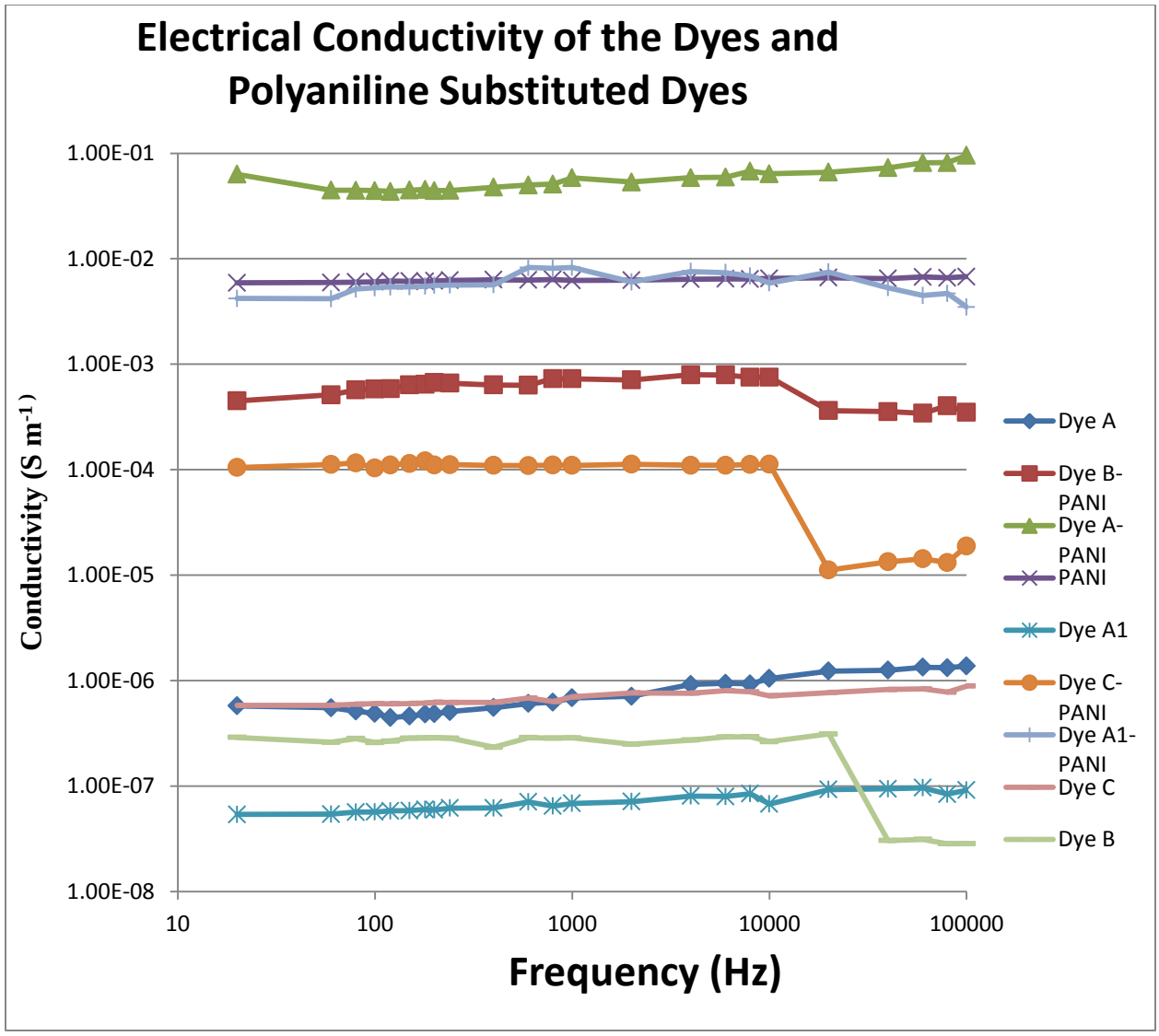


Fig 4.2: Electrical Conductivity of the Synthesize Polyaniline Substituted Dyes with Change in Frequency.

4.7 Fastness Properties of the Synthesized Dyes

Table 4.12-4.13 shows the dyeing properties of the dyes on polyester and nylon 6,6 fabric. The dyes gave purple, deep pink and yellow hue with good to excellent fastness to washing on polyester fabric and fair to very good fastness to washing on nylon 6,6 fabric. However the light fastness ratings of the dyes on polyester and nylon 6,6 fabric gave moderate to very good light fastness on polyester and fair to good on nylon 6,6 fabric.

Table 4.12: Wash Fastness and Light Fastness of the Synthesized Dyes on Polyester Fabric

Dyes	Change	Staining	Light Fastness	% Exhaustion	Colour on Fabric
A	5	5	6	74	Deep pink
AI	4-5	4-5	4	70	Deep purple
B	4-5	4	5	63	Purple
B1	4	4-5	4	61	Purple

Table 4.13: Wash and Light Fastness of the Synthesized Dyes on Nylon 6,6 Fabric

Dyes	Change	Staining	Light Fastness	% Exhaustion	Colour on Fabric
A	4-5	4	4	82	Deep Purple
A1	4	4	5	80	Purple
B	4-5	4	4	74	Purple
B1	3	4-5	4	75	Purple
C	3	4	3	86	Yellow
C1	3	4	4	84	Deep Yellow

CHAPTER FIVE

5.0 DISCUSSION

5.1 Physicochemical Properties of the Synthesized Intermediate, Dyes and Polyaniline Substituted Azo Dyes

5.1.1 Physical Properties of the Synthesized Intermediates

The yield of the intermediate can be described as fair to good. This is not surprising in view of the result from previous and similar works. (Sabnis *et al*., 1999), reported the fact that 1,3-dicarbonyl compound generally pose a problem of low yield and difficult purification process when compared to other ketones and aldehyde. One of the methods mentioned as a way of overcoming this is a prolonged reaction time which resulted in the percentage yield of the intermediatesfrom fair to good. This was also supported by Jack, (2005) who reported that generally ketones starting materials produced far poorer result than aldehyde. They suggested that the use of a precondensed Knoevenagel intermediate may be preferred. The melting points of the intermediates were also were also compared with those reported in similar literatures by (Shridar *et al*., 2015; Muller, 1970; Mariam Al-Sheikh, 2014) ranging from174-205 °C and were observed to falls within the range.

5.1.2 Physical Properties of the Synthesized Dyes

The dyes from low-melting diazo components tended to have low melting points themselves and the factors determining high melting points were generally preserved in the dyes from high-melting heteroaryl amine as shown in Table 4.2 above. Thienyl-2-azo dyes with 3-cyano groups had higher melting points than their analogues with alkyl esters, which may be as result of increased polarity and or the rod like shape of the cyano group being more conducive to efficient packing in the crystal structure, as earlier observed by Hallas and Towns (1996a, 1996b) For instance, dye A, A1, B and B1 had melting point of 204-209 °C, 201-205 °C, 174-178 °C, 167-170 °C respectively. These figures are close in magnitude to that of aminothiophene

intermediate 1 and intermediate 2 with melting point of 199-204 °C and 168-171 °C respectively which is conformity with Hallas and Tarek (2006) that dyes from low-melting diazo components tended to have low melting points themselves and those with high melting diazo component tend to have high melting point.

5.1.3 Physical Properties of the Polyaniline Substituted Dyes

The results from Table 4.3 shows that the percentage yield of the synthesized polyaniline is 80.12 % due to the acceptable amount of oxidant to monomer ratio (r = 1). Also, the percentage yield of 87, 75.08, 63.16 and 70 % were observed for dye A, A1, B and dye C substituted polyaniline respectively.. The result from Table 4.3 also showed the melting point 290-293 °C for polyaniline. However polyaniline substituted Dye B was observed to have decomposition temperation of 314-319 °C, this can be attributed to the chemical structures of the repeating unit and the decreasing flexibility in the polymer chain as well as the emplacement of the bulky substituent of the dyes moiety along the polymer backbones Nassar and Al-azhar (2015)

5.2 Visible Absorption of the Synthesized Polyaniline Substituted Dyes

The effect of substitution in the thiophene ring of the diazo component on the visible absorption spectrum and the colour intensity was also investigated. The colour of the azo dyes depends on the nature of both the diazo and the coupling components. The introduction of the cyano group as an electron –withdrawing substituent unto the thiophene ring produces a bathochromic shift of the absorption band while the replacement of the five membered ring sulphur heterocycles diazo component with their six-membered analogues exert a hypsochromic shift which was observed for dye A, A1, B, and B1 where the introduction of the cyano group as an electron acceptor result in a bathochromic shift of 131 nm as compared with their six membered analogue as the diazo component of the azo dyes. Thus, all the dyes shows

considerable increase in wavelength of absorption when compared generally with their six membered ring as observed by various researchers. Dyes having a thiophene diazo component generally exhibit high bathochromic shift. It is to be noted that coupling component with strong powerful electron donor groups also shows similar effect. These bathochromic shift afforded by five membered ring sulphur heterocycles have been mentioned by several authors (Griffiths, 1981, 1982); (Egli, 1991); (Towns, 1999), indicating that these system are useful in providing blue to greenish blue dyes. The origin of the large shift peculiar to this heterocyclic system and polyaniline substituted dyes could not be explain only in terms of greater stabilization of the excited state but probably correlated with the increased in diene character of the heterocycles. (Peters and Gbadamosi, 1992). Also, the sharp bathochromic shift of the polyaniline substituted dyes can be attributed to the more extensive electron delocalization and smaller steric requirements of the rod-like cyano group, (Hallas and Choi 1999a). However, bathochromic shifts of the visible absorption band were also observed on increasing the solvent polarity as seen in Table 4.6 where a difference in ʎmax was noticed upon measuring the azo dyes in acetone and DMSO. This is expected for a system in which the excited state is more polar than the groung state. (Hallas, 1979; Georgiadou and Tsatsaroni, 2002).

5.3 The Infra-Red Absorption of the Synthesized Intermediate and Dyes

Table 4.5 shows the IR-vibrational frequencies of the synthesized dyes and its intermediates and the result obtained indicates that aminothiophene intermediate 1 and 2 show absorption peaks in the range 2199-2206 cm^{-1} due to the presence of cyano group .The amino group absorption for the two intermediate appeared in the range 3198-3421.7cm^{-1} while the carbonyl absorption showed up in the range 1602-1695 cm^{-1}. However, the vibrational frequency obtained for the synthesized dyes shows the characteristics absorption peaks due to stretching frequency of the NH-group in the region 3097-3365 cm^{-1}. An absorption peak in the region

2217.8, 2221.5, 2214.0, 2206.6 cm^{-1} was observed for dye A, A1, B and B1 due to the presence of cyano group. The IR spectra of the prepared azo dye also showed an absorption peak in the region 1438.8-1599cm^{-1} attributed to $V_{N=N,}$ while the observed peak in the region 1602.8-1736.9 was due to $V_{C=O}$ as outline in Table 4.5.

5.3.1 The Infra-Red Absorption of the Synthesized Polyaniline Substituted Dyes

Table 4.6 shows the IR-vibrational frequencies of the synthesized polyaniline and polyaniline substituted dyes which indicates a band 797 and 764 cm^{-1} as the characteristics of the p-substituted chains for the polyaniline . The band 1289 cm^{-1} is described as been characteristics of the conducting polymer which might be due to the delocalization of electrical charges caused by deprotonation and might also be attributed to band characteristics of B-NH-Q or B-NH-B, where B, refers to the benzenoid ring and Q to the quinoid ring. The band 1479 and 1584 cm^{-1} are related to the stretching of the C-N bonds of the benzenoid and quinoid rings, respectively, while the broad band 3220.4 cm^{-1} is assigned to the N-H stretching vibration of amine group and the peak C-H-stretching vibration is 2922.2 and 2780 cm^{-1}. However, the IR-vibrational frequencies of the polyaniline substituted dyes shows an absorption peaks due to stretching frequency of the NH group in the region 3213-3242.8 cm^{-1}. An absorption peak in the region 1461-1487 due to the presence of C-C stretch of the benzeniod ring while 1580-1595 cm^{-1} was due to the presence of C=C stretch of the quinoid rings and the absorption peak in the region 1263-1285 cm^{-1} which is attributed to V_{C-N} stretching. Comparing to polyaniline some shifted band in the spectra of polyaniline substituted dyes were observed as shown in Table 4.6. The result also suggest that the shifting of the IR absorption peaks might be a signature of the conversion of the quinoid rings to the benzenoid rings due to proton induced spin-unpairing mechanism, which was considered to be an indication of increasing degree of charge delocalization on the polyaniline backbone due to substitution (Nirmala *et al*., 2015). IR- shift

also indicates that the degree of charge delocalization of polymerization increases by introducing dye moieties into polyaniline backbone. This regions are in conformity with the characteristics of IR absorption peaks (Khopkars, 2008).

5.4 GC-MS Spectra of the Synthesized Intermediates and Dyes

The result from Table 4.7 showed the fragmentation of the intermediate, dyes and their respective mass (m/z). The mass spectra of the intermediate 1 and 2 are fully consistant with the assigned structures: In most cases, intense molecular ion peaks were observed. Thus intermediate 1 and 2 showed intense molecular ion peaks at m/z 259 ± 2 and 282 ± 3, consistant with the theoretical molecular weight 257 and 285g/mol respectively. The molecular ion of the intermediate 1 shown in Table 4.7 underwent fragmentations to produce peaks at m/z 139 and 123 corresponding to its molecular weight. While the intermediate 2 underwent fragmentation to produce peaks at m/z 117 and 165 respectively. However, Dye A and B showed molecular ion peaks at m/z 394.2 ± 5 and 414.6 ± 3, consistant with the theortical molecular weight 389 and 417g/mol respectively. The molecular ion of Dye A shown in Table 4.7 underwent fragmentation to produce three fragments with peaks at m/z 81.1, 177, and 129 respectively corresponding to the theoretical molecular weight of Dye A. While Dye B underwent fragmentation to produce three fragment with peaks at m/z 91, 179 and 149 respectively corresponding to its calculated molecular weight. Thus, the molecular weight determination by GC-MS may not be the same as that calculated from atomic weights, If parent compound contains certain element with high isotopic abundances (Khopkars, 2008). This may account for the slight difference/change in numerical value of molecular weight of the samples under examination.

5.5 Antimicrobial Screening of the Synthesized Polyaniline Substituted Dyes

The synthesized polyaniline substituted dyes showed higher activity than the polyaniline and the individual dyes thus, the abstraction of the hydrogen atom from a nitrogen atom of the

imine group on the polyaniline chain backbones by butyl lithium and further attachment of the dye moieties enhance their antimicrobial activities which may be further attributed to greater extent in the alteration in chemical structure and charge delocalization which is in consonant with the work of (Nirmala *et al*., 2015) who observed that polyaniline substituted dyes has an enhance antimicrobial activity as compared to polyaniline and dyes individually which was also in agreement with (Karunanithy *et al*., 2013). From the results above in Table 4.8 the best activity was shown by the Dye A-PANI against *Staphylococcus aureus* with zone of inhibition (32mm), followed by synthesized Dye A1-PANI, Dye B-PANI and Dye C- PANI with maximum zone of inhibition of 31, 29 and 26 mm respectively on *Escherichia coli* and *Staphylococcus aureus*, however the synthesized dyes and polyaniline shows moderate zone of inhibition against *Staphylococcus aureus, Salmonella typhi and Escherichia coli, Staphylococcus aureus* is known to play a significant role in the infection of skin disease (Usman *et al*., 2007). The strong activity of the synthesized polyaniline substituted dyes against staphylococcus aureus indicates that it may be effective against skin infection and diarrhea treatment. It is pertinent to note the activity of the polyaniline substituted dyes against *Candida albican and Aspergellus niger* which also indicate that they can be used as antifungal especially for the treatment of skin disease such as vaginitis and other generalized infections including endocarditis caused by candida albicans. Also, the synthesized polyaniline substituted dyes demonstrated an interesting activity against Escherichia coli, this bacteria causes infections that are difficult to combat due to multi drug resistant (Salie *et al*., 1996, Afolayan and Aleiro, 2006). Also the results obtained indicated the existence of the presence of quarternery ammonium cation in various synthesized polyaniline substituted dyes and showed a good correlation between the reported uses of these dyes against infectious diseases. For example the inhibitory

and biocidal activities of *Escherichia coli* by all the polyaniline substituted dyes justifies their use in the treatment of diarrhea and dysentery. Hence, it is clear from the above mentioned results that the possible causes for better and enhance antimicrobial activities of polyanilines substituted dyes when compared to acid doped polyaniline are the delocalization of electron density in side chain groups and the presence of quaternary ammonium ion.

5.6 Electrical Conductivity of the Polyaniline Substituted Dyes.

The observed relative stability of the electrical conductivity of Dye B, Dye C-PANI and Dye B-PANI over the frequency range in fig 4.1 may be ascribed to the fact that at low frequencies the materials may have had time for both fast dipole polarizations to occur as well as slower segmental polarization to occur, thus influencing the electrical behavior of the material. This may also be linked to the ability of the electrons within the molecules of the synthesized compound to respond to the applied current (Amitabh, 2009). The electrical conductivity of the polyanaline substituted dyes lies within the range of electrical conductivity for semiconductor which is between 10^{-12} - 10^{2} S m^{-1}. However, polyaniline substituted Dye A was observed to have the highest electrical conductivity of 4.46 x 10^{-2} S m^{-1} at 60 Hz. This can be attributed to the fact that all the dye moieties do not have continuous conjugation and hence have electrical conductivity lower than the doped polyaniline and polyaniline substituted dyes. However, due to the substitution of the dye on the polyaniline backbone, conjugation of the polyaniline substituted dyes extend in a continuous manner resulting in their high electrical conductivity value ranging from 10^{-2} - 10^{-4} S·m^{-1} which is in agreement with the work of (Nirmala *et al*., 2015) whose conductivity value for basic dyes-substituted polyaniline was 10^{-3} S·m^{-1}. Thus, the electrical conductivity value of synthesized polyaniline was in agreement with literatures (Fariz, 2007; Carolin *et al*., 2015). It was pointed out by Fariz and Carolin *et al* that the synthesis of polyaniline lead to an effective site-selective interactions between the quinoid ring of the

polyaniline and the dyes which facilitates charge transfer processes between the two components thereby resulting in an enhance electrical conductivity of all the dyes-substituted polyanilne. Hence, as a result of the degree of conjugation and presence of positive charge in form of quaternary ammonium cation, electrical conductivity of the polyanilines substituted dyes increases when compared to acid doped polyaniline and the dyes individually.

5.7 Fastness Properties of the Synthesized Dyes

The disperse dye A, A1, B and B1 were applied at 2 % depth on polyester and nylon 6,6 fabric. These dyes gave purple, deep purple and deep pink hues with brighter and deeper shades, tinctorial strength and excellent levelness on the fabric. The variation in the shade of dyed fabric results from alteration in the diazo and coupling component. The remarkable degree of levelness and brightness after washing indicate good penetration and excellent affinity of the dyes to the fabric. However, dye C and dye C1 gave yellowish to deep yellowish hues with excellent tinctorial strength and brightness on the nylon 6,6 fabric. In addition the result obtained showed that the dyed fabrics have excellent fastness level to washing which may be due to the absence of solubilizing group, which affect solubility and washing ability of the dye-out of the fabric. Also, the fastness properties are interrelated since they depend, among other things such as the rate of diffusion of the dyes on fabric. This rate is a function of the geometry of dye molecule, the concentration of the dye in the fabric which appeared to be the most influential factor in the fastness of dyeing. (Dawnson, 1991).

However, the light fastness ratings of the dyed polyester and nylon are shown in Table 4.11-4.12 showing moderate to very good light fastness. light fastness value of 6, 4, 5 and 4 for Dye A, A1, B and B1 respectively can be attributed to the introduction of acetamido group ortho to the azo group resulting in a significant improvement in light fastness (Patel *et al.*, 2003). Also

the intramolecular hydrogen bonding between acetamido and azo group can also be ascribed to be responsible for higher value of light fastness as compared to dye C and dye C1 (Divyesh *et al*., 2014). In a related work by (Evans and Staplenton, 1978). Maradiya *et al*., (2010) also observed that there is no absolute value for the light fastness of a dye. The rating obtained for a giving colourant for any fading test depends on many factors most of which are: concentration and degree of aggregation of dye within the fabric, nature of the fabric in which the dye is dispersed, the molecular structure of the dye and substantivity. Finally the result from Table 4.11-4.12 show the percentage exhaustion on nylon 6,6 ranging from 75-86 % compared with polyester fabric with percentage exhaustion ranging from 61-74 %. This can be attributed to greater accessability of the pore structure in nylon 6,6. The very good exhaustion may also be expected due to the diffusion of the dye within the fabric which proceeded rapidly under dyeing condition. Hence the rate of diffusion of dye molecules on the fabric is higher which increases the exhaustion value.

CHAPTER SIX

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusion

Different polyaniline substituted azo dyes were synthesized by the substitution of the dyes moieties on the polyaniline backbones. Their physicochemical properties were assessed and spectroscopic analysis such as visible spectrometry, Fourier Transform Infra red Spectrometry, and Gas chromatography-mass spectroscopy were used to elucidate the structures. An Agar well diffusion method was used for the assessment of their antimicrobial properties on different microorganism and the result showed zone of inhibition ranging from 14-34 mm, which implies that this compound can be effective against infectious diseases which these microorganism can cause. The electrical conductivity of the polyaniline substituted dyes were observed to be in the range of 10^{-2} - 10^{-4} $S \cdot m^{-1}$. Finally, the dyes synthesized in the course of these research were successfully applied on polyester and nylon 6,6 fabrics and their washing and light fastness were evaluated. The dyes gave mostly deep purple, orange and yellow shades on the fabric and exhibited good to excellent washing fastness properties on substrate and moderate to very good light fastness. This research work therefore has justified that substitution of dye moieties on polyaniline backbones increases the antimicrobial properties and electrical conductivities as compared to polyaniline and the individual dyes.

6.2 Recommendations

I. Other analytical methods of characterization such as Nuclear magnetic resonance spectroscopy (NMR) and high resolution Mass Spectroscopy should be carried out to further elucidate the structure of polyaniline substituted dyes.

II. Acute toxicity test and other pharmacological screening should be carried out

III. Further investigation using the synthesized polyaniline substituted dyes on other antibiotic resistant microorganism should be conducted

IV. Other types of conducting polymers such as polypyrrole, polythiophene, polyfuran and polyacetylene should be worked upon to synthesize polyaniline substituted dyes

V. Low frequency dielectric spectroscopy should be performed to study charge transport in the polyaniline substituted dyes.

VI. Further investigation should be performed on the application of polyaniline substituted dyes on textile and leather substrate to produce electronic textile and electronic leathery material.

6.3 CONTRIBUTIONS TO KNOWLEDGE

I. Acetoacetanilide was used to synthesized 2-aminothiophene intermediate as the diazo components and p-N,N-dimethylaminobenzaldehyde was used as the coupling component in the synthesis of new azo dyes and new polyaniline substituted dyes.

II. The dyes synthesized from these intermediate were successfully applied to polyester and nylon 6,6 fabric and gave purple to brilliant pink shades with fair to very good light fastness and very good to excellent washing fastness properties.

III. A new approach using LCR meter was used to determine the electrical conductivity of the synthesized polyaniline substituted azo dyes at a frequency range of 20-100,000 Hz.

IV. Antimicrobial properties of the synthesized polyaniline substituted dyes were investigated and were found to be more potent than the polyaniline and individual dyes against bacteria and fungi.

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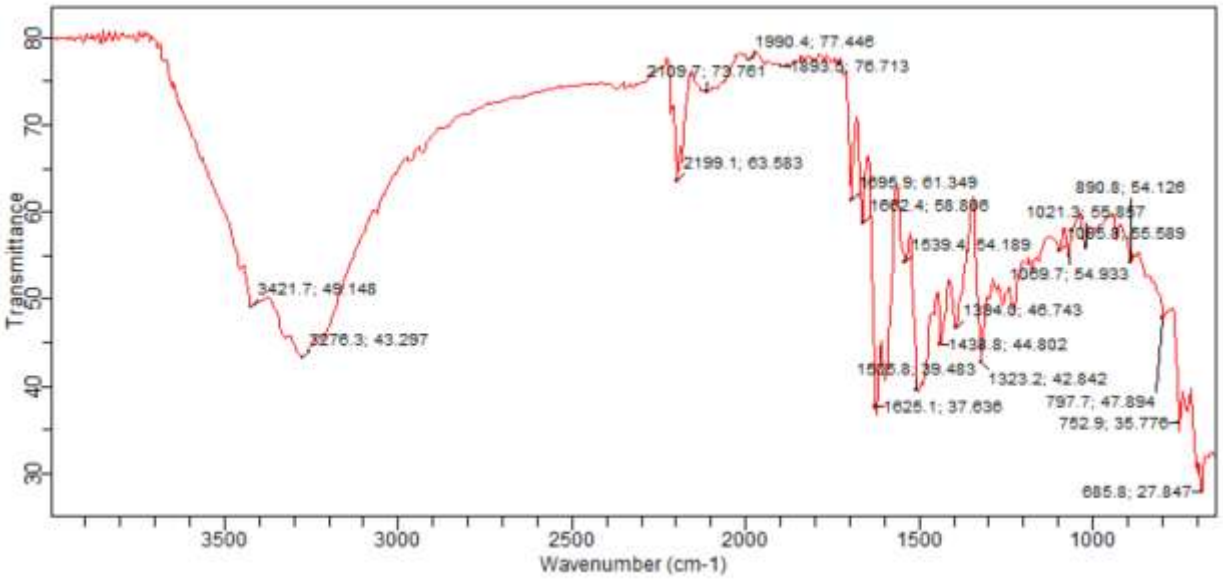
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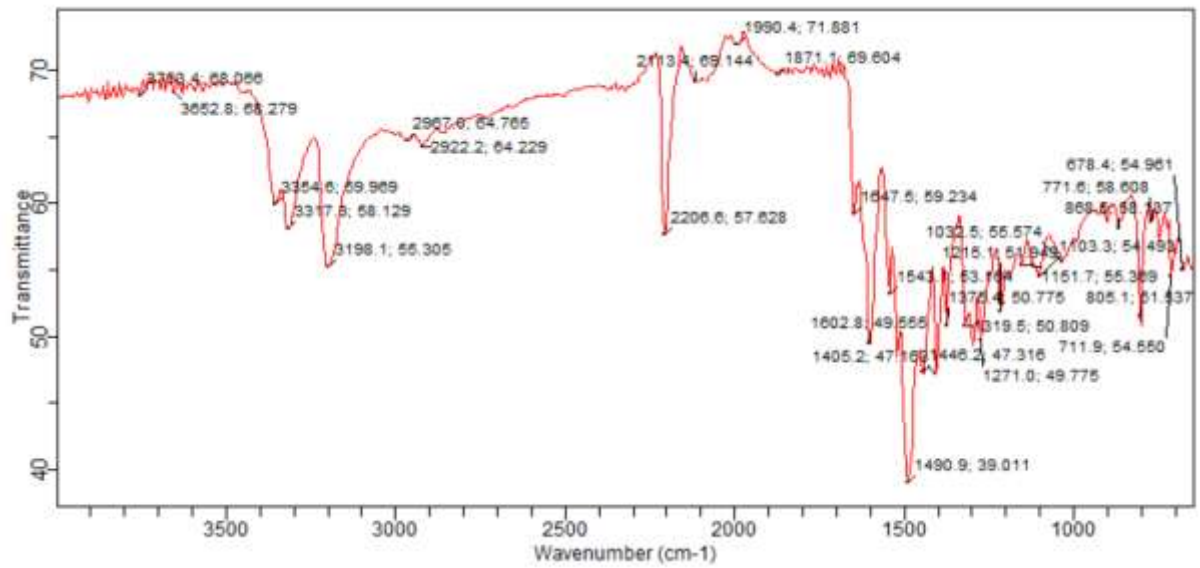
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APPENDIX 1

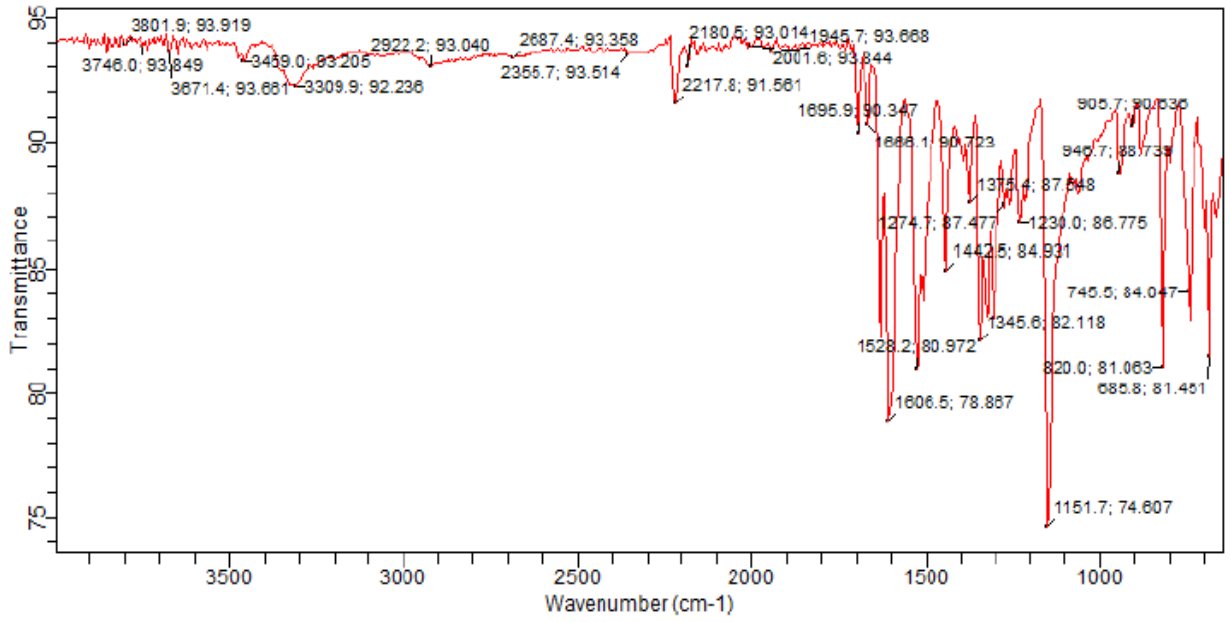
FT-IR Absorption of the Synthesized Intermediate, Dyes And Polyaniline Substituted Dyes.



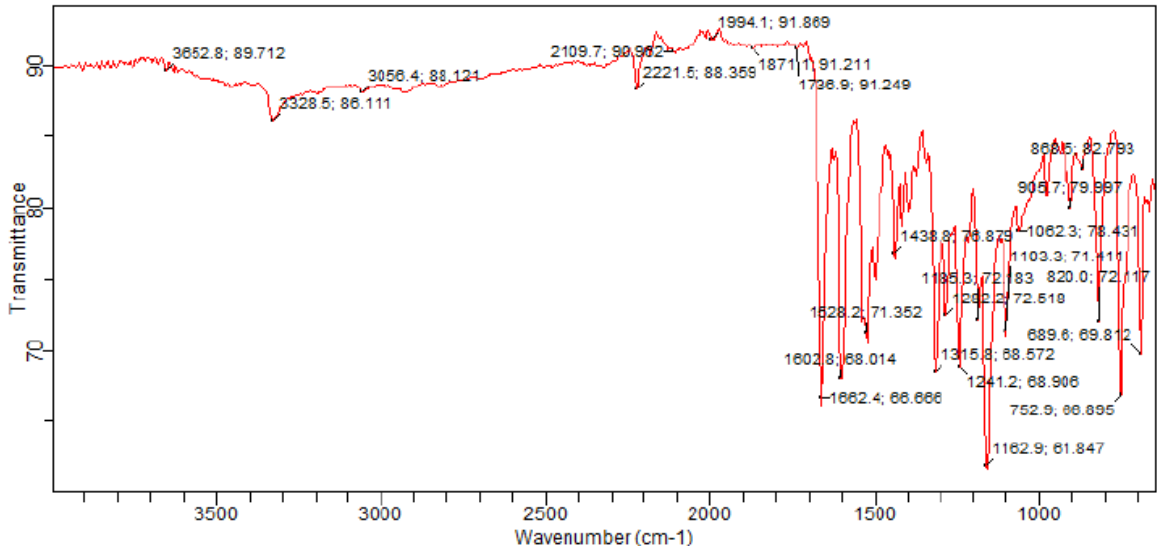
INTERMEDIATE 1



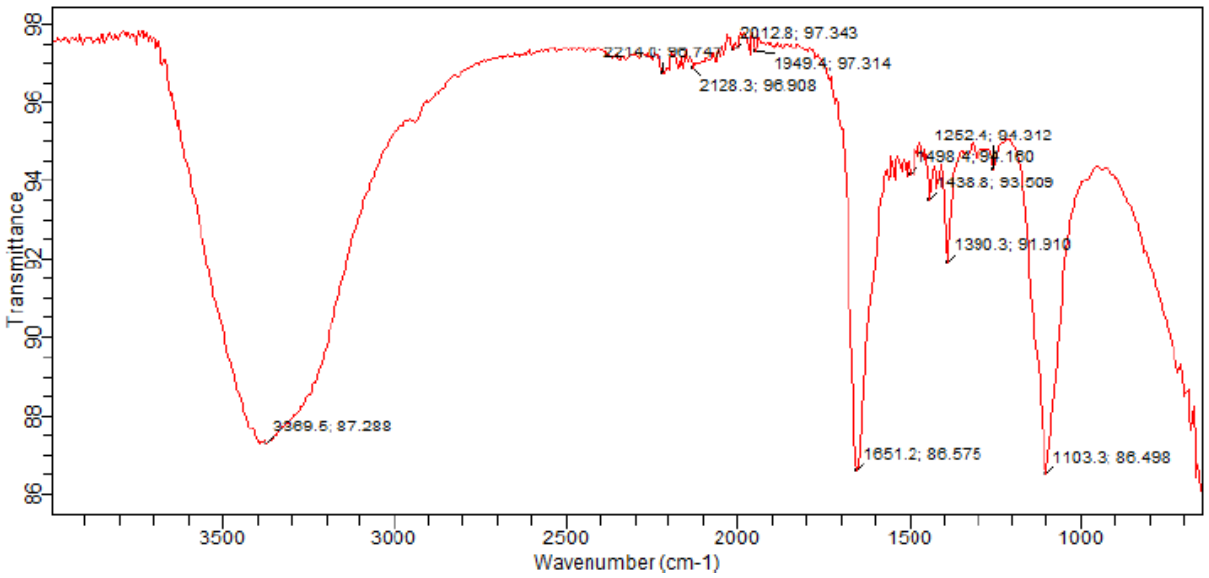
INTERMEDIATE 2


Transmittance
Wavenumber (cm-1)
3801.9; 93.919
3746.0; 93.849
3671.4; 93.661
3459.0; 93.205
3309.9; 92.236
2922.2; 93.040
2687.4; 93.358
2355.7; 93.514
2180.5; 93.014
2217.8; 91.561
1945.7; 93.668
2001.6; 93.844
1695.9; 90.347
1666.1; 90.723
1375.4; 87.648
1274.7; 87.477
1230.0; 86.775
1442.5; 84.931
745.5; 84.047
1345.6; 82.118
1528.2; 80.972
820.0; 81.063
685.8; 81.451
1606.5; 78.857
1151.7; 74.607

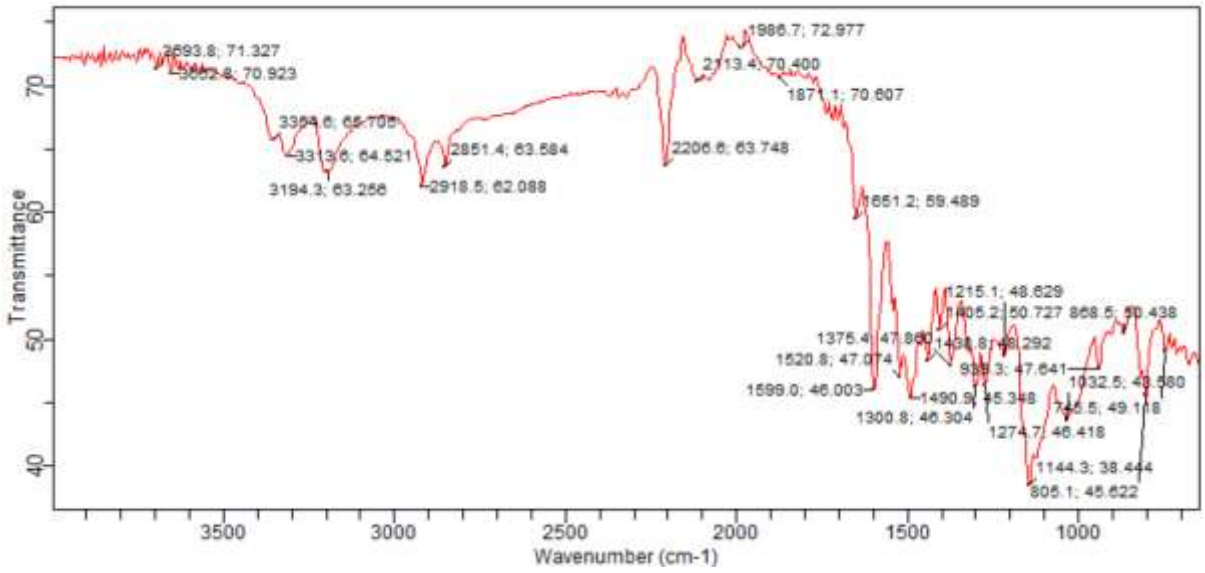
DYE A


Transmittance
Wavenumber (cm-1)
3652.8; 89.712
3328.5; 86.111
3056.4; 88.121
2109.7; 90.962
1994.1; 91.869
2221.5; 88.358
1871.1; 91.211
1736.9; 91.249
1438.8; 79.879
1062.3; 78.431
1103.3; 71.411
1135.3; 72.183
820.0; 72.117
1528.2; 71.352
689.6; 69.812
1602.8; 68.014
1315.8; 68.572
1241.2; 68.906
1662.4; 66.666
752.9; 66.895
1162.9; 61.847

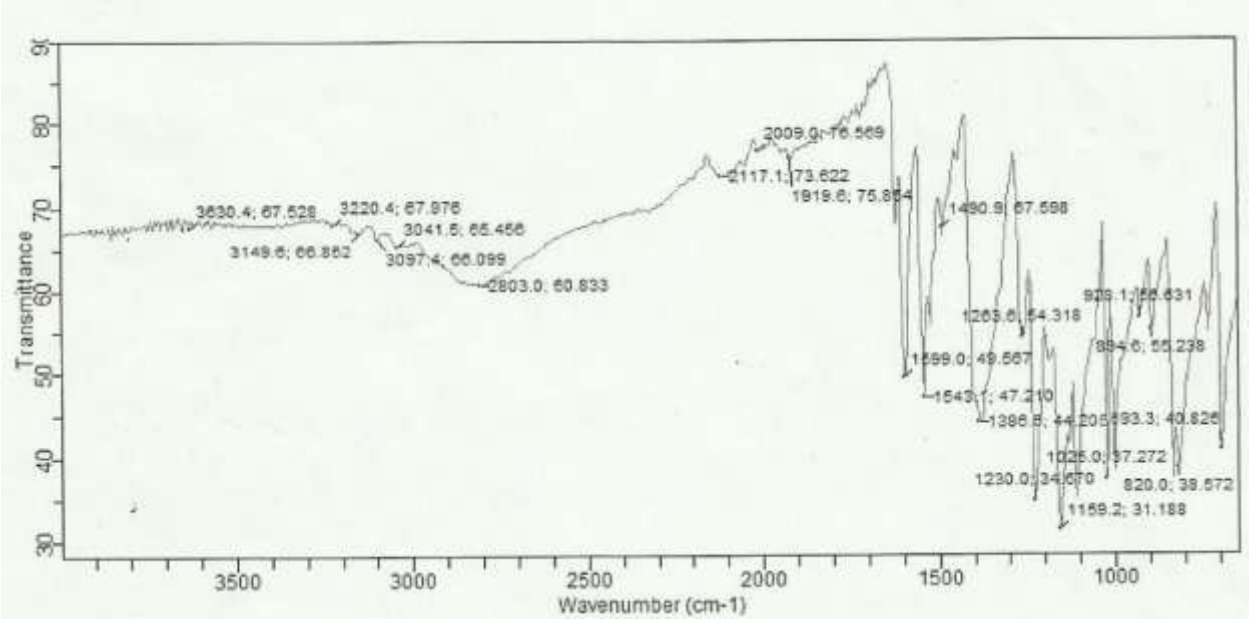
DYE A1


Transmittance
Wavenumber (cm-1)
2012.8; 97.343
2214.0; 80.747
1949.4; 97.314
2128.3; 96.908
1252.4; 94.312
1498.4; 94.160
1438.8; 93.509
1390.3; 91.910
3369.5; 87.288
1651.2; 86.575
1103.3; 86.498

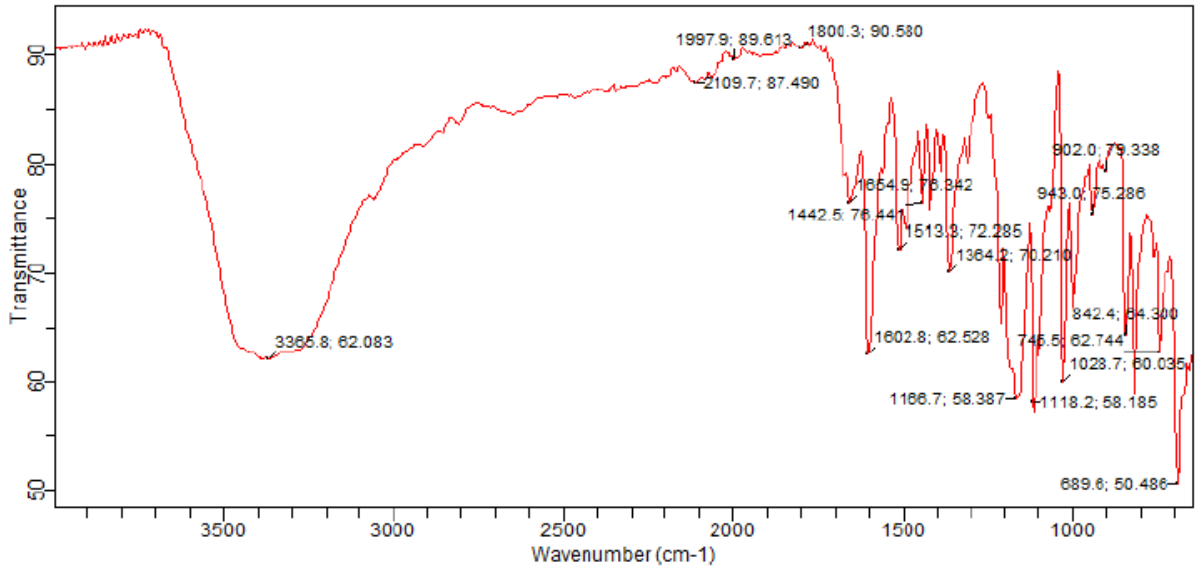
Dye B


Transmittance
Wavenumber (cm-1)
1986.7; 72.977
2693.8; 71.327
2113.4; 70.400
1871.1; 70.607
3313.6; 64.521
2851.4; 63.584
2206.6; 63.748
3194.3; 63.256
2918.5; 62.088
1651.2; 59.489
1215.1; 48.629
1375.4; 47.860
1520.8; 47.074
1599.0; 46.003
1490.9; 45.348
1300.8; 46.304
1274.7; 46.418
1144.3; 38.444
805.1; 45.622

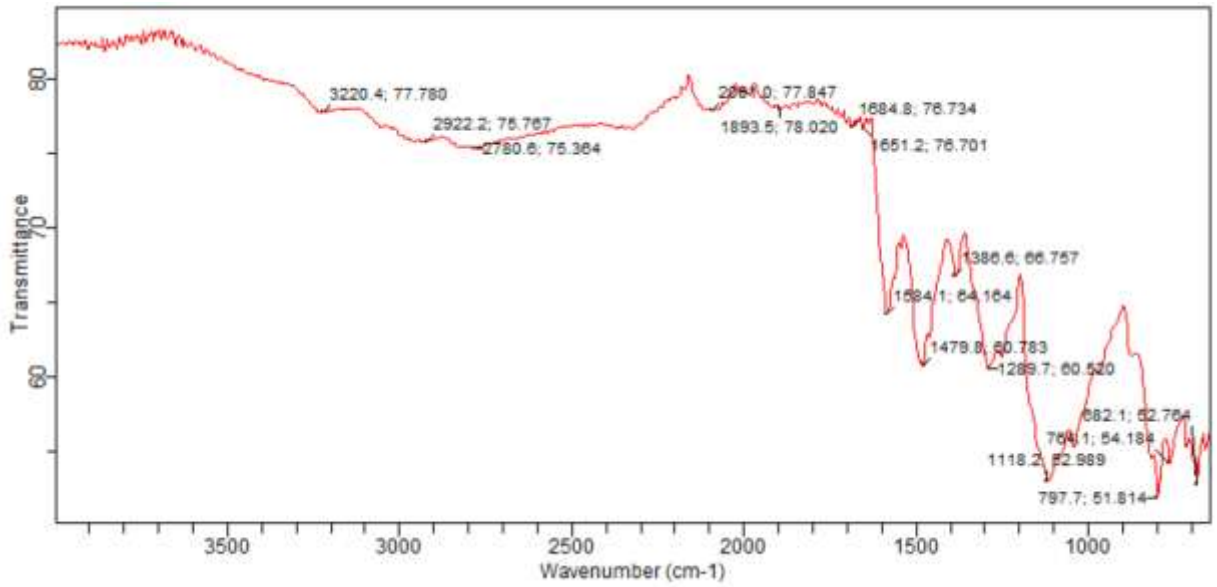
Dye B1


Transmittance
Wavenumber (cm-1)
3630.4; 67.528
3220.4; 67.976
3149.6; 66.852
3041.6; 66.456
3097.4; 66.099
2803.0; 60.833
2009.9; 76.569
2117.1; 73.622
1919.6; 75.854
1490.9; 67.598
1543.1; 47.210
1230.0; 34.670
1159.2; 31.188
820.0; 39.572

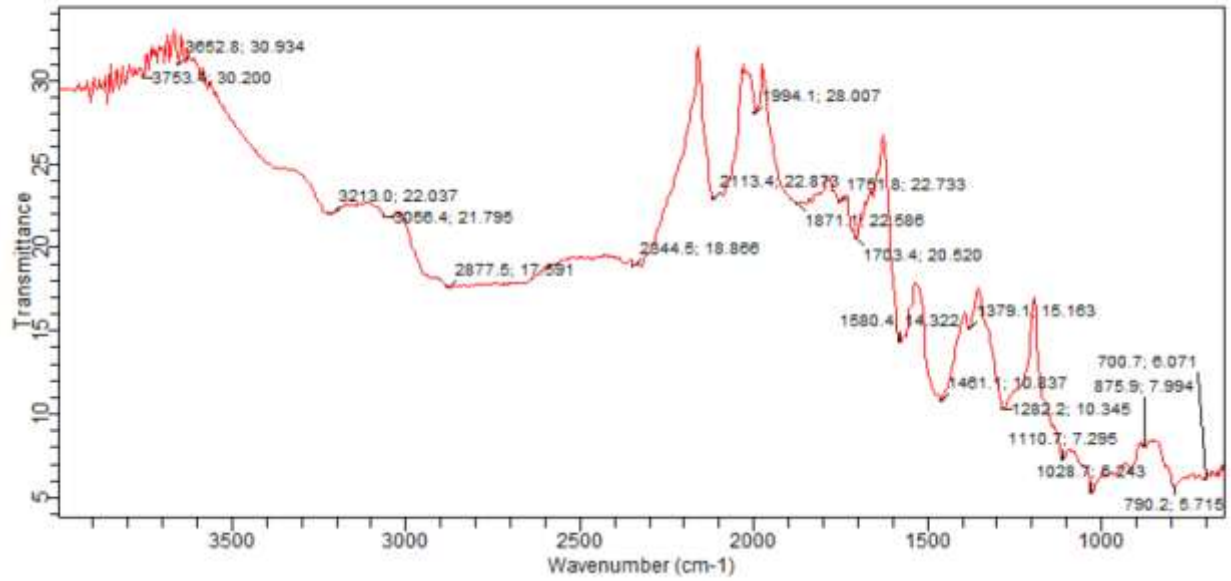
Dye C


Transmittance
Wavenumber (cm-1)
1997.9; 89.613
1800.3; 90.580
2109.7; 87.490
3365.8; 62.083
1654.9; 76.342
1442.5; 76.441
1513.3; 72.285
1364.2; 70.210
902.0; 79.338
943.0; 75.286
842.4; 64.300
1602.8; 62.528
745.5; 62.744
1028.7; 60.035
1166.7; 58.387
1118.2; 58.185
689.6; 50.486

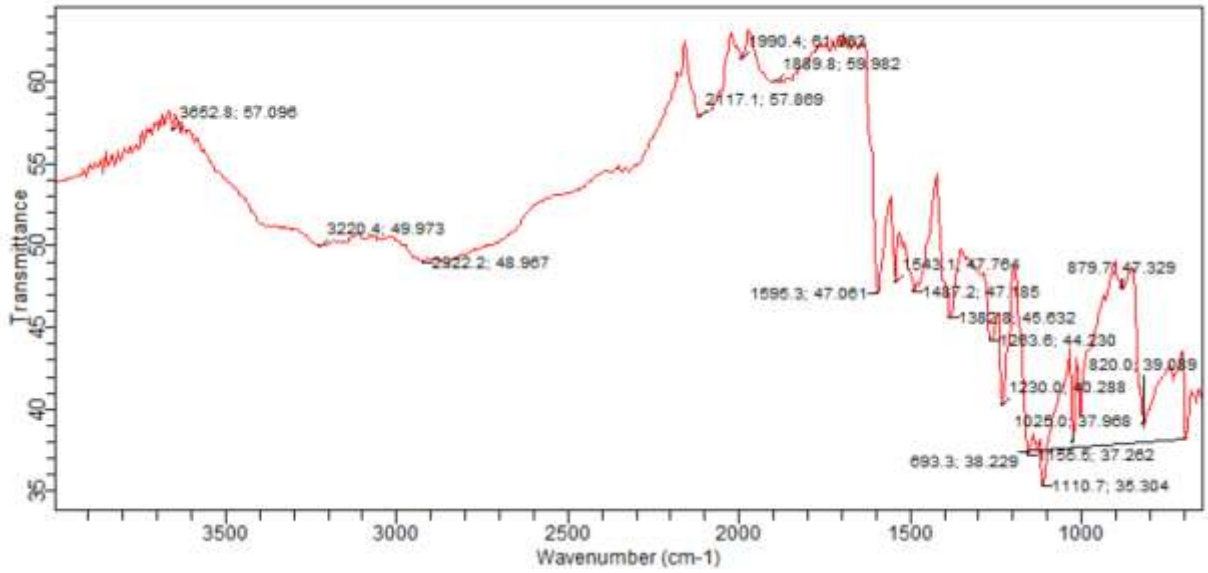
Dye C1



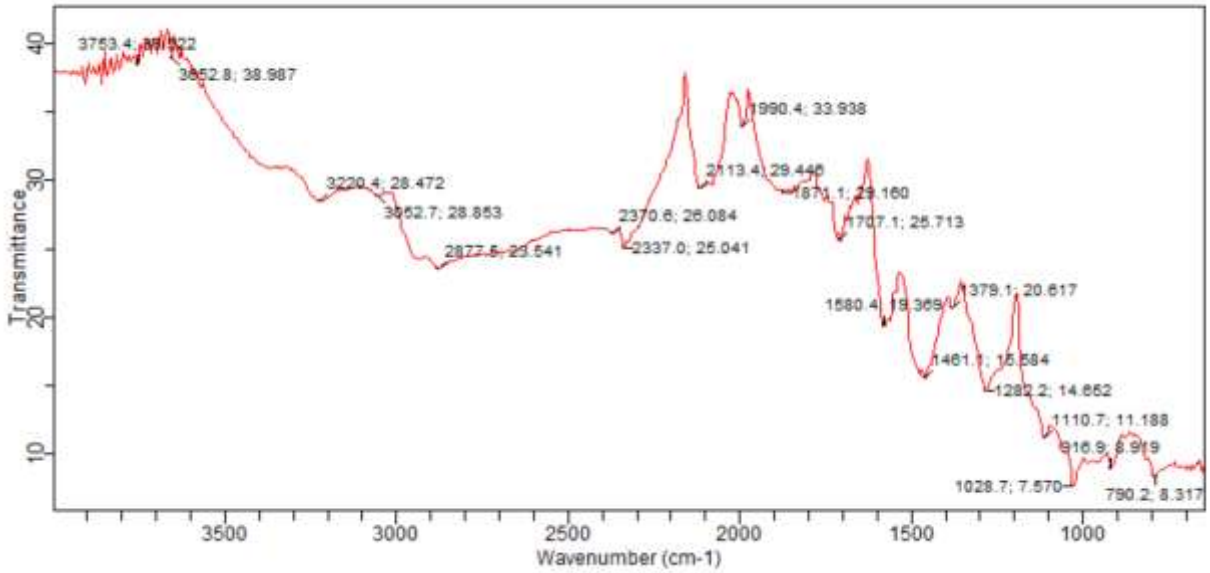
PANI



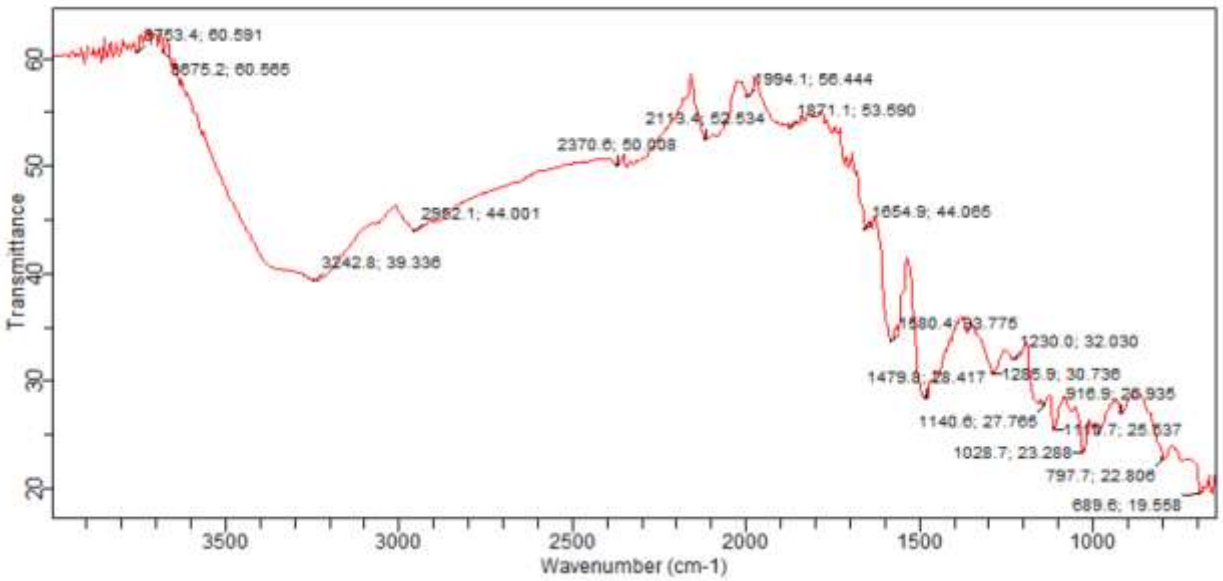
DYE A-PANI



DYE A1-PANI



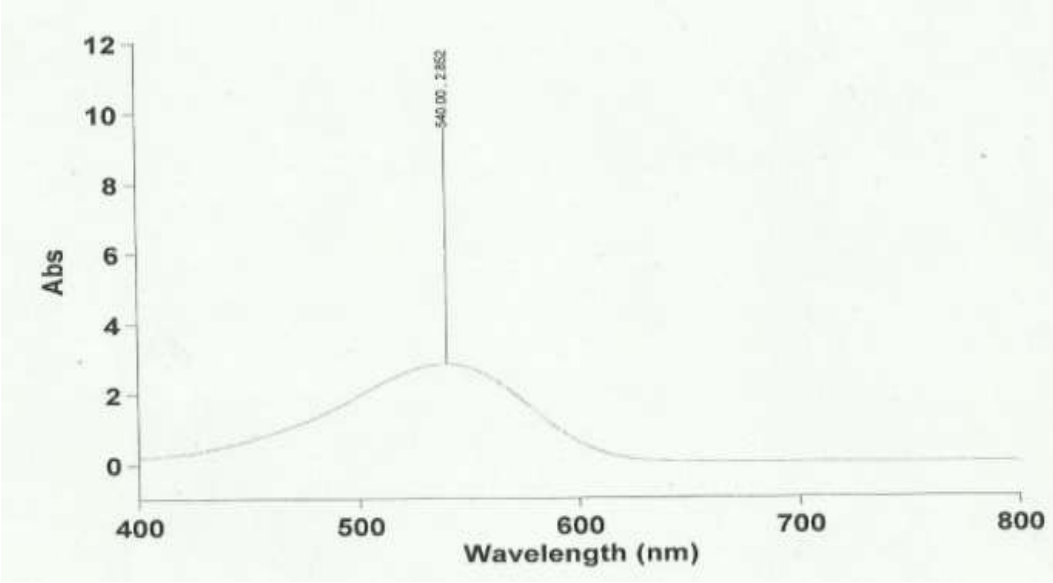
DYE B-PANI


3753.4; 60.591
3675.2; 60.565
3242.8; 39.336
2562.1; 44.001
2370.6; 50.008
2113.4; 52.534
1994.1; 56.444
1871.1; 53.590
1654.9; 44.066
1580.4; 33.775
1230.0; 32.030
1479.8; 28.417
1285.9; 30.736
916.9; 26.935
1140.6; 27.765
1028.7; 23.288
797.7; 22.806
689.6; 19.558
Transmittance
Wavenumber (cm-1)
3500
3000
2500
2000
1500
1000
60
50
40
30
20

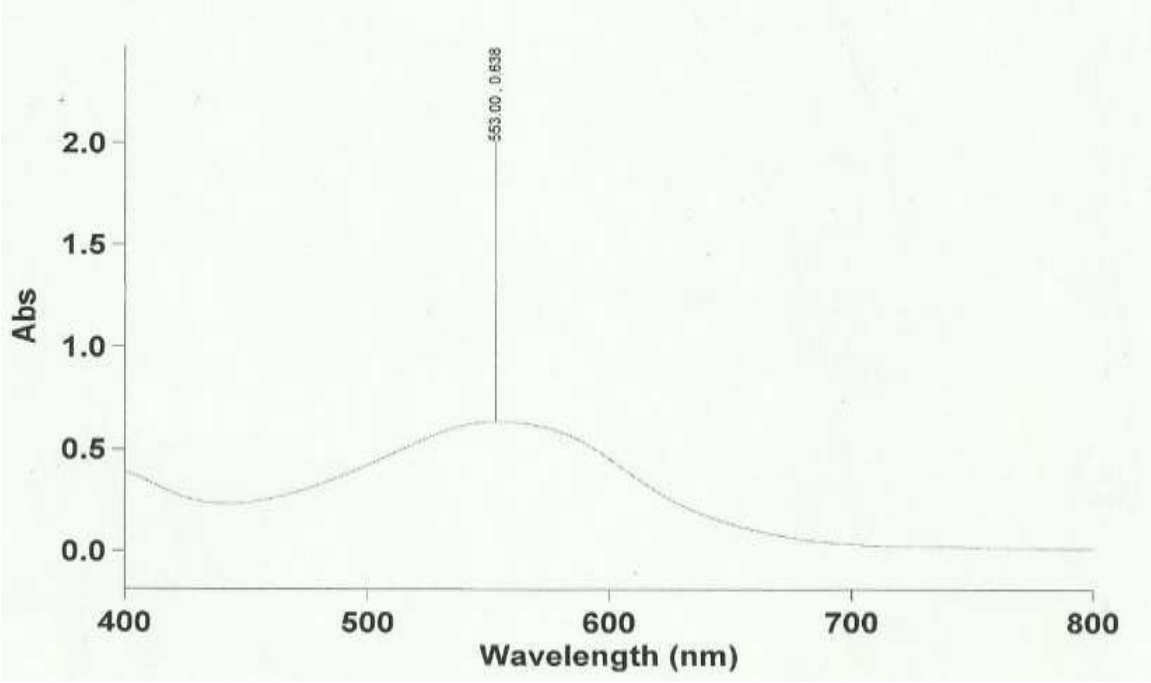
DYE C-PANI

APPENDIX II

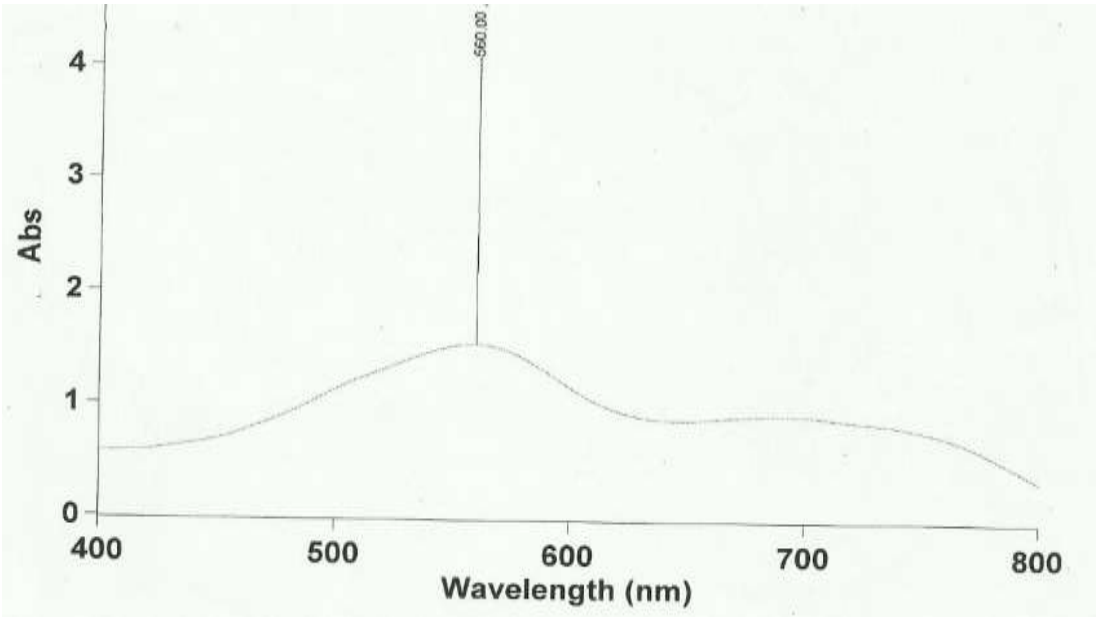
Uv- Visible Absorption Spectrum of the Synthesized Dyes and Polyaniline Substituted Dyes



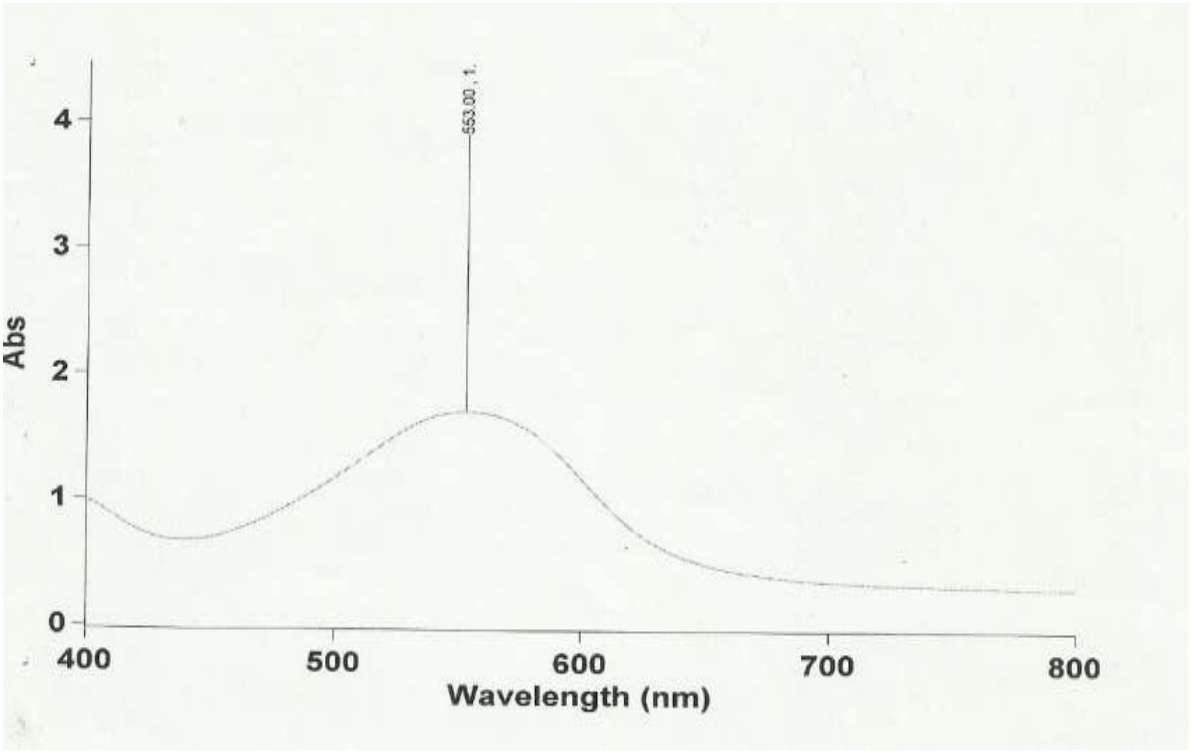
Dye A in DMSO



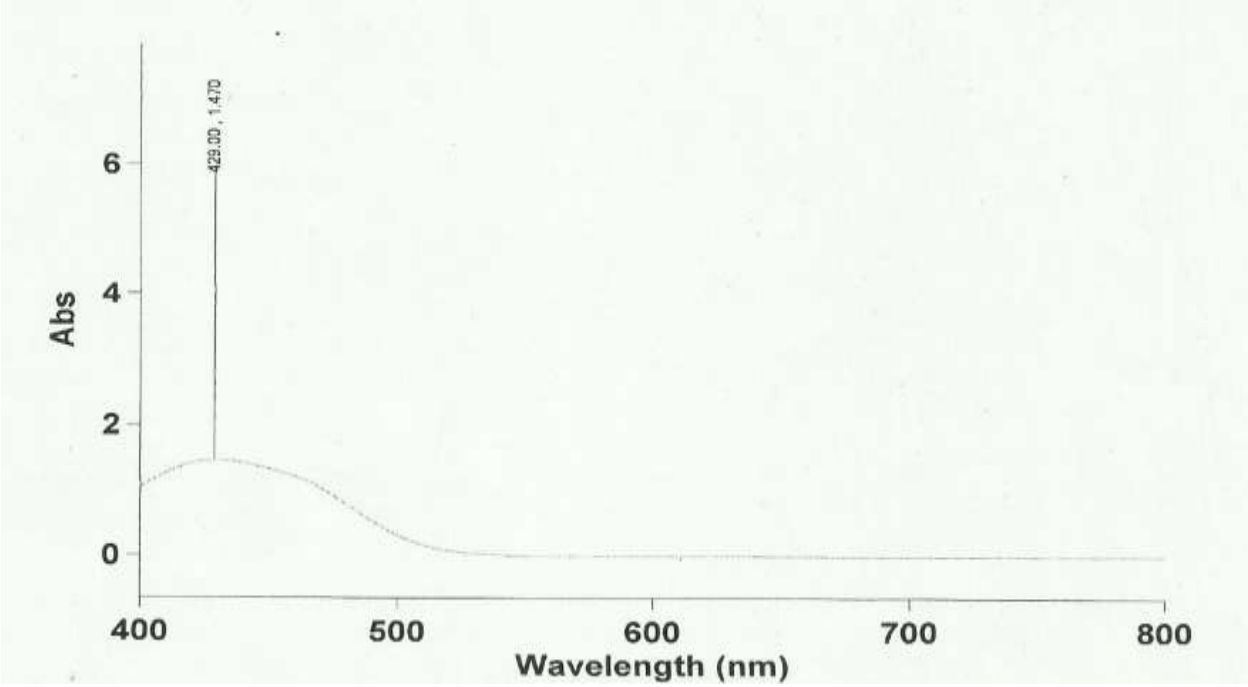
Dye A1 in DMSO



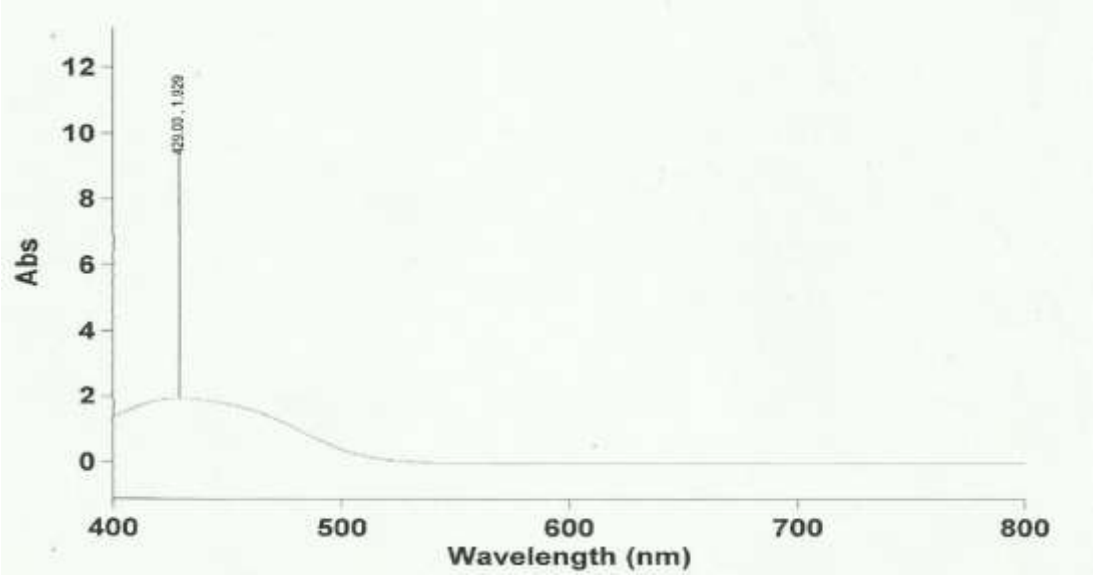
Dye B in DMSO



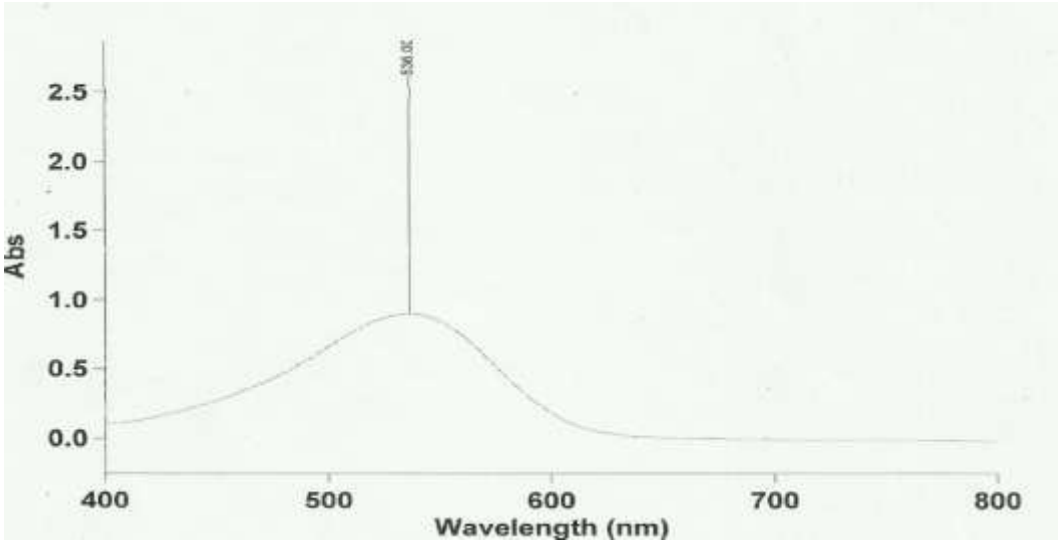
Dye B1 in DMSO



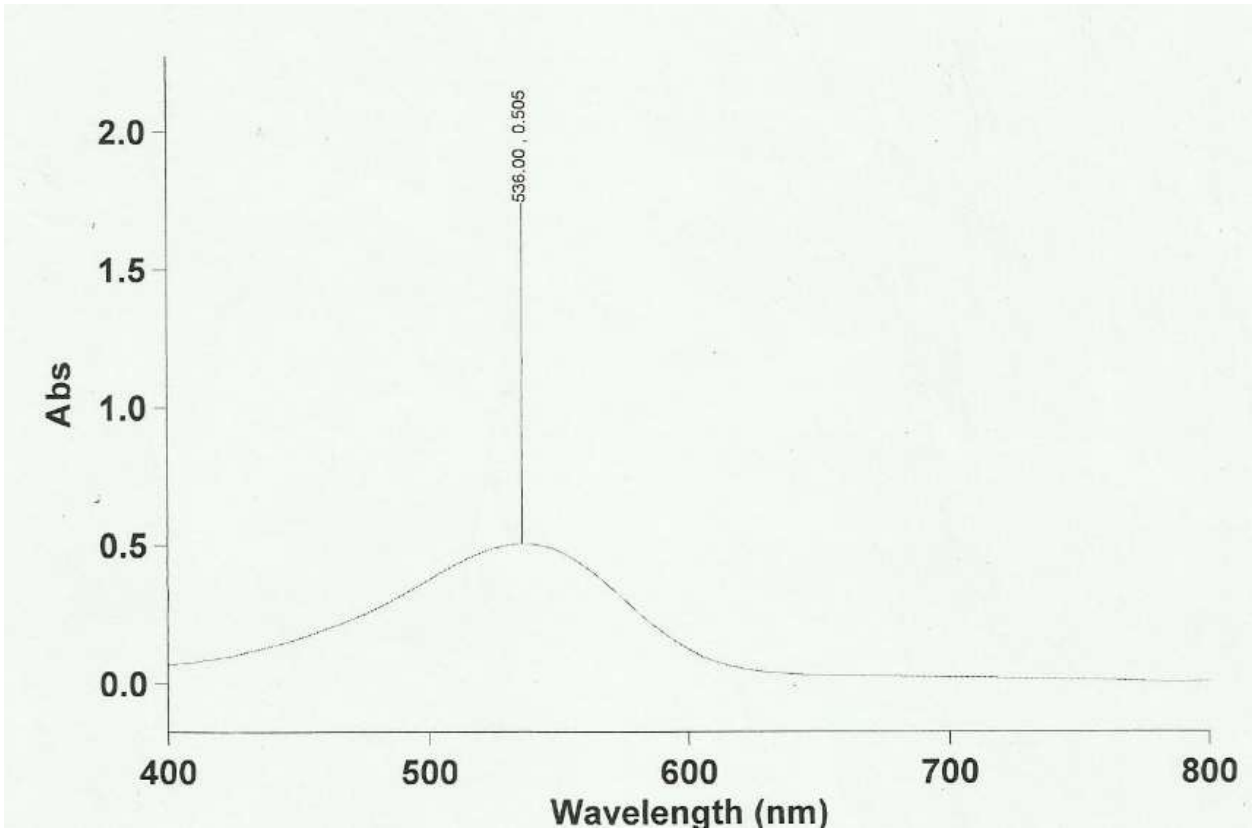
Dye C in DMSO



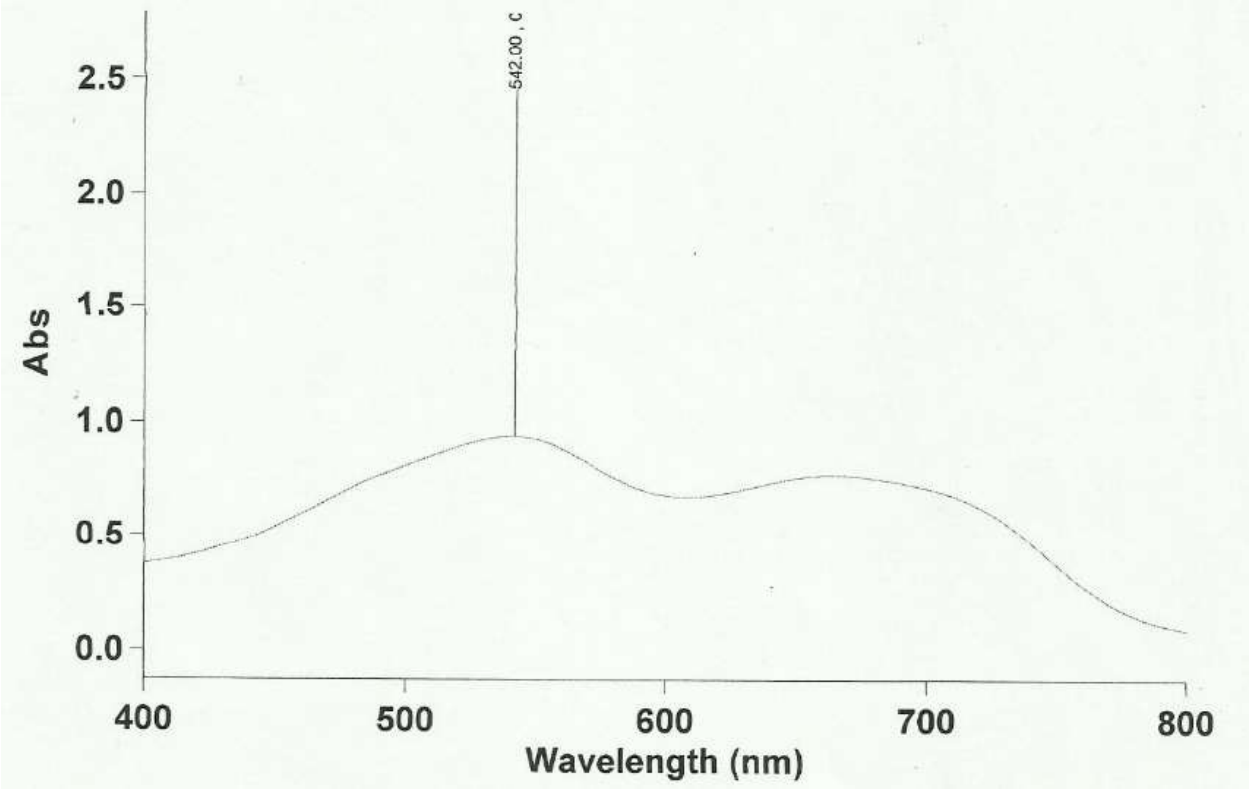
Dye C1 in DMSO



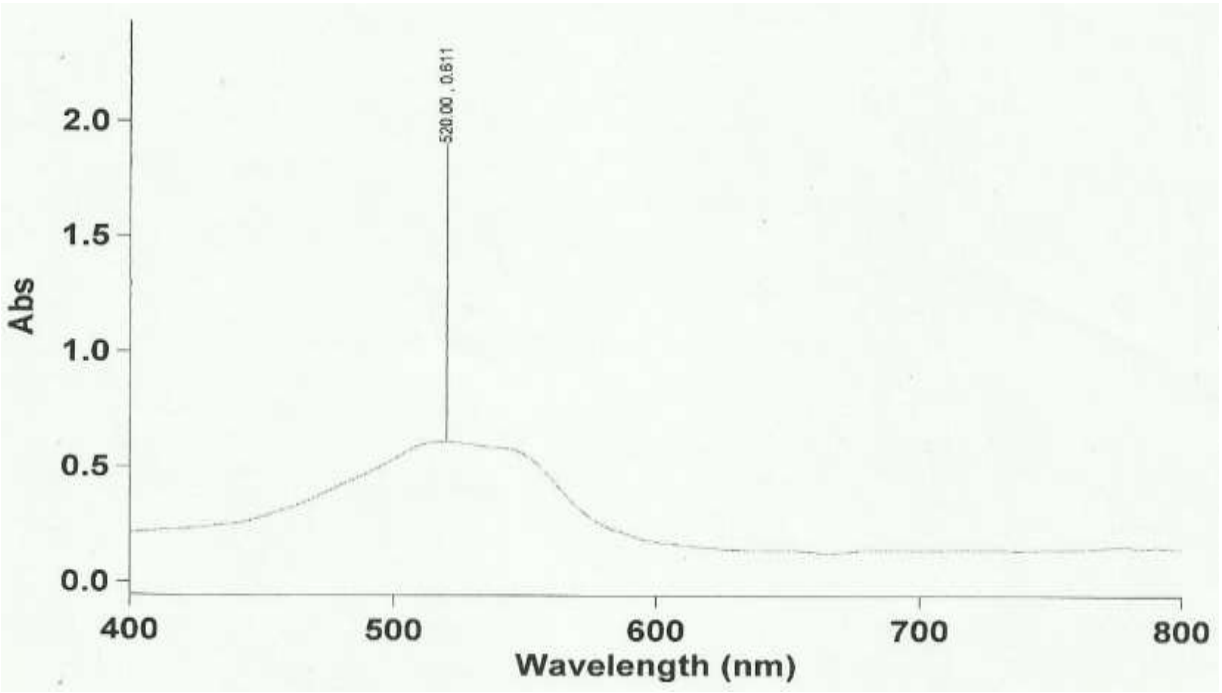
Dye A in Acetone



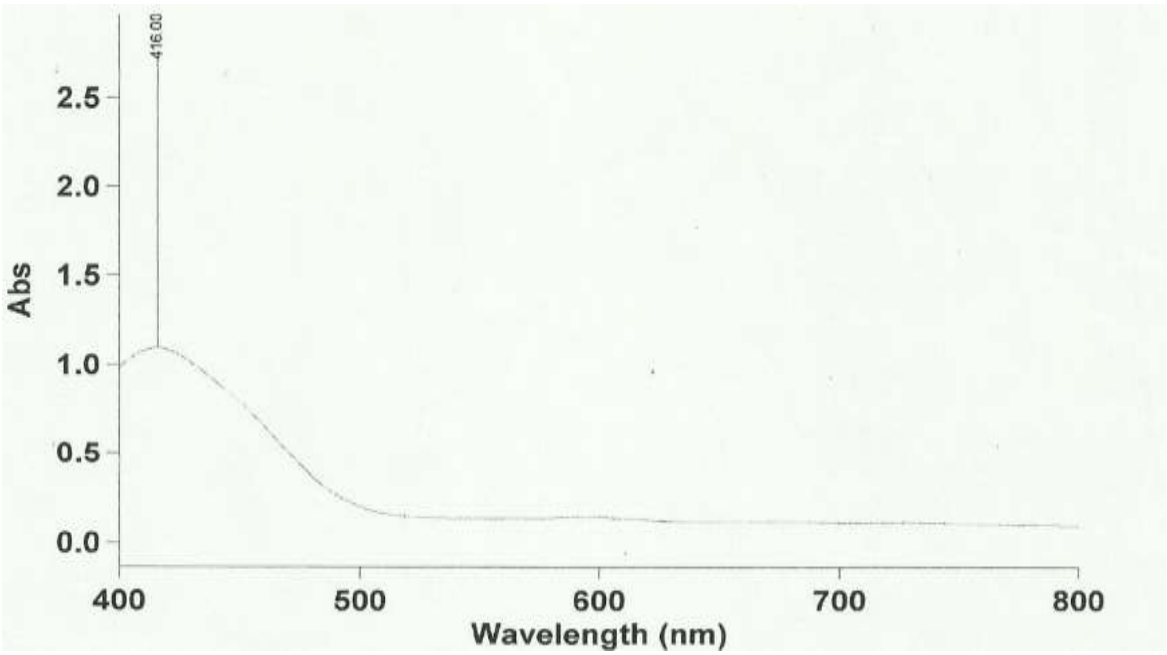
Dye A1 in Acetone



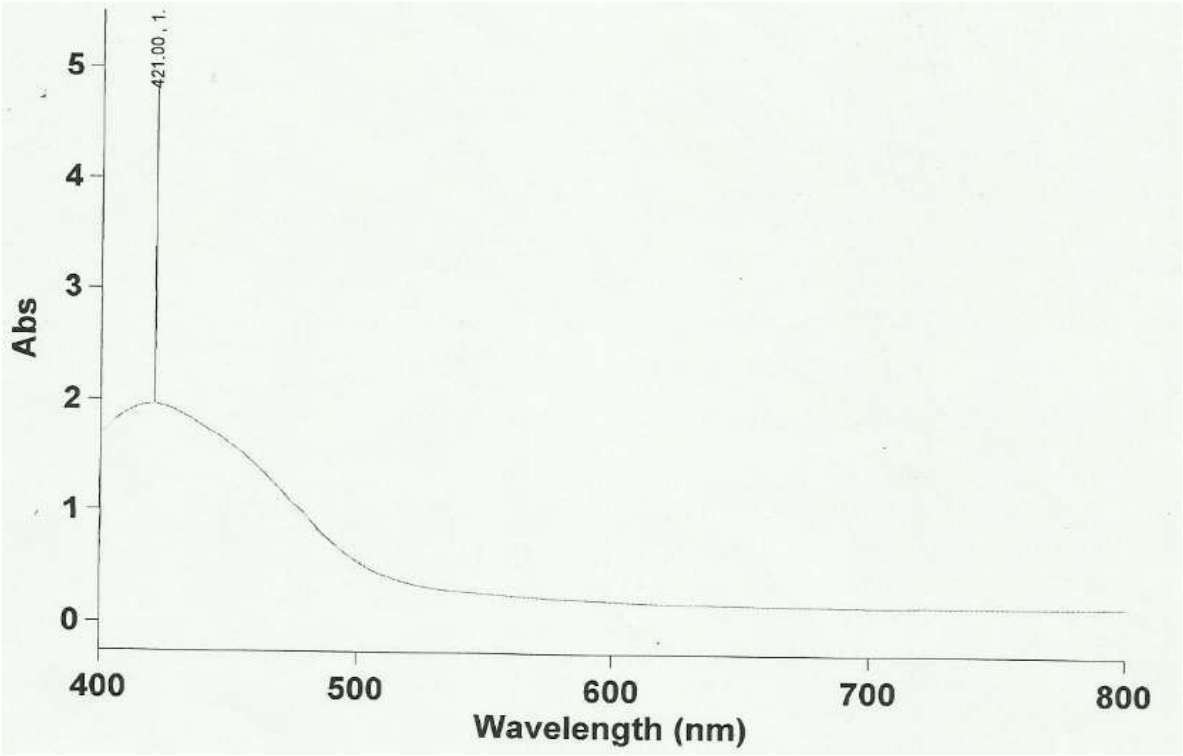
Dye B in Acetone



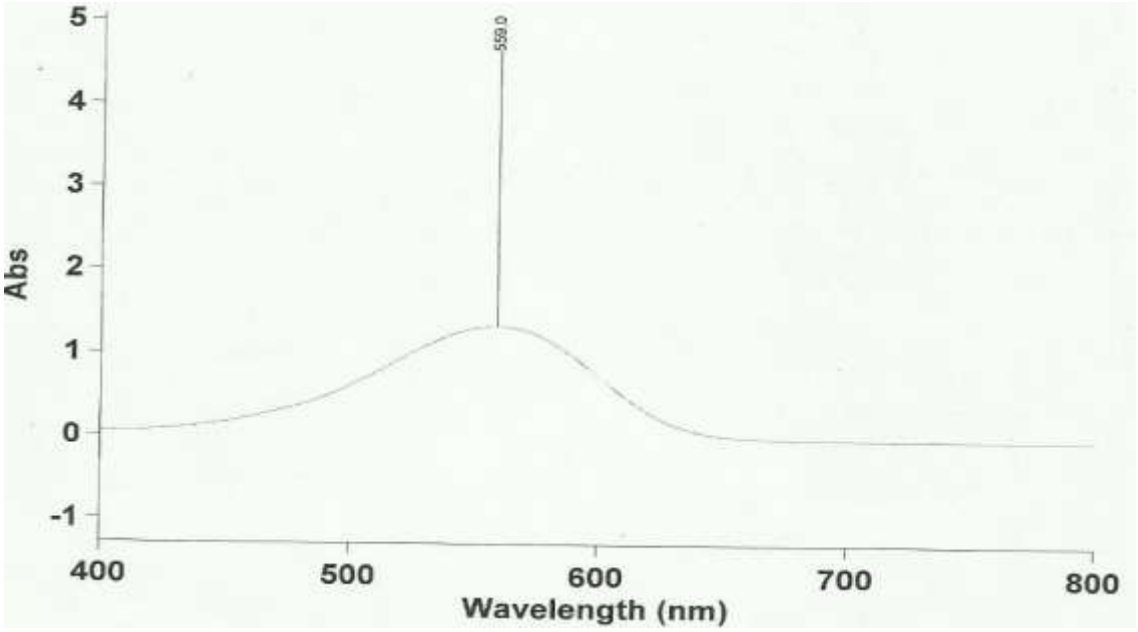
Dye B1 in Acetone



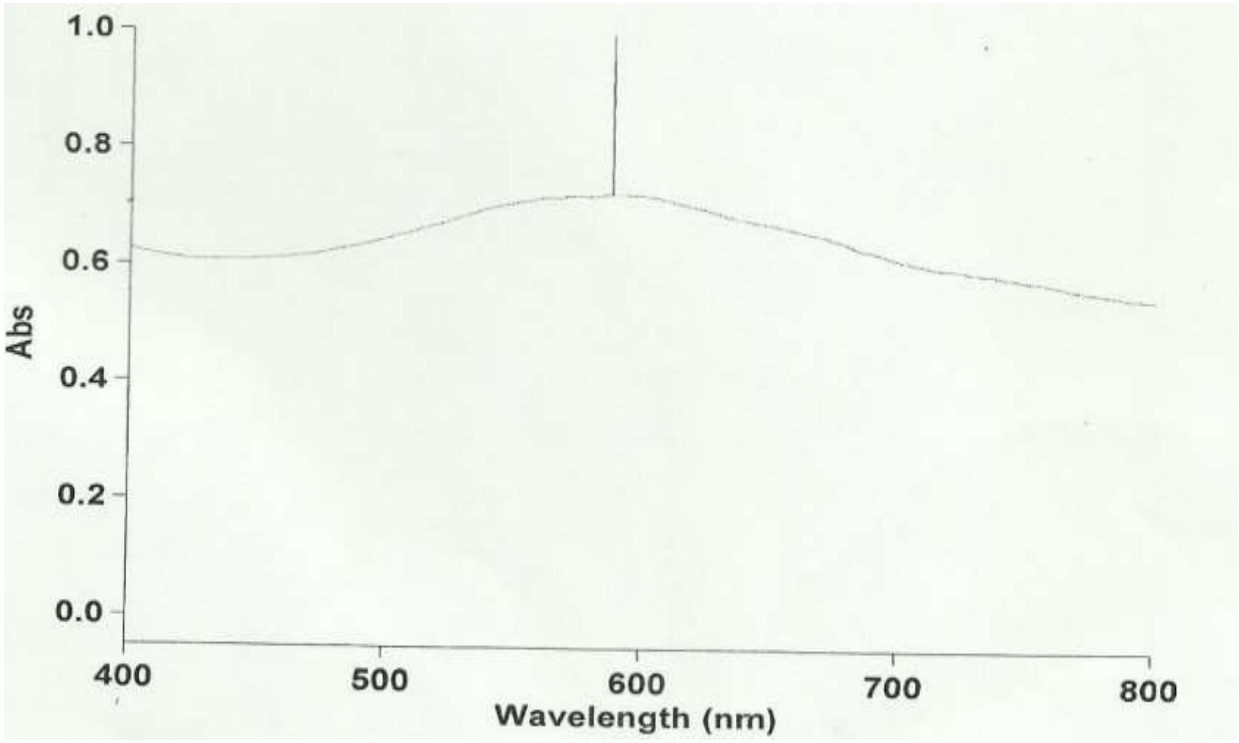
Dye C in Acetone



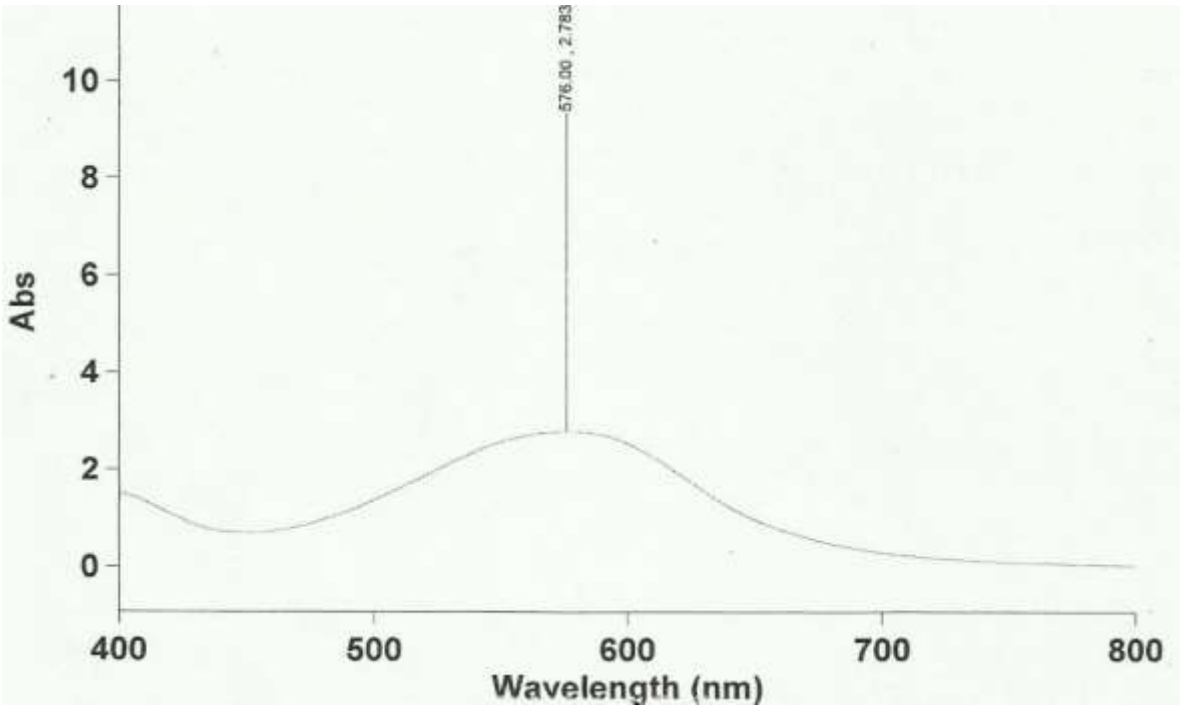
Dye C1 in Acetone



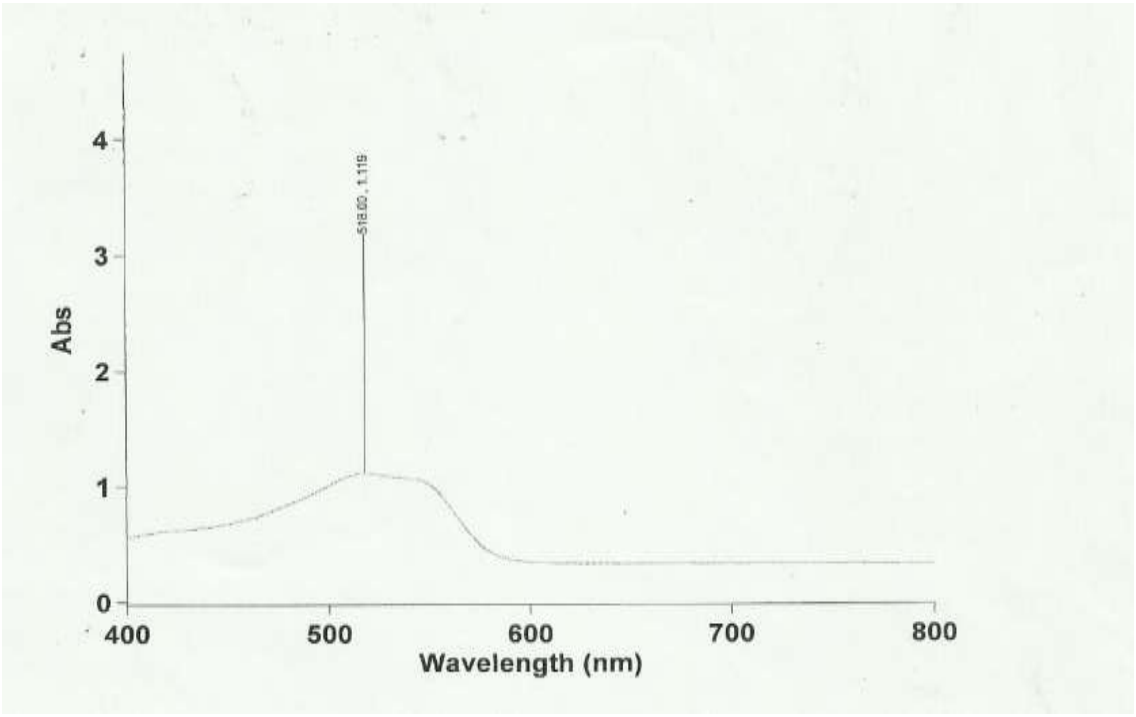
Dye A-PANI in DMSO



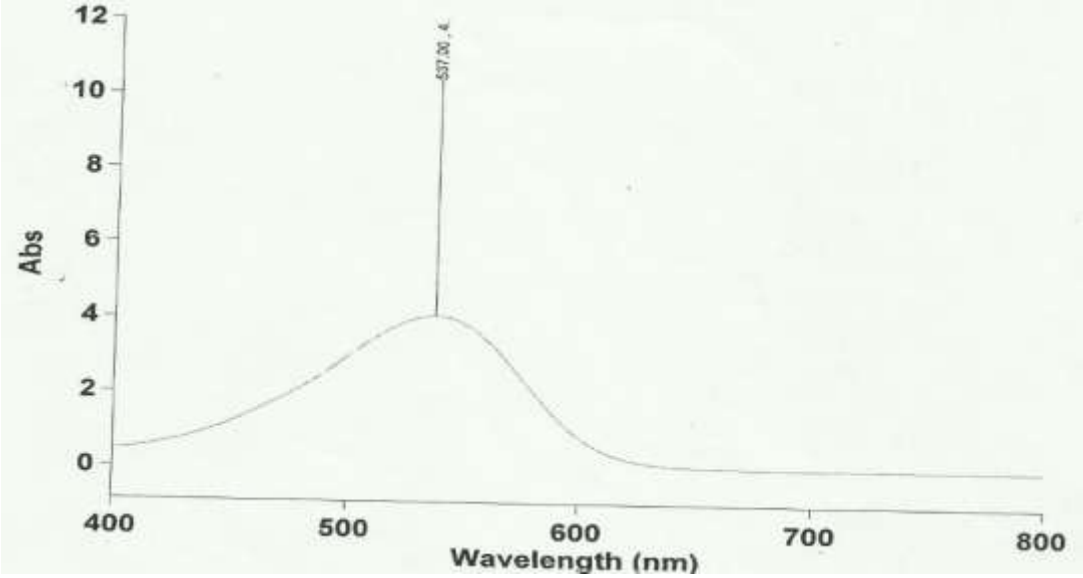
Dye A1-PANI in DMSO



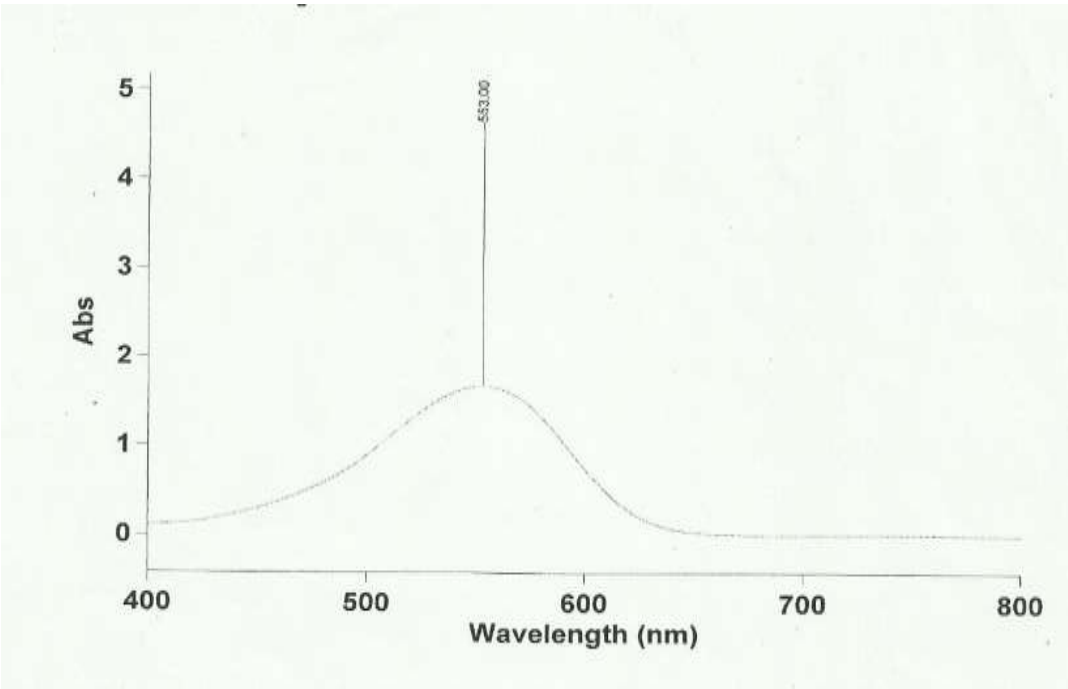
Dye B-PANI in DMSO



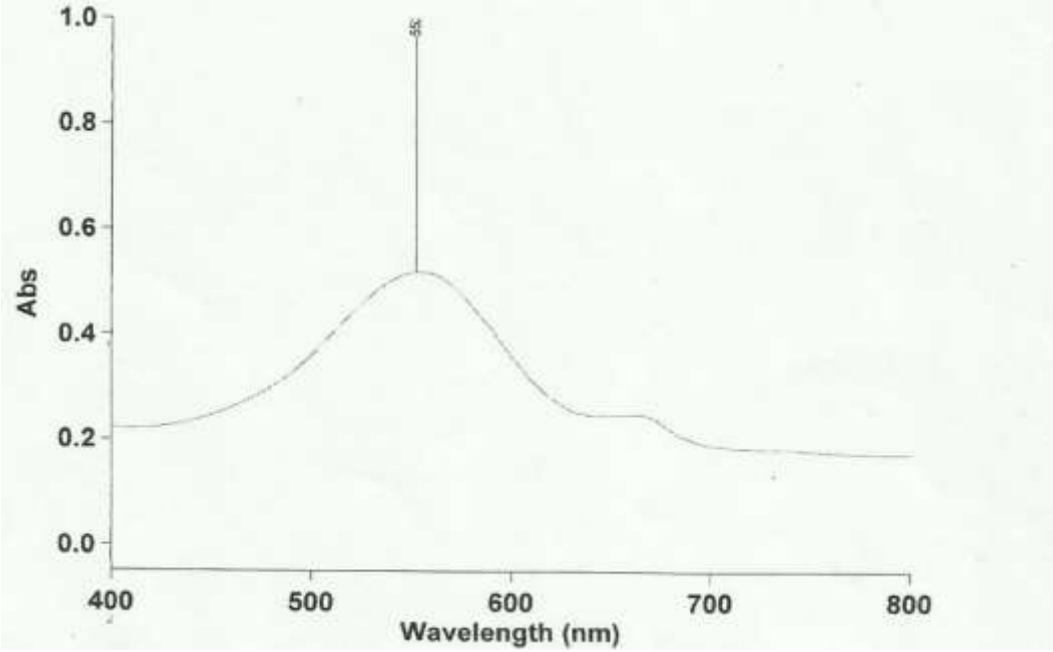
Dye C-PANI in DMSO



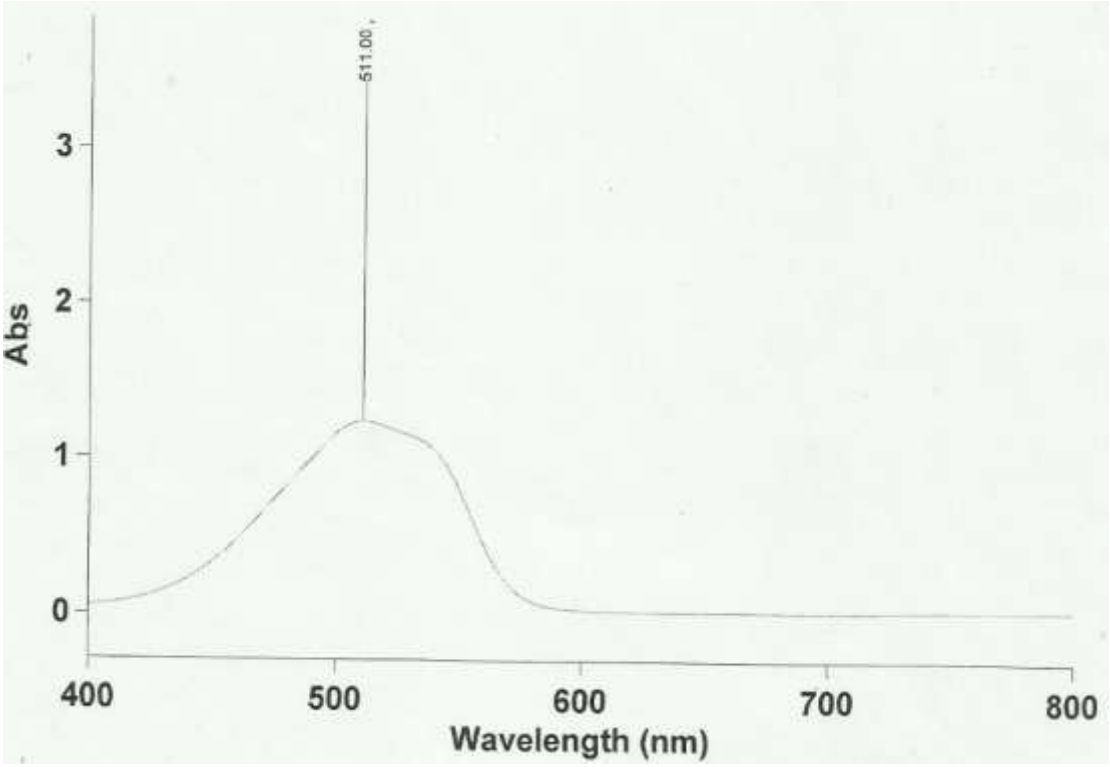
Dye A-PANI in Acetone



Dye A1-PANI in Acetone



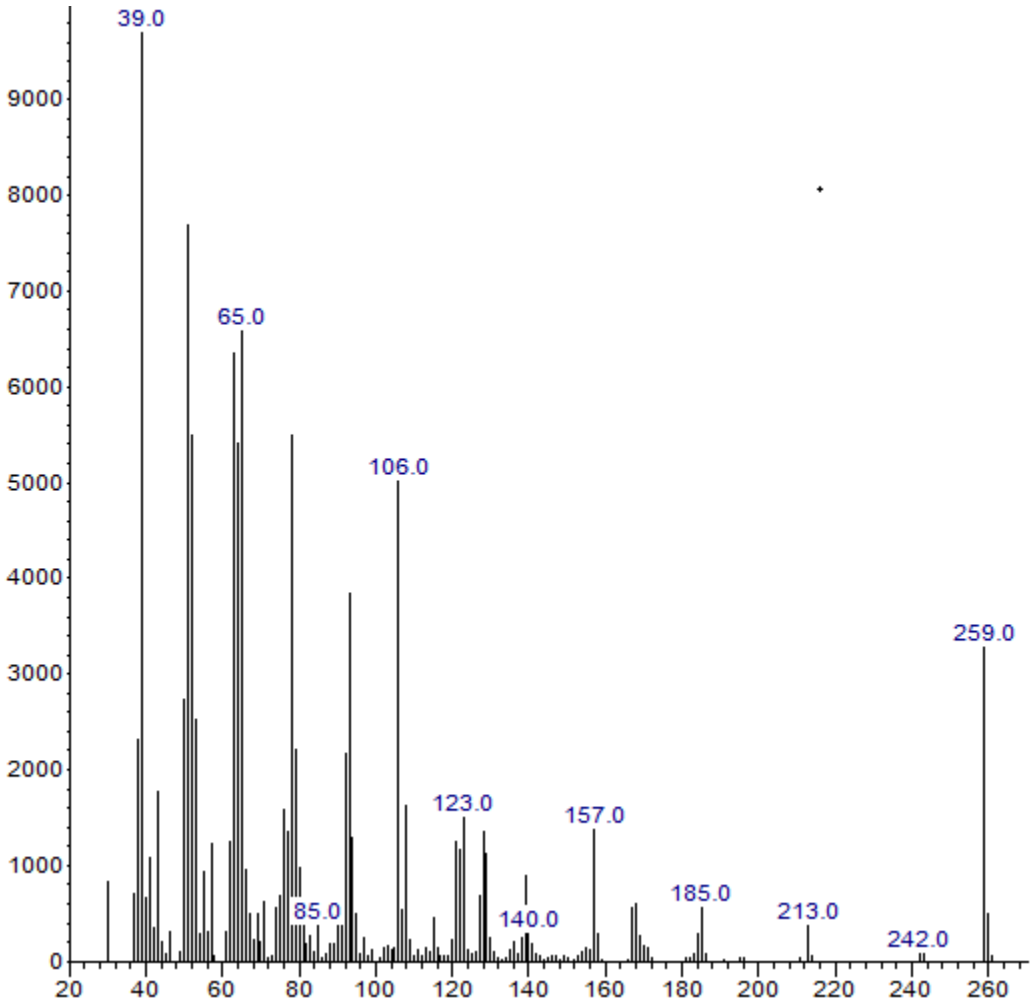
Dye B-PANI in Acetone



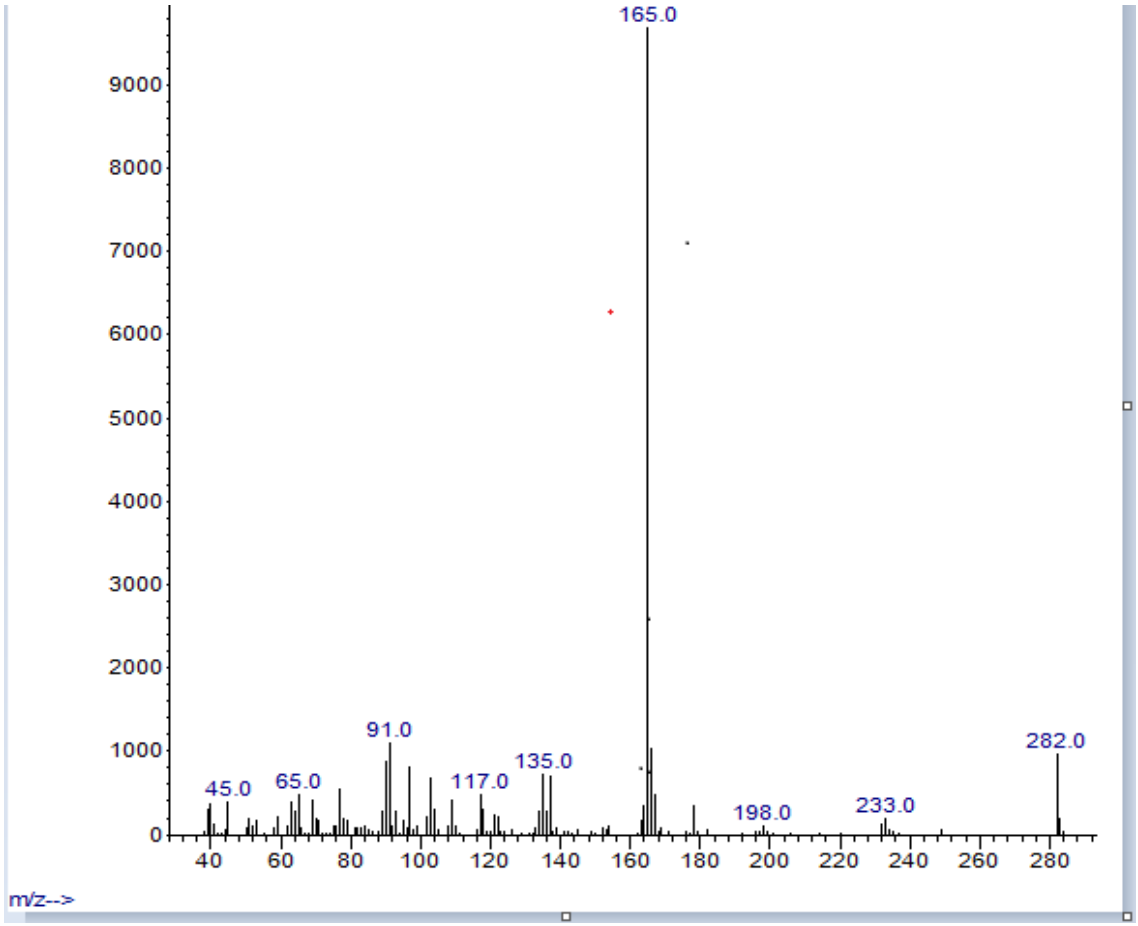
Dye C-PANI in Acetone

APPENDIX III

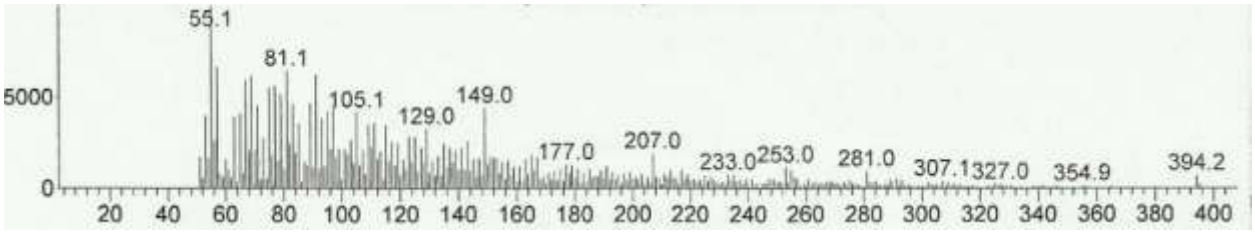
GC-MS Spectra of the Synthesized Intermediate and Dyes



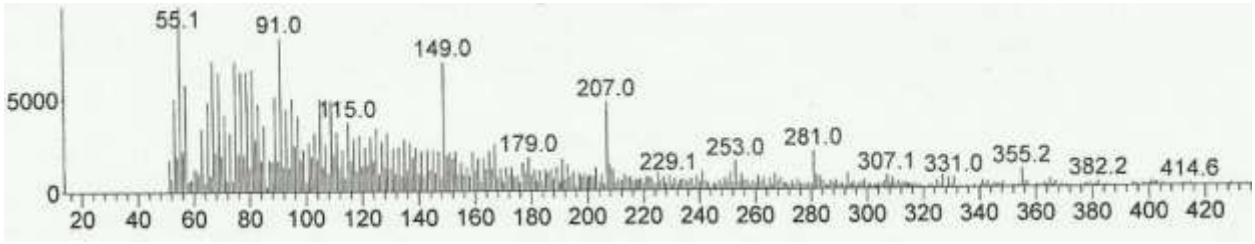
Intermediate 1



Intermediate 2


55.1
81.1
105.1
129.0
149.0
177.0
207.0
233.0
253.0
281.0
307.1
327.0
354.9
394.2
5000
0
20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400

Dye A


55.1
91.0
149.0
207.0
115.0
179.0
229.1
253.0
281.0
307.1
331.0
355.2
382.2
414.6
5000
0
20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420

Dye B