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Chemistry Department

Synthesis and Characterization of New Heterocyclic Polymers Containing 2,6-Pyridine Derivatives and Study Some of Their Applications

A Thesis

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in a Partial Fulfillment of the Requirements for the Degree

of Doctor of Philosophy in Chemistry Science

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2019 AD   **1441 H**

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

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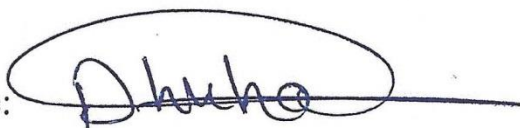
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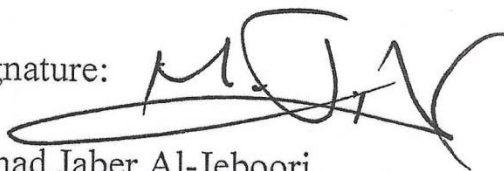
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We, the examining committee, certify that we have evaluated this thesis (Synthesis New Copolymers containing 2,6-Pyridine Derivatives and Investigation some of Their Physical Properties) presented by the student (Nawar Jamal Abdul Rada) and examined her in its contents and that, we have found its worthy to be accepted for the degree of **Doctor of Philosophy** in Chemistry with grade "Excellent".

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Dedication

Every Challenging work, needs self-efforts as well as guidance of elders especially those who close to our heart my humble effort I dedicate to my sweet and loving

Family

Whose affection love, encouragement and pays of day and night make me able to get such success

My completion of this work project could not have been accomplished without the support and encouragements of

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With all my respect

And above all to the

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Finally, I would like to thank all my friends and family members who encouraged and helped me overcoming the difficulties I have faced in this project.

Abstract

In this study, two series of bis oxadiazole polymers were synthesized. The first series was synthesized by converting the solution of 2,6-pyridine di carboxylic acid in the presence of concentrated H_2SO_4 to diethyl pyridine-2,6-dicarboxylate Compound (1) (**comp.1**), was converted to its corresponding di hydrazide (**comp.2**), this compound reacted with oxalyl chloride in dry pyridine and N-methyl-2-pyrrolidone (NMP) to obtain(**Polymer 1**) P_1. was converted to P_2 by cyclized it in the presence of poly phosphoric acid (PPA) as dehydrating agent to obtain P_2 as bis oxadiazole polymer.

P_3-P_7 were synthesized by reacting compound **2** with five different di carboxylic acid in PPA as illustrated in scheme **I** and **II.** These polymers were characterized by FTIR but cannot characterize by ^{1}H-NMR because the synthesized polymers were insoluble in most of known deutrated solvents except P_1.

The second series was P_8-P_{13} these polymers were synthesized by reacting (**comp.2**) with 2 moles of 4-hydroxy benzaldehyde in the presence of acetic acid to give (compound **3**) N'2,N'6-bis(4-hydroxybenzylidene)pyridine-2,6-dicarbohydrazide (**comp.3**), which converted to 4,4'-(pyridine-2,6-diylbis(1,3,4-oxadiazole-2,5-diyl) bisphenol (Compound **4**) by adding bromine solution in the presence of glacial acetic acid and anhydrous sodium acetate. Then (**comp.4**) enter in two path first was reacted with oxalyl chloride to get **P8.**

The second path was reacting of **(comp4)** with five different di acid chloride to prepare (**P9-P13)** as demonstrated in the scheme.
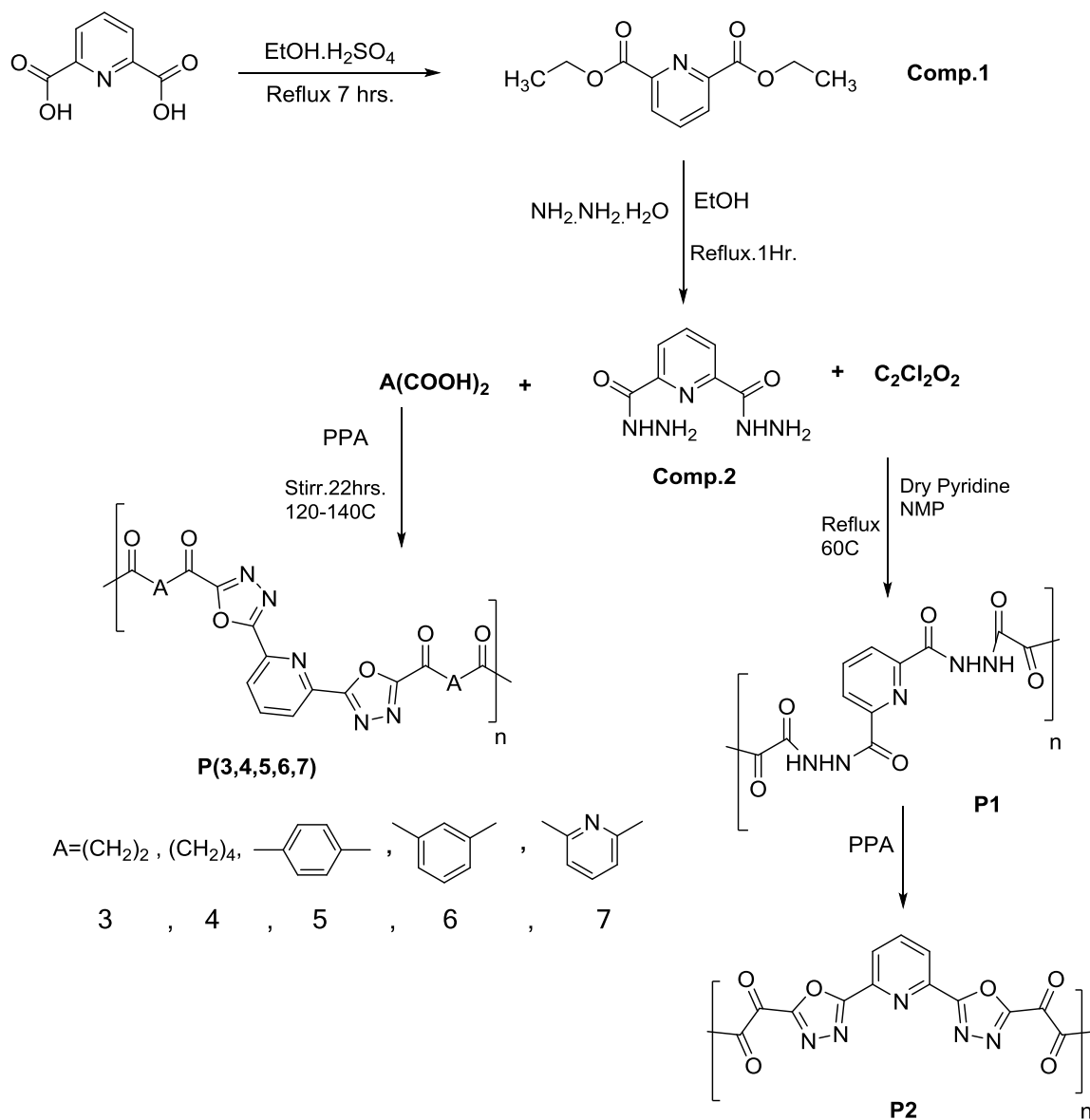
These polymers were characterized by FTIR and [1] H-NMR except polymer **8** which did not show ^{1}H-NMR results.

Thermal stability studied for **(P2-P7)**, polymers **(P5-P7)** which afforded from aromatic di carboxylic acid showed higher stability in comparison with those prepared from aliphatic di acid chloride.

The electro conductivity of **(P2-P7)** was tested at (50-1MHz), at (25-75° C), all these polymers recorded moderate to good conductivity at different temperature. Anti-bacterial activity was screened against *Escherichia coli* (gram-negative bacteria), *Bacillus subtilis* and *Staphylococcus aureus* (gram-positive bacteria), and the fungus *candida albicans*.
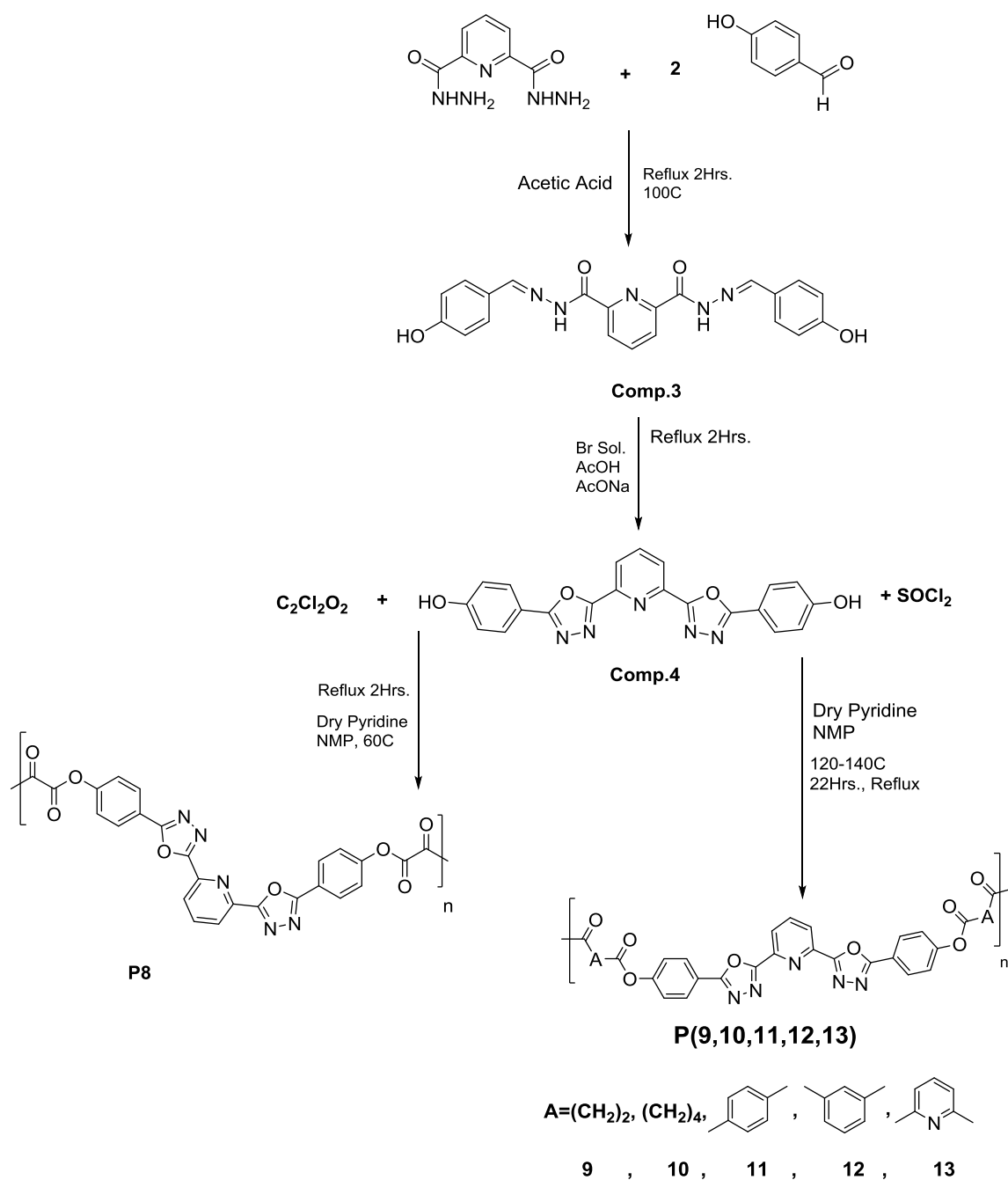
Polymers (5, 6, 7, 11, 12, 13) displayed highest inhibition against all microorganisms under test.

Scheme I: Synthesis of Polymers

P (1-7)

III

Scheme II: Synthesis of Polymers

P (8-13)

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Abbreviation

Symbol	Name
AcOH	Acetic acid
aliph.	Aliphatic
Ar	Aromatic
CHN	Carbon ,Hydrogen and Nitrogen Elemental analysis
DCE	Dichloroethane
DMF	Di methyl formamid
DMSOd$_6$	Dimethyl sulfoxide deuterated
DPPH	2,2-diphenyl-1-picrylhydrazyl
DSC	Differential scanning calorimetry
DTBP	di-tert-butyl peroxide
eq	Equivalent
Et$_3$N	Triethylamine
FTIR	Fourier Transform Infrared Radiation
^{1}H-NMR	Proton Nuclear Magnetic Resonance
Hrs.	Hours
Hz	Hertz
IUPAC	International union of pure and Applied chemistry
KHz	Kilohertz=1000Hz
M.F	Molecular formula
M.p.	Melting point
MeCN	Acetonitrile
MeOH	Methanol
mL	Millliter
mmol	Millimole
min.	Minute
MHz	Megahertz=1000000Hz
MPOX	Methyl phenyl oxadiazole
NMP	N-Methyl-2-pyrrolidone
R.t	Room temperature
pH	Potential of hydrogen
POCl$_3$	phosphorus oxychloride

PPm	Part per million
PPA	Poly phosphoric acid
t-Bu	Tert-butyl
TEAB	tetraethyl ammonium bromide
Td	Degradation temperature
Tm	Melting point
Tg	The glass transition temperature
TGA	Thermo gravimetric analysis
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TMS	Tetra methylsilane
TsCl	Tosyl chloride
UV	Ultraviolet
Ω	conductivity

Chapter One

Introduction

Chapter 1

1. Introduction

1.1 Oxadiazole Ring

Oxadiazoles are an important type of oxygen and nitrogen containing aromatic heterocyclic compounds, possess desirable electronic and charge-transport properties and the various functional groups can easily introduced into the structurally rigid oxadiazole ring. These characteristics afford extensive potential applications of oxadiazole based derivatives in the field of medicinal chemistry. Among the heterocyclic compounds, 1, 3, 4-oxadiazole building motif has become an essential for development of new drugs [1].

Oxadiazoles are five member hetero cyclic rings containing two carbons, two nitrogen and one oxygen atom[2].

The oxadiazoles exist in different isomeric forms such as 1,2,4-, 1,2,5-, 1,3,4- and 1,2,3-oxadiazoles(**a-d**)[3]. 1, 3, 4-oxadiazole is the only isomer which does not consist nitrogen-oxygen bond.
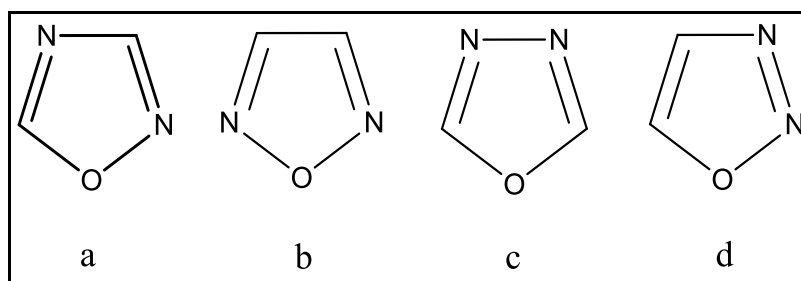
Figure 1–1: Oxadiazole isomers

1.1.1 Synthesis of 1, 3, 4-oxadiazole

In the mid of last century, two separated researchers reported the first method for synthesizing the 1,3,4-oxadiazole[4].

Ainsworth & Hackler in 1966, synthesized some alkyl 1,3,4-oxadiazole by heating the 1-acyl-2-ethoxymethylene hydrazine at atmospheric pressure[5].

$$RCONHN=CHOC_2H_5 \xrightarrow{\Delta} \text{(oxadiazole)}$$
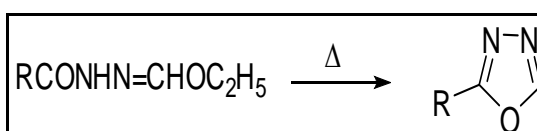
Figure 1-2: synthesis of oxadiazole using 1-acyl-2-ethoxy methylene

Generally, 2, 5-di substituted oxadiazole is synthesized either from reaction carboxylic acid and hydrazide in the presence of dehydrating agent such as $POCl_3$, PPA, conc. H_2SO_4, P_2O_5 and $BF_3.Et_2O$[6-9].

From cyclization their corresponding hydrazone in the presence of oxidative agent such as Br_2, bis (trifluoroacetoxy) iodobenzene and chloramine-T [10-13].

A series of substituted 1,3,4-oxadiazole derivatives were synthesized as anti-inflammatory agents. The target compounds were obtained by cyclodesulfurization of the corresponding thio semicarbazides using either di cyclo hexyl carbo di imide DCC, or I_2/NaOH. Intermediates are readily accessible through conversion of the carboxylic acids to the respective hydrazides followed by treatment with appropriate isothiocyanate derivatives[14].
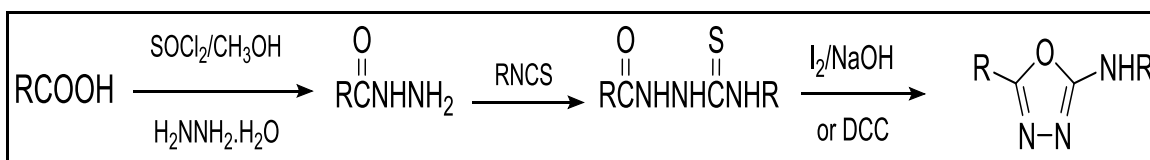
Figure1-3: Synthesis of oxadiazole using sodium hydroxide and iodine

A fast and convenient approach to synthesis of fully substituted 1,3,4-oxadiazoles via three-component reaction of aromatic carboxylic acids, acenaphthoquinone, and (*N*-isocyanimino) triphenylphosphorane under ultrasound irradiation. Utilization of easy reaction conditions, very high to excellent yields, and short reaction times makes this manipulation potentially very useful[15]. as shown in Figure (1-4).
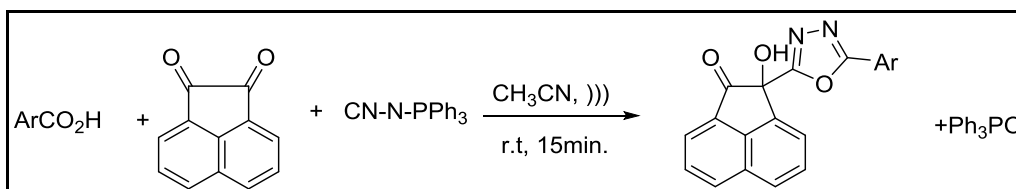
Figure 1-4: Synthesis of di substituted 1,3,4-oxadiazole derivatives under ultra sound irradiation

Series of novel 1,3,4-oxadizole derivatives containing 1,4-benzodioxane ring system were synthesized starting from 2,3-dihydro-1,4-benzodioxane-2-carbohydrazide. The synthesized compounds were characterized and evaluated for anti-bacterial activity against *Staphylococcusaureus*, *Escherichiacoli*, and *Bacillus subtilis,* and anti-fungal activity against *Aspergillus niger*, *Aspergillus flavus* and *Candida albicans* [16]. Figure (1-5).
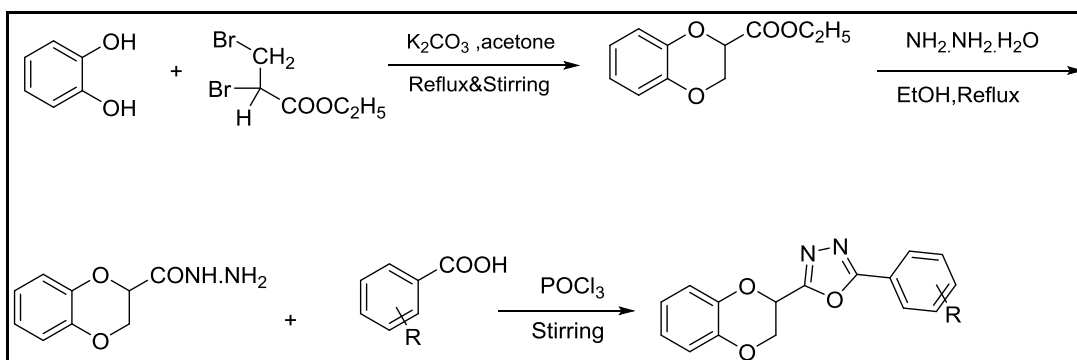
Figure 1-5: Synthetic route for the preparation of 1,3,4-oxadiazole derivatives

Liang Wang *et.al*[17] in 2015 synthesized di aryl 1,3,4-oxadiazole from direct reaction of aryl tetrazoles with aryl aldehydes using di-tert-butyl peroxide as oxidative reagent as shown in Figure(1-6).
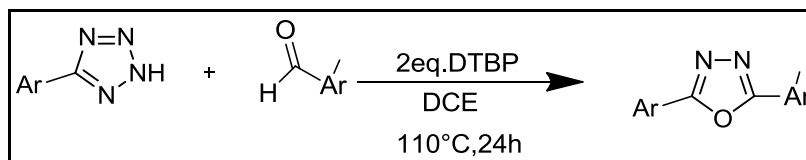
Figure 1-6: Synthesis of oxadiazole by using aryl tetrazoles

Symmetric and asymmetric 1,3,4-oxadiazoles were synthesized in situ from hydrazine hydrate and the corresponding 2-acyl-4,5-dichloropyridazin-3-ones as acylation agents in polyphosphoric acid (PPA) or $BF_3 \cdot OEt_2$ in excellent yields[18] as in figure(1-7).
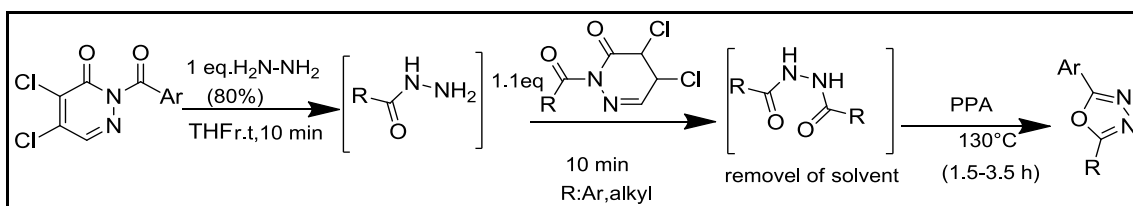
Figure 1-7: Synthesis of symmetrical and asymmetrical oxadiazole by hydrazine hydrate

Alpha-keto-1,3,4-oxadiazoles with significant yield were synthesized under reasonable conditions, using 2-iodoxybenzoic acid and tetraethyl ammonium bromide as oxidative cyclization agents [19]between aryl hydrazide or hydrazones and aryl glyoxal as shown in Figure(1-8).
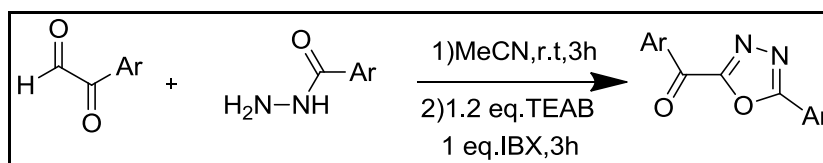
Figure 1-8: Synthesis of oxadiazole by using 2-iodo oxybenzoic acid

Navin B. Patel and Jaymin C. Patel synthesized 1,3,4-oxadiazole amine from the reaction of aryl hydrazide with cyanogen bromide. [20] have synthesized 5-aryl-1,3,4-oxadiazole-2-amine as shown in Figure (1-9).
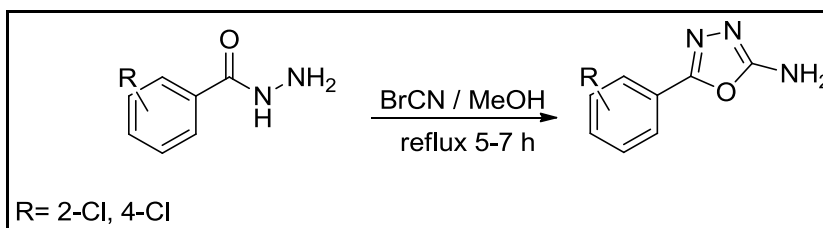
Figure 1–9: Synthesis of oxadiazole by using aryl hydrazide

Alan R. Katritzky *et. al* [21]reported that the Di(benzotriazol-1-yl) methanimine is too useful for synthesizing different heterocyclic included 2-amino-5-phenyl-1,3,4-oxadiazole as in figure(1-10).

5

R= (a) Ph,(b) 4-t-BuC$_6$H$_4$,(c) 4-NH$_2$-C$_6$H$_4$
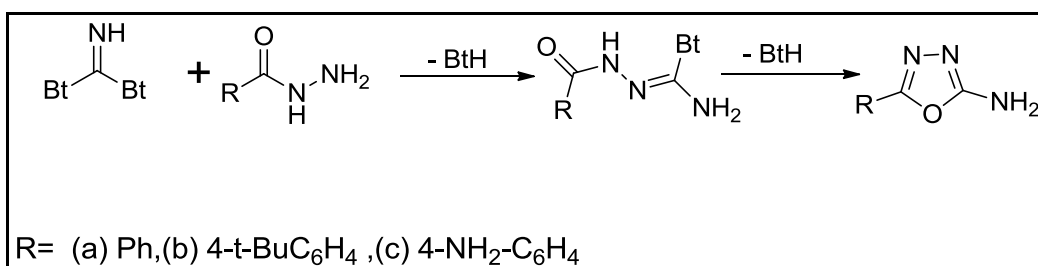
Figure 1–10: Synthesis of oxadiazole using di(benzotriazole-1-yl) methanimine

The oxadiazole amine was, also synthesized from reaction of aldehyde with semicarbazide in the presence of iodine in potassium carbonate [22] as displayed in Figure(1-11).
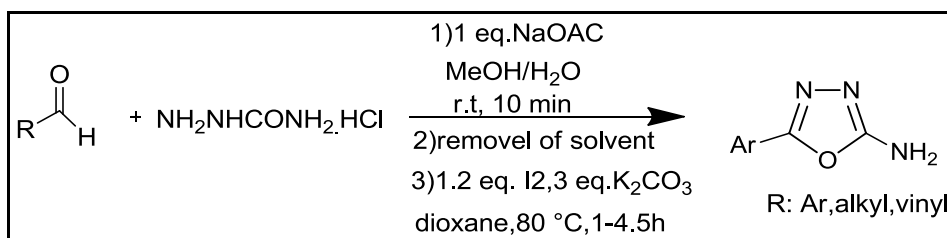
Figure 1-12: Synthesis of oxadiazole by using aldehyde

R. Kapoorr *et.al* [23] synthesized the oxadiazole amine from oxidation of semicarbazones by eosin Y under visible-light photo redox catalysis using CBr$_4$ as a bromine source as in Figure(1-12).
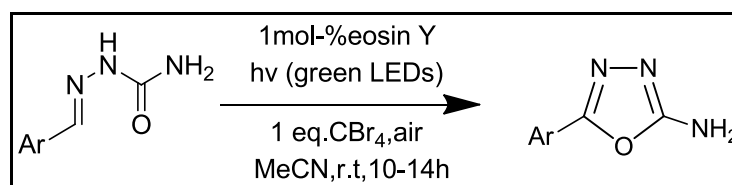
Figure1-13: Synthesis of oxadiazole by using semicarbazones

T. Fang *et.al*[24] In 2014, reported the synthesis of N alkyl-2-amino-1,3,4-oxadiazoles from N-acetyl aryl hydra alkyl iso thio cyanides as depicted in Figure(1-13).
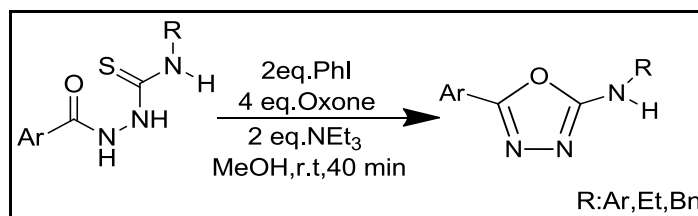
Figure 1-14: Synthesis of oxadiazole by using oxones as catalyst

H.-J. Kwak *et.al* in 2013 [25] has been reported same reaction by using N-(3-Dimethylaminopropyl)-N′-ethyl carbodiimide hydrochloride (EDC HCl) in DMSO instead of iodobenzene and oxone as depicted in Figure(1-14).
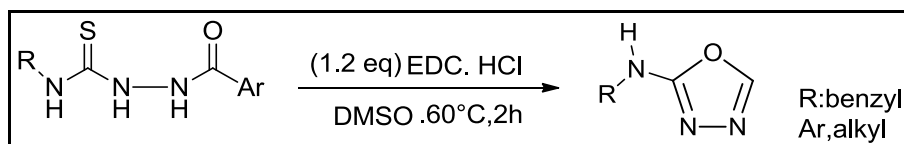
Figure 1-15: Synthesis of oxadiazole by using (EDC HCl)

M. Adib. *et.al* [26]reported the synthesis of 2-aryl-5-hydroxyalkyl-1,3,4-oxadiazoles in one pot from the reaction of *N*-Isocyanimino triphenyl phosphorane, aldehydes and benzoic acid to afford target compounds with good yield as shown in Figure(1-15).
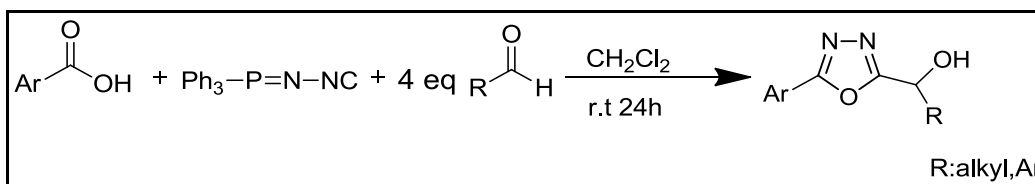
Figure 1-16: Synthesis of oxadiazole by using-N-isocyanimino tri phenyl phosphorene

The suggested mechanism for this interesting cyclization is illustrated in Scheme (1-1).
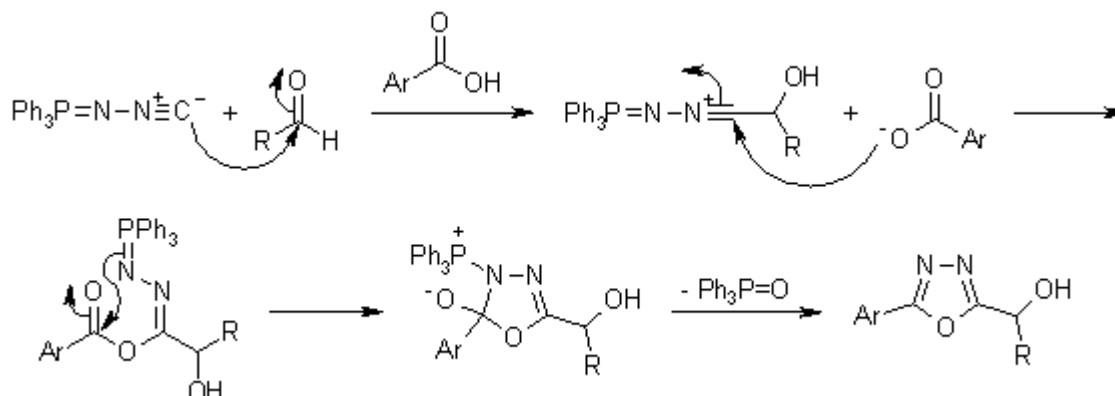
Scheme 1--1: Suggested mechanism of oxadiazole cyclization

Green and rapid method, solvent-free, for synthesis of 1,3,4 - oxadiazoles and 1,3,4-thiadiazoles by condensation of acid hydrazide and triethyl orthoalkanates under microwave irradiations reported by Polshettiwar.V *et et.al* . This method was catalyzed efficiently by solid supported Nafion, NR50 and phosphorus pentasulfide in alumina (P_4S_{10}/Al_2O_3) with high yields[27] as shown in figure(1-16).
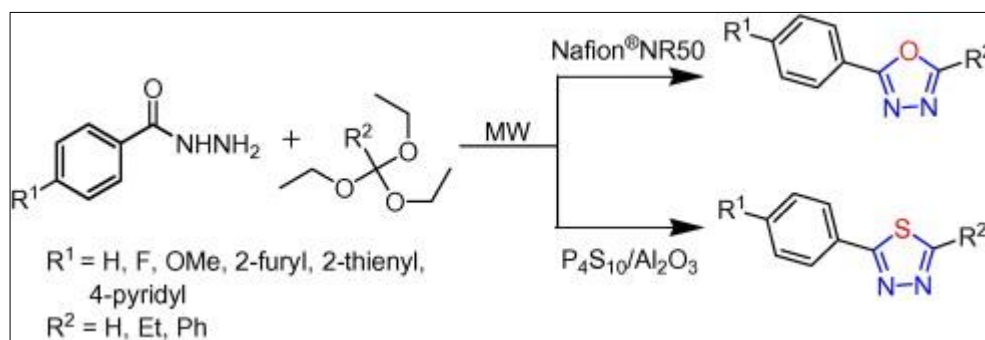
Figure 1–17: Synthesis of oxadiazole by condensation of acid hydrazide and triethyl orthoalkanates

1.1.2 Biological activity of 1, 3, 4-oxadiazole

1, 3, 4-oxadiazole have a wide range of biological activities ranging from anti- cancer[28, 29], radical scavenging [30], anti-malarial [31], anti-microbial[32], anti-HIV[33], anti-protozoal[34], anti- inflammatory[35], anti-diabetic[36, 37], anti-oxidant[38, 39], anti-tubercular[40], anti- convulsing[41], anti- fungal[42], activity against human rhino virus[43], as alpha glucosidase inhibitors[44], antibacterial[45, 46], anti-viral[47], anti-depressant[48], act as selective carbonic anhydrase[49], anti-Alzheimer disease[50], anti-leishmanial[51], inhibition of leukemia cell[52], and act as a biological scaffold with DNA[53].

1.1.3 Physical properties of 1, 3, 4-oxadiazole

1,3,4-oxadiazole have received considerable attention during the last two decades for their photo physical properties[54], photo sensitizer[55], light emitting diodes[56], in liquid crystal[57], fluorescent brightening agent[58], photo luminescent[59, 60], also act as semiconductor[61], optical properties[62, 63],used in solar cells [64], in electronic field[65], anti-corrosion[66], in agriculture field[46], as energetic material[67], and thermal stability[68].

1.2. Poly (1, 3, 4- oxadiazole)s

High molecular weight poly hydrazide gained from low temperature solution reaction of hydrazine or arylene dihydrazide with aromatic dicarboxylic acid are precursors for the genesis of thermally stable poly 1,3,4-oxadiazole [69]. A.H. Frazer and F.T.Wallenberger described this work [70-72].

1,3,4-oxadiazoles polymer belong to the class of polymers with heterocyclic rings, high heat-distortion temperature and thermal stability. Furthermore, the comparative accessibility of the raw materials used in their preparation, dicarboxylic acids and their derivatives afford rise to considerable interest in these polymers.

Aromatic poly-1,3,4-oxadiazoles, like most known heat-resistant polymers of cyclic structure are mainly high-melting polymers and are insoluble in organic solvents [70].

Gateway into the polymer molecules of bulky, cyclic side groups, at least one carbon atom of which forms part of the main polymer chain, cause an obvious boost in the thermal stability of the polymers and to considerable refinement in their solubility [73].

1.2.1 Synthesis of poly (1, 3, 4- oxadiazole)s

Generally, aromatic poly (amid-hydrazides) has been synthesized by solution polycondensation at low temperature of aromatic hydrazides with aroyl dichlorides. By heating these polymers at temperatures about 300° C, dehydrocyclization take place to give polymers containing the oxadiazole ring in the main chain [74, 75].

New silicon-containing aromatic polyhydrazides were synthesized by low-temperature solution polycondensation reaction of bis(p-chlorocarbonylphenyl)diphenylsilane with several aromatic di

hydrazides, or of bis(p-carbohydrazidophenyl)diphenylsilane with di acid chlorides. The corresponding poly(arylene-1,3,4-oxadiazole) were synthesized by thermal cyclodehydration in the solid state at 250-300C [76].

Poly(1,3,4-oxadiazole-imide)s were synthesized from a diamine containing 1,3,4-oxadiazole ring, 4,4′-diamino-4″-[(2-(4-phenoxy)-5-(4-dimethylaminophenyl)- 1,3,4- oxadiazole] triphenylmethane, and various aromatic dianhydrides: 4,4′-(hexa fluoro iso propylidene) diphthalic anhydride, 9,9-bis[(3,4-di carboxy phenoxy phenyl]fluorene dianhydride, 4,4′-(4,4′-isopropylidene diphenoxy) bis(phthalic anhydride) and perylene-3,4,9,10-tetra [77].

Carboxylic di anhydride, sulfonated poly (1,3,4-oxadiazole) was synthesized and it was composited with pristine MWCNT of 0.1–10.0 wt% by an ultrasonicated solution mixing [78].

Tawade.B.V, and Valsange.N.G, reported the synthesis of diacylhydrazide monomer, 4-(4-(4-(4(hydrazinocarbonylphenoxy)-2-pentadecylphenoxy) phenoxy) benzohydrazide (HPPDPB), which was synthesized at the first from 4-(4-hydroxyphenoxy)-3-pentadecylphenol. HPPDPB was poly condensed with terephthalic acid chloride (TPC), isophthalic acid chloride (IPC) and a mixture of TPC and IPC (50:50 mol %) to gain polyhydrazides including multiple arylene ether linkages in the backbone and pendent penta decyl chains. Polyhydrazides were posteriorly cyclized in the presence of phosphorus oxychloride to afford the corresponding poly (1,3,4-oxadiazole)[79].

1.2.2 Poly (1, 3, 4- oxadiazole)s properties

Aromatic poly (1, 3, 4 -oxadiazole)s comprise a group of specialized-performance polymers that are meant to be used in small quantities, but have remarkable values in their end-uses. "Specialized performance" includes:

High thermal stability [80], photo catalytic degradation of organic dyes[81], U.V resistance[82], high modulus[83], optical properties[84], electrical and di electrical properties[85-87], fire retardant[88], stabilizers[89] and anti-microbial[90].

1.3 Hydrazide

Type of organic compound sharing a common functional group characterized by hydrazine core in which at least one of the hydrogen atoms is replaced by a substituent of an acyl group. General structure for a hydrazide is E (=O)-NR-NR$_2$, where the R are usually hydrogens. Moreover, hydrazides can be categorized by atom connected to the oxygen: carbohydrazide (R-C (=O)-NH-NH$_2$), and sulfonohydrazide (R-S (=O)$_2$-NH-NH$_2$.

1.3.1 Synthesis of Hydrazide

Several hydrazide–hydrazone derivatives denoted 2′,4′-difluoro-4-hydroxybiphenyl-3-carboxylic acid [(5-nitro-2-furyl / substituted phenyl)methylene] hydrazide have been synthesised. Methyl 2′,4′-difluoro-4-hydroxybiphenyl-3-carboxylate and 2′,4′-difluoro-4-hydroxybiphenyl-3-carboxylic acid hydrazide were also synthesised and used as intermediate compounds [91], figure(1-17) shown 2,4-

di fluoro-4-hydroxy biphenyl-3-carboxylic acid that bears biological activity was chosen as starting compound to designed several novel hydrazides-hydrazones.
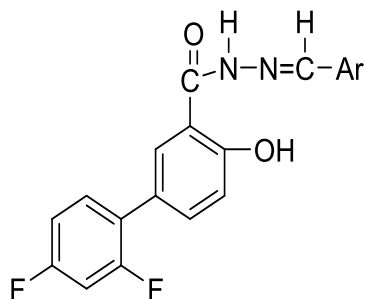
Figure 1-87: (2,4-di flouro-4-hydroxy bi phenyl-3-carboxylic acid)

Perdicchia et.*al*, [92] synthesized hydrazide by oxidizing Fischer carbenes, predominately hydrazinocarbene complexes. The reagents traditionally used to oxidize Fischer carbenes have failed because of the stability of hydrazinocarbene complexes and simple oxidation of prepare hydrazides in the reaction conditions. Three newly developed methodologies are very moderate, fast, active, and complementary. Differently functionalized hydrazinocarbene complexes can be oxidized to give new hydrazides as shown in figure (1-18).
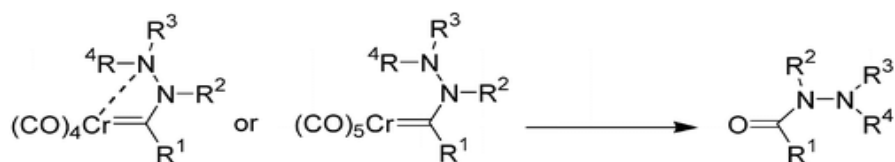
Figure 1-18: Synthesis of hydrazide by oxidize Fischer carbenes

Synthesis of different mono-, di- and tri substituted hydrazines with high yield by reduction step can be followed by an in situ reaction with a carboxylic acid making possible a one-pot synthesis of tri substituted hydrazides. This method is comparatively suitable for industrial applications[93] as displayed in figure(1-19).
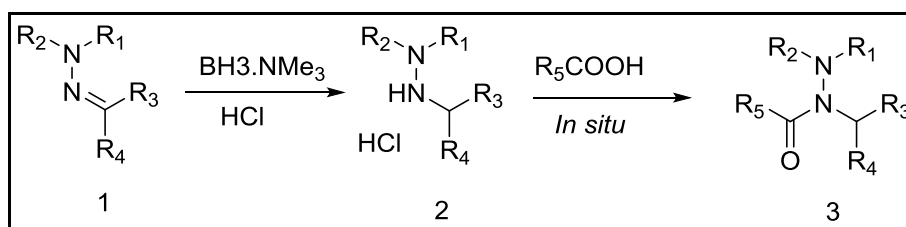
Figure 1–19: Synthesis of different substituted hydrazide

Joshi *et.al* [94], reported synthesis a new series of 4-pyrrol-1-yl enzoic acid hydrazide analogs,5-substituted-2-thiol-1,3,4-oxadiazoles, 5-substituted-4-amino-1,2,4-triazolin-3-thione and 2,5-dimethyl pyrroles as shown in figure(1-20).
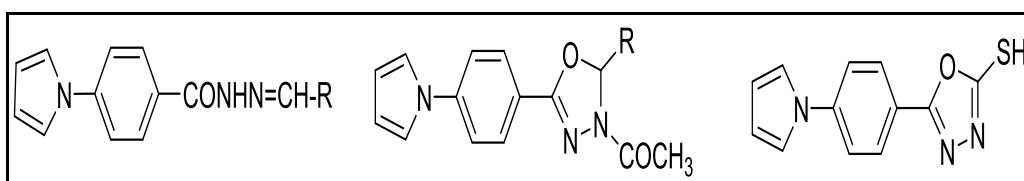
Figure 1–20: Synthesis of a new series of 4-pyrrol-1-yl-benzoic acid hydrazide

Salgin-Goksen *et al.*[95] in 2007 reported synthesis of arylidene hydrazides as cis–trans conformers. Among the synthesized compounds (X) ,3-[(5-methyl-2-benzoxazolinone-3-yl) methyl]-4-phenyl-1*H*-1,2,4-triazole-5(4*H*)-thione, exhibited high anti-inflammatory activity figure (1-21).
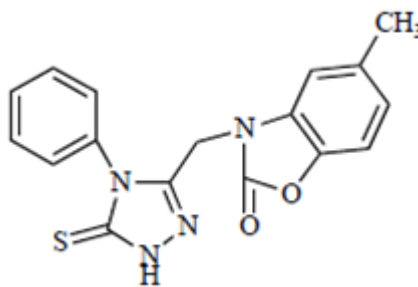
Figure 1-21: Compound X possess anti-inflammatory activity

Kulandasamy *et al.* [96], synthesized a series of new 3,4-dipropyloxy-N2,N5-bis(substituted)thiophene-2,5-dicarbhydrazides from ethyl thiodiglycolate and diethyloxalate. The anticonvulsant activity of all compounds was investigated against maximal electroshock induced seizures and subcutaneous pentylenetetrazole models and their neurotoxicity was also estimated compound 3,4-dipropyloxy-N2,N5-bis[1-(2-thienyl)ethylidene]thiophene-2,5-dicarbohydrazide protrude as a lead with less neurotoxicity compound XI As displayed in Figure (1-22).
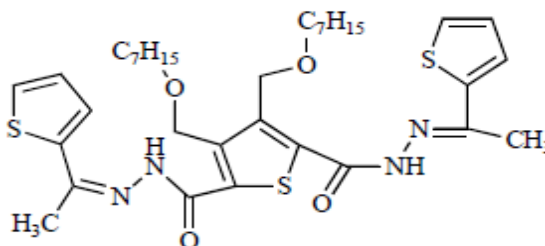
Figure 1-22: Compound XI exhibited less neurortoxicity

New bis-benzylidene-hydrazides were synthesized via a condensation reaction of the corresponding azo dyes with adipic acid dihydrazide. Nitro bis-benzylidene-hydrazide derivative shown

highly sensitive and selective chromogenic sensor for naked-eye detection of CN⁻ and AcO⁻ ions, with a discret color change from yellow to blue and yellow to purple[97].

Last years, indole-indazolyl hydrazide-hydrazone derivatives with strong cell growth inhibition and apoptosis creation characteristics are being strongly screened for their cancer chemo-protective.

Das Mukherjee *et.al* [98] in 2016 reported synthesis a series of bis(indolyl)- hydrazide−hydrazones, labeled as (NMK-BH), from indole- 2(3)-carboxylic acid hydrazide and indole-3-carboaldehyde, where in the indole rings were linked by an active pharmacophore (−CO−NH−NCH−), shown anti-cancer activity. N-methyl and N,N-dimethyl bis(indolyl)hydrazide-hydrazone analog derivatives were designed, synthesized and allowed to evaluate for their anti-cancer activity[99] figure (1-23).
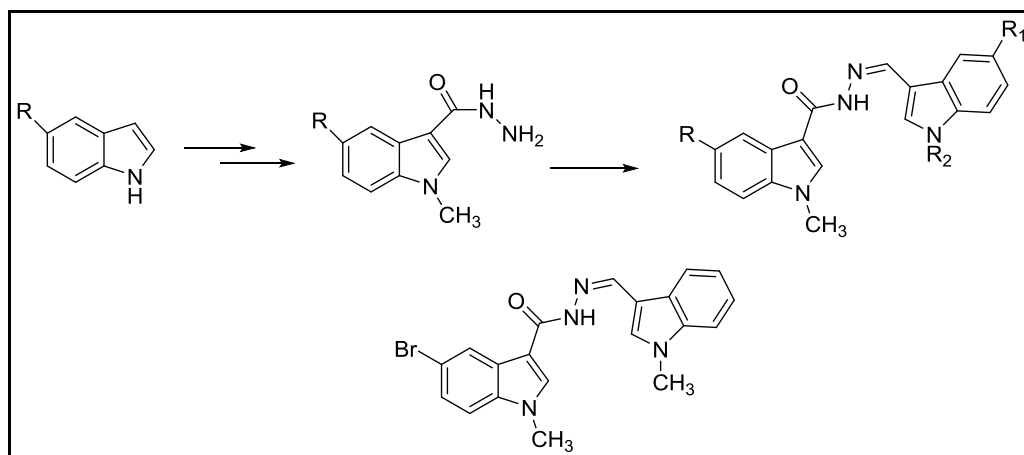
Figure 1-23: Compound possess anti-cancer activity

Ru,Chen-Hao *et.al*[100] described a new chemistry of azo compounds that is a radical generation and addition in situ od azo carboxylic tert-butyl esters in the presence of hexa fluoro iso propanol to synthesize hydrazine, figure(1-24).
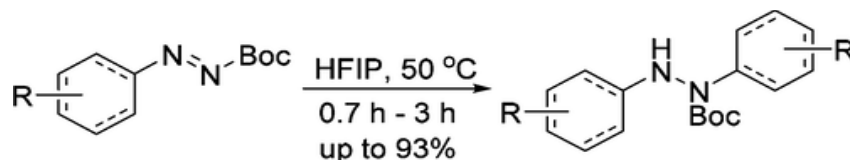
Figure 1–24: Synthesis of hydrazide from azo compounds

1.3.2 Hydrazide properties

Hydrazides have been the focus of considerable interest owing to their biological activities such as:

Anti-tuberculosis[101], anti-tumor[102], anti-leishmanial and ani-plasmodial[103], mimics for some protein[104], anti-cancer[105], anti- pancreatic carcinoma and hepato cellular carcinoma and leukemia[106], anti-inflammatory[107], anti-oxidant[108], anti-microbial[109, 110], anti-bacterial[111], anti-viral[112], anti-fungal[113], anti-convulsant[114], anti-infectious[115], anti-giogenic activity[116], anti-HIV[117], and anti-diabetic[118].

Also displayed physical properties like:

Optical activity[119], electrical properties[120], photochromic materials[121],electrochemical activity[122], recognition of metal ions[123], anti-corrosion[124], with adhesion[125], improving of hydrogel[126], improving energetic materials[127], and in laser[128].

1.4 Hydrazone

Hydrazone constitute an azo methine R-C(H)=N-N(H)-Ar group which may be derivatives of aldehydes and ketones by replacement of oxygen atom with the (=NNH$_2$) group.

Hydrazones is a privileged moiety has significant position in the field of medicinal chemistry due to its worthy chemo therapeutic potential [129, 130].

Hydrazone receives much attention of today s researchers in the field of drug recovery, so its act as intermediate for development of novel compounds with anti-bacterial[131], cartilage tissues engineering[132], anti- diabetic[133], anti-hyperglycemic[134], anti- oxidant[135], anti-convulsant[114], DNA binding[136], anti-tuberculosis[137, 138], anti-inflammatory[139], anti-microbial[140, 141], anti-viral[142], anti-HIV[143], anti-malarial[144], anti-cancer[145], photo protective agent[146], anti-platelet[147], anti-protozoal[148],anti-leishmanial[149],anti-analgesic[150], cardiovascular disease[151], anti-depressant[152], anti-Alzheimer disease [153], and anti-proliferative[153].

Also shown various physical properties such as:

Catalyst[154],anti-corrosion[155], photosensitive material[156], selective and detection of metal ions[157], and luminescent properties[158].

1.5 Polymers

The word *polymer* is derived from Greek words meaning "many parts".

Polymers are synthesized by a process known as *polymerization*, which includes the chemical incorporation of many small chemical units known as *monomers* "single parts". The repeating units in a polymer molecule may be either single atom as in sulfur molecules

or groups of atoms such as the methylene units,$\_CH_2\_$,in   poly ethylene[159].

$$-S-S-S-S-S-S-S-S-S-S-S-S$$

$$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$$

Natural polymers are considered as a first polymers, such as cotton, starch, proteins, and wool[160]. In 1900s, scientists started collecting knowledge of polymers.

Herman Staudinger in 1910 was the first who began search and studied the large molecules, Staudinger suggested that rubber and other polymers were indeed collected of giant molecules that he named (Macromolecules) [161].

The first synthesized polymers were Bakelite and nylon, which considered promising materials[160].

The total number of repeating units in polymer is known as the degree of polymerization or **Dp**.

Some polymers have a linear or thread like structure. Others are branched or cross-linked in three dimensional networks.

Still others have less prevalent shapes resembling combs, stars, or ladders[162].

Polymers have flexible linear or branched structures are thermoplastic, so, they can be molded or extruded under pressure and high temperature. While, the cross-linked thermosetting resins are rigid materials[163].

Homo polymer consist only of one type of repeating unit, whereas

Copolymers are composed of two or more different monomers units arranged in either random or alternating sequences.

A few copolymers possess block or graft structures. With relatively long sequences of one repeating unit bonded to similar sequences of other. Polymer formulation involves either chain or step reactions. The terms addition and condensation, consequently, were used for characterizing those processes[164].

1.5.1 Classification of Polymers

There are different ways used to classify polymers according to some special respect. The figure display some of polymers classifications [165], as illustrated in figure(1-25).
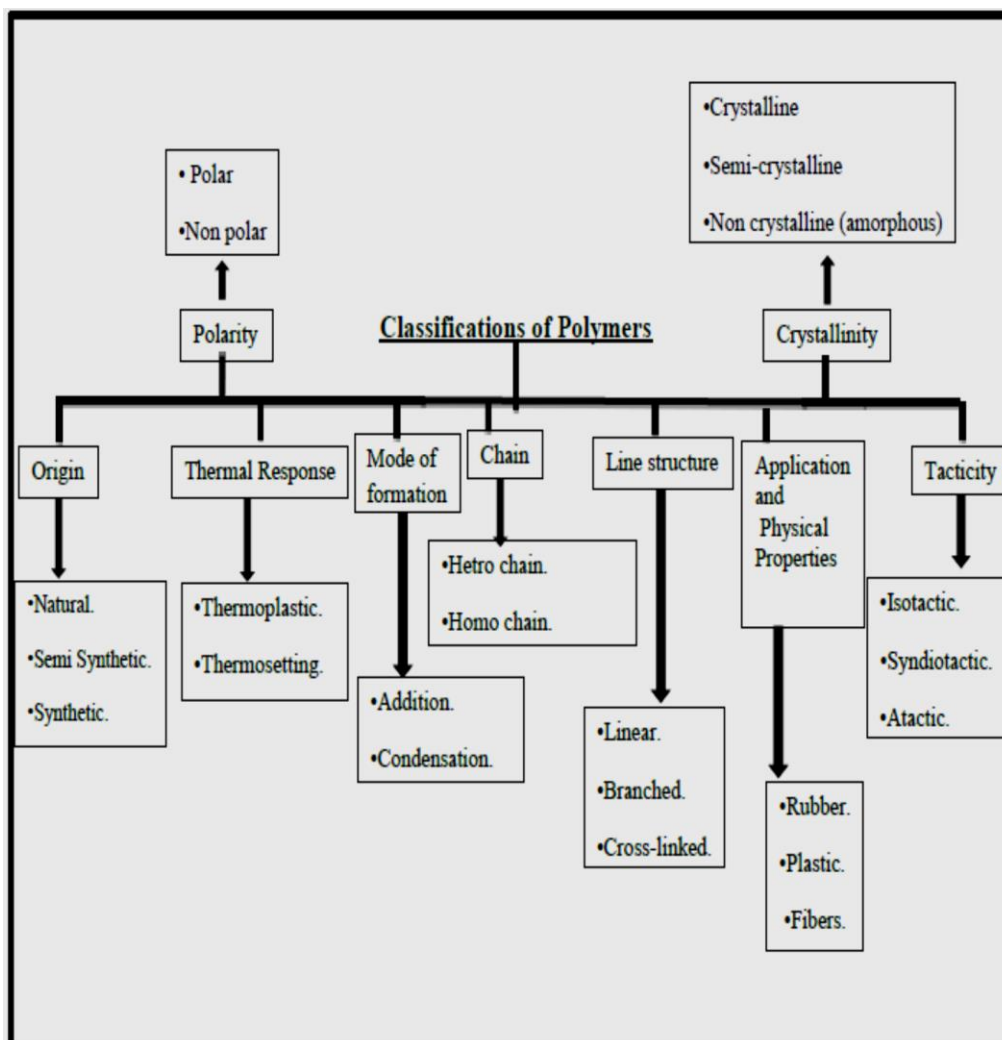
Figure 1–25: Polymers classifications

1.5.2 Type of Polymerization

1.5.2.1 Condensation (step-Growth):

Condensation polymerization, also named step growth or simple step polymerization, one simply traditional organic reactions that are used to produce linear macromolecules starting from bi functional monomers (that is, monomers containing two functional groups per molecule), or to produce polymer networks from mixture of bi functional and multi- functional monomers having three or more functional groups per molecule[166].

The polymerization of bi functional monomers may be described as a step wise or progressive conversion of monomers with two reactive end groups to higher molecular weight homologues, which themselves retain two reactive end groups. It may happen either by a poly condensation reaction. However, a low- molecular weight by products is formed a long with the polymer as is exemplified by poly esterification.

$$nHOOC(CH_2)_X COOHnHO(CH_2)_y$$

$$HO\text{-}[\text{-}OC(CH_2)_x COO(CH_2)_y OOCNH\text{-}]\text{-}(CH2)_x NCO$$
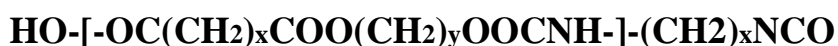
The equations exhibit the overall reactions in the particular step-growth polymerization, the polymer molecules growth, however happen by a stepwise intermolecular reaction.

A dimer reacts with monomer to form a trimer or with dimer to creat tetramer and so on.

Actually, any two species in the reaction mixture can react with each other.

Step polymerization can be expressed by the general reaction:

$$\text{n-mer} + \text{m-mer} \longrightarrow \text{nm-mer}$$
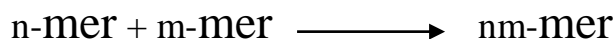
Where (n) and (m) can have any number from 1 to very large number.

Furthermore, the polyesterification reaction mixture of diacid and diol at any time will consist different sized diacid, diol, and hydroxy acid react and the chemical reaction in each step is the same, that can be written as:

$$..........\text{-COOH}+\text{HO-}.........\text{-COO-}........+H_2O$$

Similarly, polyamidation and poly urethane-forming reactions can be written as:

$$.......\text{-COOH}+H_2\text{N-}.....\ \ ......\text{-CONH}.....+H_2O$$

$$.......\text{-NCO}+\text{HO-}.....\ \ ......\text{-NH-COO-}.....$$

Implied in this equation is the assumption that the functional group on the end of monomer has the same reactivity as similar group on a n-mer of any size and that the reactivates of both functional species: Like COOH groups of a diacid and OH groups of diol in the reaction mixture are the same.

These simplifying assumptions are known as the concept of equal reactivity of functional groups [167, 168].

1.5.2.2 Chain Polymerization:

Ionic mechanisms in which the growing chain end carbon bears a negative charge (carboanion) so the polymerization known as anionic polymerization , while with positive charge (carbocat ion), it is known as cationic polymerization[169, 170].

1.5.2.3 Ring Opening Polymerization:

Polymerization can be classified into two wide category condensation and olefin polymerization.

The third type is ring opening polymerization (ROP) of cyclic compounds[171].

One of the most commercially important polymers synthesized by (ROP), polyethers which synthesized from three-memberd ring cyclic ethers (epoxides), polyamides from cyclic amides(capro lactam) nylon 6, and poly siloxane from cyclic siloxanes[172, 173].

1.5.2.4 Free Radical Polymerization:

A large number of unsaturated monomers, like ethylene (CH_2CH_2) the simplest olefin, A-olefins (CH_2CHR; where R is an alkyl group), vinyl compounds (CH_2CH_X), where X=Cl, Br, I, Alxoy, CN, COOH, COOR, C_6H_5, etc., atoms or groups), and conjugated diolefins(e.g., butadiene $CH_2CHCHCH_2$, and isoprene $CH_2C (CH_3) = CHCH_2$) easily submit chain growth polymerization, and also known as addition or simple chain polymerization [174, 175].

1.5.2.5 Coordination Addition Polymerization:

Coordination polymerization originated by the German chemist Karl Ziegler and Italian Giulio Natta in 1950s.

In the beginning of 1950s Ziegler found out that aluminum alkyls when react with certain transition metal compounds such as $TiCl_4$or VCl_4 created complexes that would polymerize ethylene at low temperatures and pressures producing polyethylene with linear structure.

That now pointed to high density polyethylene (HDPE).

Natta's work led to the realization that catalytic complexes described by Ziegler were capable of polymerizing 1-alkenes (usually known as alpha olefins in the chemical industry) to yield stereo regular polymers[176].

This type of catalysts, known as Ziegler Natta catalyst, was posteriorly prolonged to produce polymers exhibiting a wide range of stereo regular structure including those afforded from dienes and cycloalkenes. Many polymers are now manufactured on a commercial level using Ziegler-Natta catalysts the most important among them being stereo regular (isotactic) polypropylene of high molecular weight [177, 178].

Aim of the Study

The aim of this study is to synthesis some poly (1,3,4-oxadiazole)$_S$ characterize their biological activity against some microorganisms, study of their thermal stability and their electrical behavior for use as semi-conductors.

Hetero cyclic compounds are a highly versatile class of organic materials. 1,3,4-oxadiazole and their polymers are some of them which consider as a privilege materials have a significant position due to their wide spectrum of biological activities ranging from anti-bacterial, anti- fungal, anti-cancer, anti-diabetic, anti-viral, anti-malarial, anti-oxidant, etc.

Besides to their importance in the field of medicinal chemical because of their worthy chemo potential, that made them receives much attention of today researchers.

Poly (1,3,4-oxadiazole)$_S$ have been the focus of interest with aspect to the production of high performance materials, especially due to their thermal stability, high chemical resistance ,etc.

Poly(1,3,4-oxadiazole)$_S$ have many eligible properties such as low di electric constant, tough mechanical properties, have semi-conductive properties, some of them have liquid crystalline characteristic, precursors for some oriented graphite fibers, films.

Chapter Two

Experimental

Chapter Two: Experimental

2.1 Table of Chemicals

Table 2-1: Chemicals, Manufactures and their purity

Name of Chemical	Name of Company	Purity
Acetone(C_3H_6O)	Romil	99%
Acetonitrile anhydrous(CH_3CN)	Sigma-Aldrich	99.8%
Bromine solution	Sigma-Aldrich	80%
DMF	Sigma-Aldrich	99.8%
Ethanol(EtOH)	Romil	99.9%
Ethyl acetate($C_4H_8O_2$)	Romil	99.5%
Hexane(C_6H_{12})	Romil	95%
Hydrazine hydrate (N_2H_4)	Merck	80%
Hydrochloric acid(HCl)	Sigma-Aldrich	36.4%
4-Hydroxy Benzaldehyde	Sigma-aldrich	98%
Isophthalic acid	Sigma-Aldrich	99%
Magnesium sulphate ($MgSO_4$)	Romil	97%
Methanol(MeOH)	Romil	99.8%
N-Methyl-2-pyrrolidinone	Sigma-Aldrich	99%
Oxalyl Chloride	Sigma-Aldrich	98%
Poly phosphoric acid (PPA)	CDH	99%
Potassium carbonate(K_2CO_3)	Romil	99.99%
Potassium hydroxide(KOH)	Romil	98%
2,6-Pyridine di carboxylic acid	Sigma-Aldrich	99%
Pyridine	Merck	99.5%
Sodium hydrogen carbonate($NaHCO_3$)	Romil	98%
Sodium hydroxide (NaOH)	Romil	98%
Sodium sulfate(Na_2SO_4)	Romil	99%
Succinic acid	HIMEDIA	99%
Sulfuric acid	CDH	98%

Name of Chemical	Name of Company	Purity
Terphthalic acid	Sigma-Aldrich	99%
Thionyl chloride	Merck	99%
Thiosemicarbazide	Sigma-Aldrich	99%
Toluene($C_6H_5CH_3$)	Romil	99%
Tri chloro phosphoric acid	Sigma-Aldrich	99%

2.2 Instruments

1. Melting point apparatus Stuart-automatic were used to determine melting points in open capillary tube.

2. Thin layer chromatography (TLC) were carried out using alumina plates recoated with silica-gel; were used to confirm the synthesis of the compounds and to monitor the reaction proceeding. Two different solvents systems (hexane: ethyl acetate) were used to run the TLC. The spots were located under iodine vapors /UV light.

3. Infrared spectra were recorded on Shimadzu 8400 Fourier Transform Infrared spectrophotometer (FT-IR) by using the KBr disc or thin film in the wave number range (400-4000) cm^{-1}, in College of Education For Pure Science (IbnAl-Haitham), University of Baghdad.

4. ^{1}H-NMR spectra were recorded on a BRUKER 60 MHz, operating at 60MHz, (DMSO-d6) was used as the solvent with TMS as internal standard, measurements were made at Central Service

Laboratory/ College of Education for Pure Science (Ibn Al-Haitham), University of Baghdad.

5. The Element analysis (CHN) was recognized by EURO EA 3000 at Central Service Laboratory/ College of Education For Pure Science (Ibn Al-Haitham), University of Baghdad.

6. Thermal analysis (TGA, DSC) were carried out using LINSEIS (STA TT-1000) instrument in Central Service Laboratory/ College of Education For Pure Science (Ibn Al-Haitham), University of Baghdad.

7. The biological activity at Central Service Laboratory /College of Education For Pure Science (Ibn Al-Haitham), University of Baghdad.

8. The conductivity measurement of the prepared polymers were carried on using Hewlett Packard 4274A multi Frequency LCR meter at Central Service Laboratory/ College of Education For Pure Science (Ibn Al-Haitham), University of Baghdad.

2.3 Synthesis of monomer

2.3.1 Synthesis of diethyl pyridine-2,6-dicarboxylate comp.1

Comp. 1
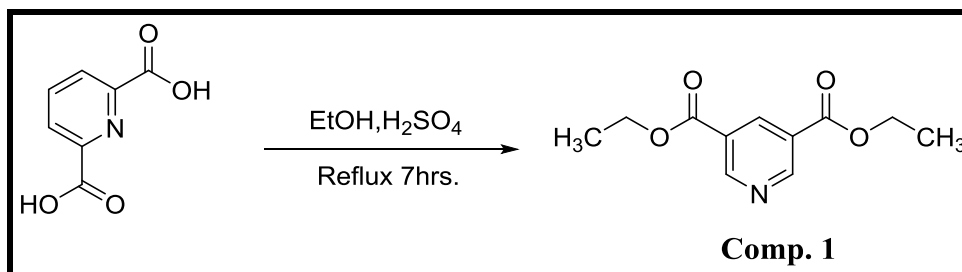
A solution of 2,6- pyridine di carboxylic acid (15g, 89.8 mmol) in absolute ethanol (25 mL) and three drops of concentrated sulfuric acid was heated under reflux for 7 hrs. The reaction was monitored by TLC utilizing hexane: ethyl acetate (3:1) as eluent. The excess of solvent was evaporated under reduced pressure and then extracted three times with25 mL ethyl acetate. The organic layer washed with saturated solution of sodium hydrogen carbonate (5%) several times then washed with distilled water. The combined organic layer was dried under anhydrous sodium sulfate, filtered and evaporated under reduced pressure to afford pale yellow oil, Yield 80%, B.P 43-45°C. (lit44-46°C) [179]. The ranger of differences between the boiling point of (compound 1) and the literature was about (2-3°C) that could be attributed to the differences in percentage of purity.

2.3.2 Synthesis of pyridine-2,6-dicarbohydrazide comp.2

Comp. 2
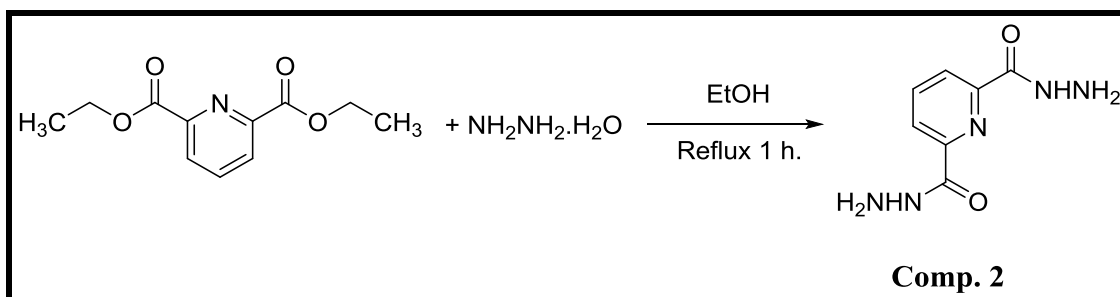
Excess of hydrazine hydrate(80%) was added to warm solution of diethyl pyridine2,6-dicarboxylate (8g,36mmol) in absolute ethanol(65mL)The mixture was refluxed for 1hr.Upon cooling the product was filtered, washed with distilled water and recrystallized from ethanol to give white precipitate (7.1g), Yield 89%, MP 278-282°C, (lit 280-284°C)[180].

2.4 synthesis of polymer 1

P₁
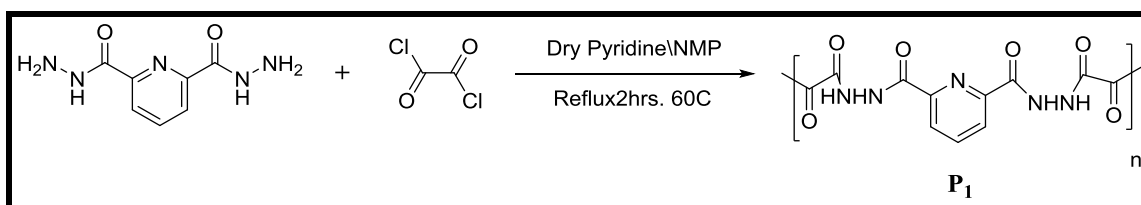
Oxalyl chloride (0.18g, 1.64mmol) was added drop wise through additional funnel within 15min. to a solution of pyridine-2,6-dicarbohydrazide (0.5g,2.56mmol) in dry pyridine and NMP (3:1)

at ambient temperature. After completion the addition the mixture was refluxed for 2hrs at 60°C.Upon cooling, the mixture was poured into (50mL) crashed ice. Hydrochloric acid (2%, 10mL) was added to adjust pH at (5-7) then the mixture was evaporated under reduced pressure to afford dark brown liquid polymer.

2.5 synthesis of polymer 2
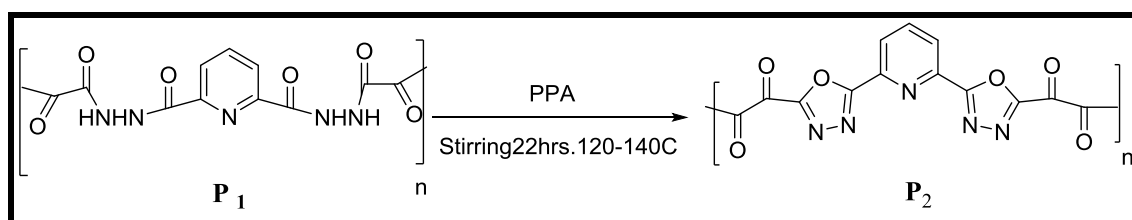
P_1 (0.5g) was added into hot stirring liquid of poly phosphoric acid at (120-140°C).The mixture was left under heating and stirring for 22 hrs. After cooling the mixture was poured into50mL ice water and stirred for 15 minutes. The pH of the solution was adjusted to (7-8) by adding a solution of sodium hydroxide 10%. The product was evaporated under reduced pressure to give blackish gray amorphous polymer.

2.6 General synthesis of Bis 1,3,4-oxadiazole polymerization (P3-P7)

P(3,4,5,6,7)

$A = (CH_2)_2$, $(CH_2)_4$,   ,   ,

          3   ,   4   ,   5   ,   6   ,   7
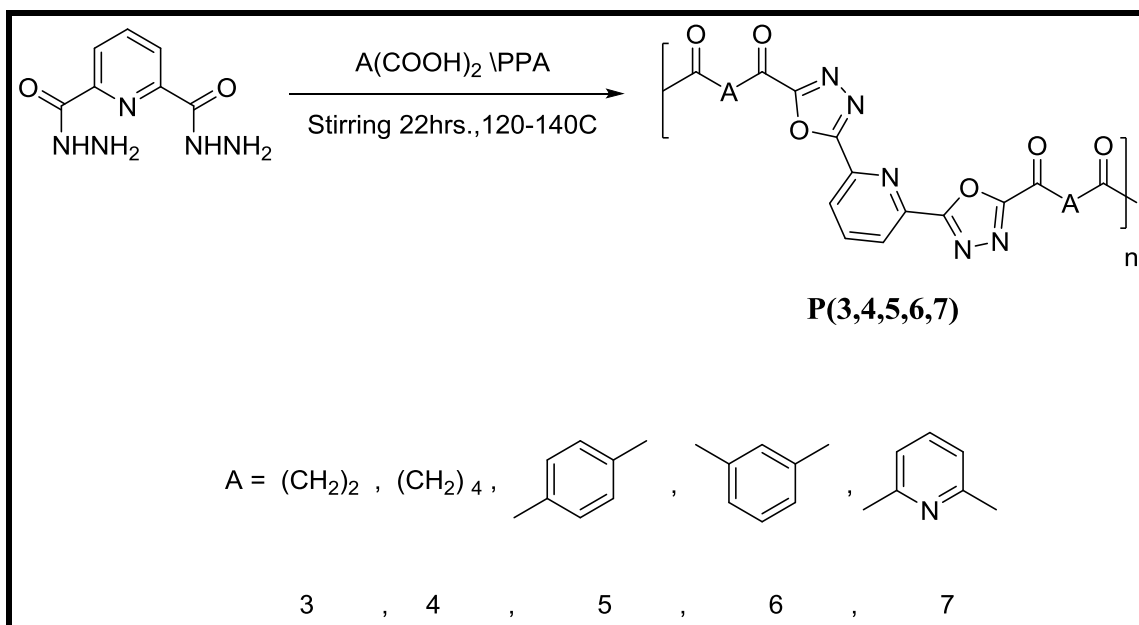
Pyridine -2, 6-dicarbohydrazide (0.5g, 2.56mmol) and dicarboxylic acid (1gm) was mixed and grinding to finny powder then poured into hot stirring liquid of poly phosphoric acid at 120-140°C. The mixture left under heating and stirring for 22 hrs, after cooling the mixture poured into (50mL) crashed ice.

 The pH of the solution was adjusted to (7-8) by adding a solution of sodium hydroxide 10%. The mixture was evaporated under reduced pressure to get the target polymer. The resulting polymers were tabulated in Table (2-2).

Table 2-2: The synthesized polymers and their physical properties

NO.	Structure	Color
P$_1$		Dark Brown
P$_2$		Blackish Grey
P$_3$		Pale pink
P$_4$		white
P$_5$		Greenish Yellow
P$_6$		Blue
P$_7$		white

2.7 synthesis of N'2,N'6- bis(4-hydroxybenzylidene) pyridine-2,6-dicarbohydrazide comp.3

Comp.2   +   **2mol.**   4-hydroxybenzaldehyde   Acetic Acid, Reflux 2hrs., 100C   Comp. 3
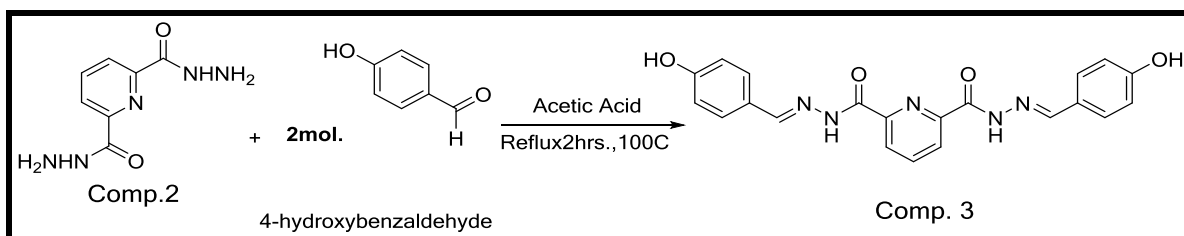
Pyridine-2, 6-dicarbohydrazide (5.8g, 29.7mmol) and 4-hydroxy benzaldehyde (7.25g, 59.4mmol) in (25mL) of acetic acid was heated under reflux for 2hrs at 100°C. After cooling the precipitate was filtered and washed by warm distilled water (30mL) then dried and recrystallized from DMF to give yellow precipitate MP up to 300°C, Yield 90%.

2.7.1 Synthesis of 4, 4'-(pyridine-2,6-diylbis(1,3,4-oxadiazole-5,2-diyl))bisphenol comp4.

Comp 4
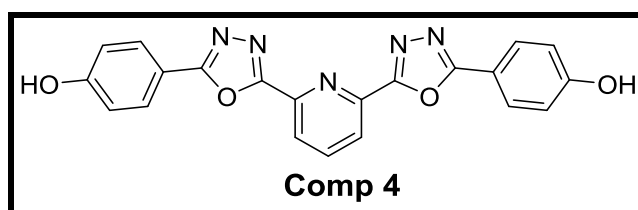
To a suspension of N'2, N'6-bis (4-hydroxybenzylidene) pyridine-2,6-dicarbohydrazide (10g ,24.7mmol) in 10 ml glacial acetic acid and (8.1g, 98.8mmol) anhydrous sodium acetate, solution of bromine (7.9g, 49.4mmol) in (30mL) acetic acid was added carefully at room temperature with vigorous stirring.

The mixture was refluxed for 2hs at 100°C. Upon cooling, the mixture was poured in to (25ml) ice water and left stirred for 15 minutes the crud product was filtered and washed with distilled water. Then dried the precipitate and recrystallized from methanol to give pale yellow powder (6.1g), Yield 62%, MP 218°C.

2.8 synthesis of polymer 8

Oxalyl chloride (0.18g, 1.64mmol) was added drop wise through additional funnel within 15 minutes to the mixture of (0.5g) of (**compound 4**) [4, 4'-(pyridine-2, 6-diylbis(1,3,4-oxadiazole-5,2-diyl))bisphenol] in (10mL) of dry pyridine – NMP(3-1) at ambient temperature and was left stirring for one hour. After that the mixture was heated and refluxed for further 2hrs at 60° C. Then cooling crushed ice (20mL) was poured into the mixture and stirred for 15 minutes, adjusted the pH to 5-7 by added solution of 2% HCl.

The mixture was evaporated until dryness under reduced pressure to give the target polymer.
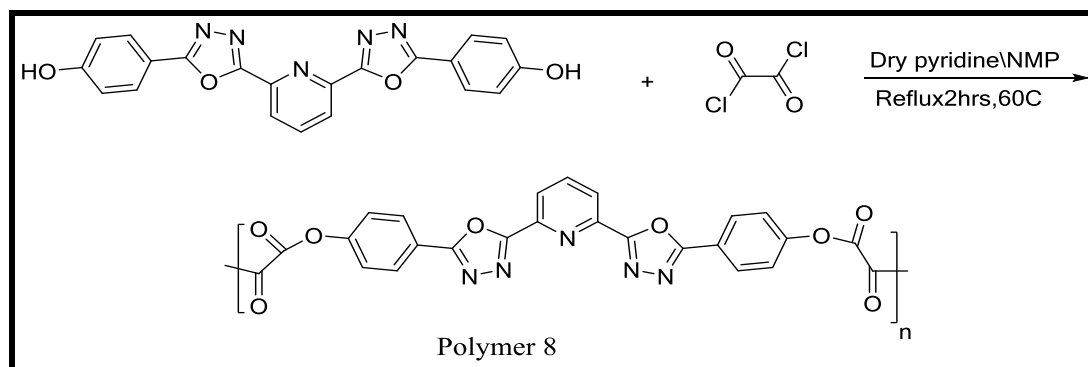
Polymer 8

2.9 General synthesis of Bis (1,3,4-oxadiazole-2,5-diyl)-4-hydroxy phenyl, (P9-P13)

A= (CH2)₂ , (CH2)₄ , [p-phenylene] **,** [m-phenylene] **,** [2,6-pyridinediyl]

9   ,   10   ,   11   ,   12   ,   13
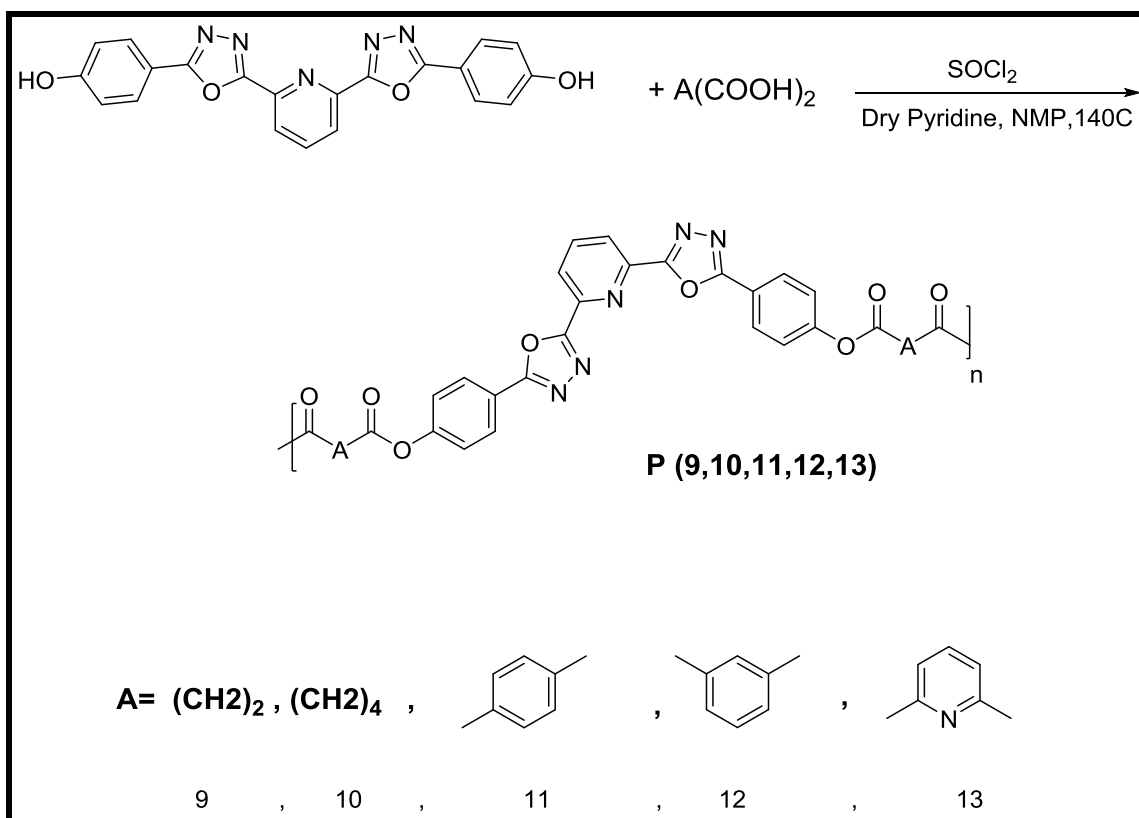
First step:

These polymers were synthesized by two steps. The first step, convert the di carboxylic acid to their corresponding di acid chloride, excess of thionyl chloride about (3mL) was added to dicarboxlyic acid (1.87 mmol) at ambient temperature. The mixture was heated under reflux for 2hrs. Excess of thionyl chloride was removed under reduce pressure. The resulting product was used at the second step without any further purification.
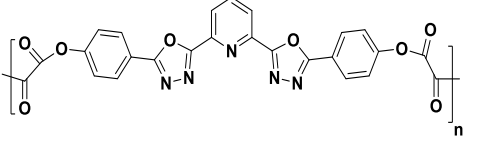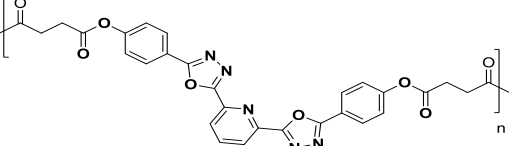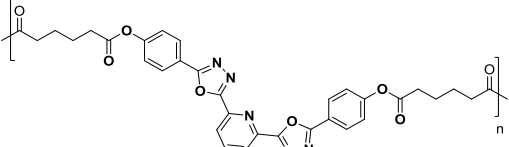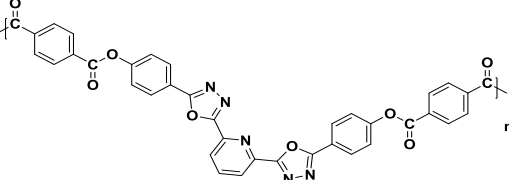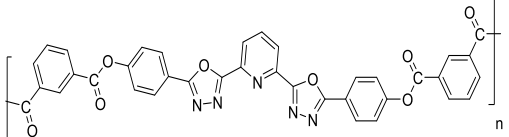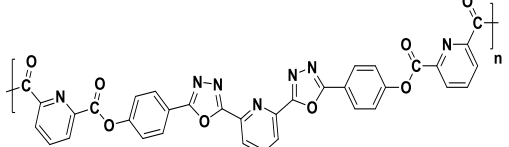
Second step:

Freshly synthesized di acid chloride (1.87mmol) in dry pyridine was added through dropping funnel within 20 minutes to a solution of compound 4,4'-(pyridine-2,6-diylbis(1,3,4-oxadiazole-5,2-diyl)) diphenol (0.75g, 1.87 mmol) in (10mL) of dry pyridine-NMP(1-methyl-2-pyrrolidinone) (3:1) at room temperature.

After that the mixture was refluxed for 24hrs. at 140° C. Upon cooling, crushed ice (20 mL) was poured into mixture and stirred for 15 minutes, then adjusted the pH to (5-7) by adding of (2%) HCl solution. The precipitate was collected and washed with distilled water, filtered and dried.

The desired product washed by (THF) to remove the solvent by decantation and dried to afford dark brown amorphous semi-solid polymers which were tabulated in Table (2-3).

Table 2-3: The Synthesized Polymers and their Physical Properties

No	Structure	color
P 8		Dark Brown
P 9		Dark Brown
P 10		Dark Brown
P 11		Dark Brown
P 12		Dark Brown
P 13		Dark Brown

Chapter Three

Results and Discussions

CHAPTER 3   Results and Discussion

3.1 Synthesis and characterization of diethyl pyridine-2,6-dicarboxylate(comp.1)

This compound was synthesized from reaction 2, 6-pyridin di carboxylic acid with absolute ethanol in the presence of concentrated sulfuric acid according to the reported procedure by Ziyadanoğulları, B *et. al*[179]. Boiling point was compared with the literature. The FTIR spectrum showed disappearing the band of acidic hydroxyl group which consists good evidence for success the reaction. Furthermore, the spectrum shown new band at 3062 cm^{-1} for (CHAr) and two bands at 2985 and 2871 cm^{-1} for (CHAliph). The band for carbonyl ester (C=O) was located at 1745 cm^{-1} and the (C=C) aromatic for pyridine ring was located at 1446cm^{1} and 1576cm^{-1}. Moreover, the bands of CH$_2$ and CH$_3$ groups appearance at 1481 and 1367 cm^{-1} respectively and the bands of (C-O) ester at the range from (1244-1209) cm^{-1} as in figure (3-1).
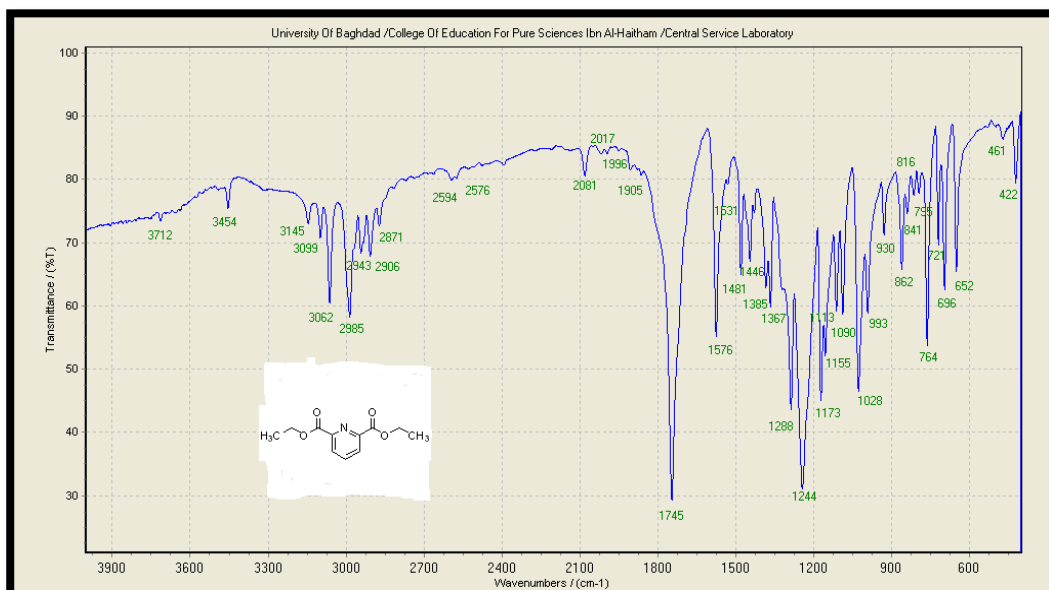
Figure 3–9: FTIR spectrum of comp.1

The ^{1}H-NMR spectrum figure (3-2) displayed disappearance of the acidic hydroxyl group and also shown the protons of (2CH$_3$) groups were located at 1.47ppm as triplet signal of six proton with coupling constant (J =7.2) and quartet signal at 3.29 ppm for 4 protons of (2CH$_2$) groups with coupling constant (J=7.2) and multiplet signal at 7.82-8.14 for three protons (d, T, d) of pyridine.
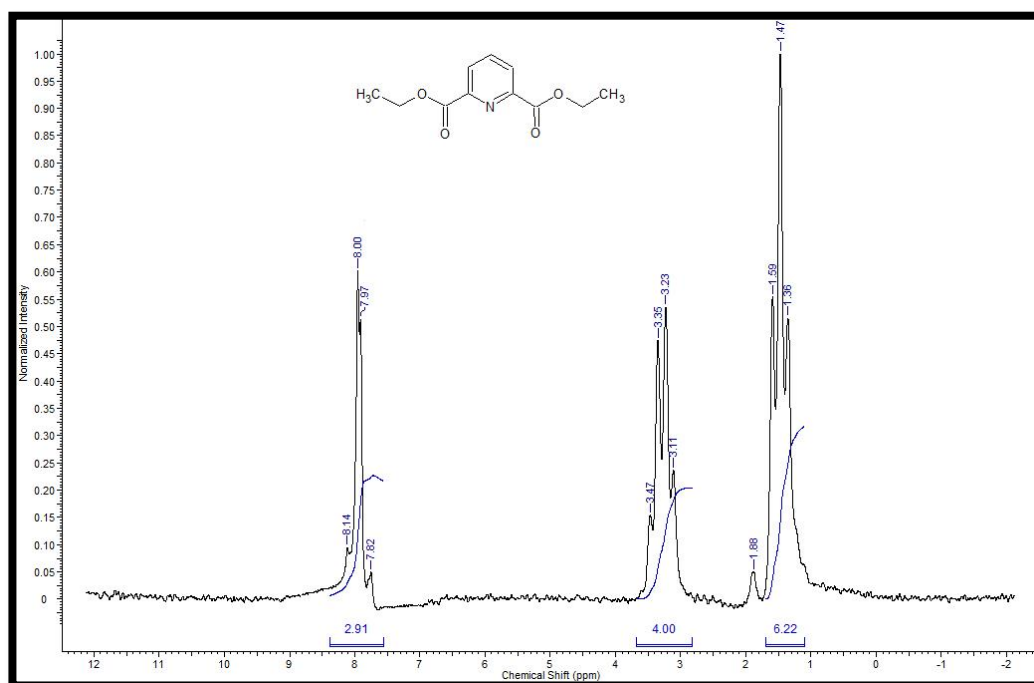
Figure 3–10: ^{1} H-NMR spectrum of comp.1

The practical percentage of CHN analysis was too matched to the theoretical results as illustrated in Table (3-1).

Table-3-Error! No text of specified style in document.: CHN Analysis of Comp.1

Compound	Theoretical Value	Practical Value
1	C:59.19 H:5.87 N:6.27	C:59.21 H:5.90 N:6.29

3.2 Synthesis and characterization of pyridine-2,6-dicarbohydrazide (comp.2)

Diethyl pyridine-2, 6-dicarboxylate was heated under reflux with excess of hydrazine hydrate (80%) to obtain bis acid hydrazide. The melting point of this compound was $280^{\circ}C$ and identified by FTIR spectrum which exhibited new bands at 3276-3186 cm^{-1} attributed to (NH$_2$ & NH) ,3016 cm^{-1} for CH aromatic (CH$_{Ar}$). The carbonyl group located at 1689 cm^{1}, besides a band at1639 cm^{-1} for (C=N) group, the band at 1589 cm^{1} referred to NH bending and two bands at 1518-1441 cm^{-1} for (C=C) aromatic as shown in figure (3-3).
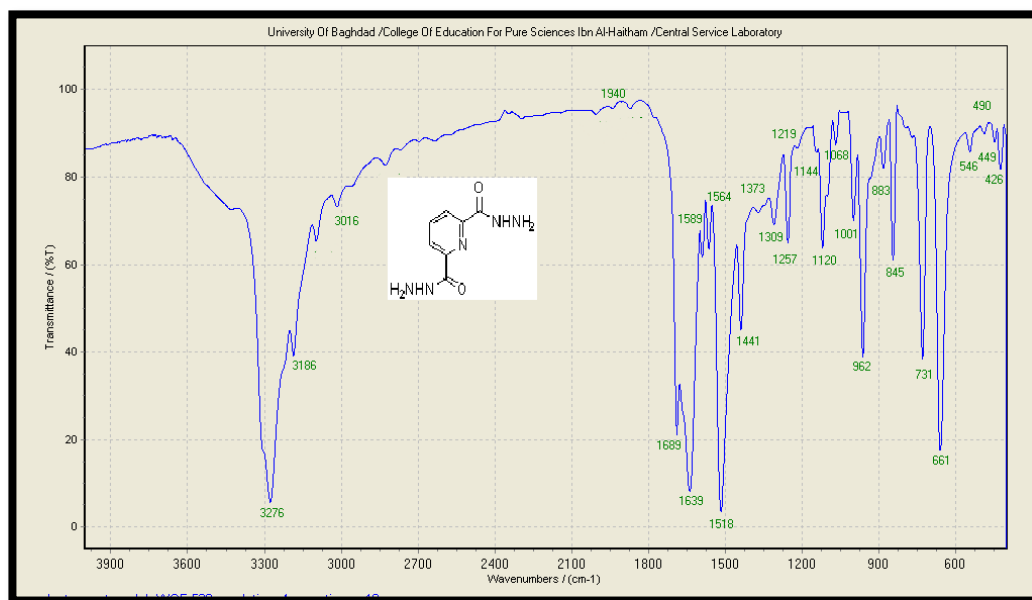
Figure 3–3: FTIR spectrum of comp.2

The ^{1}H-NMR spectrum exhibited disappearing of ten protons for two groups of OCH$_2$CH$_3$ and the existence of broad singlet signal at 4.58 ppm for two groups of NH$_2$ with integration equal to four protons. The aromatic protons were assigned as multiplet signal at

8.11-8.43 for three protons of pyridine ring. The spectrum showed a broad singlet signal at 10.58 for two NH groups with integration of two protons as shown in figure (3-4).
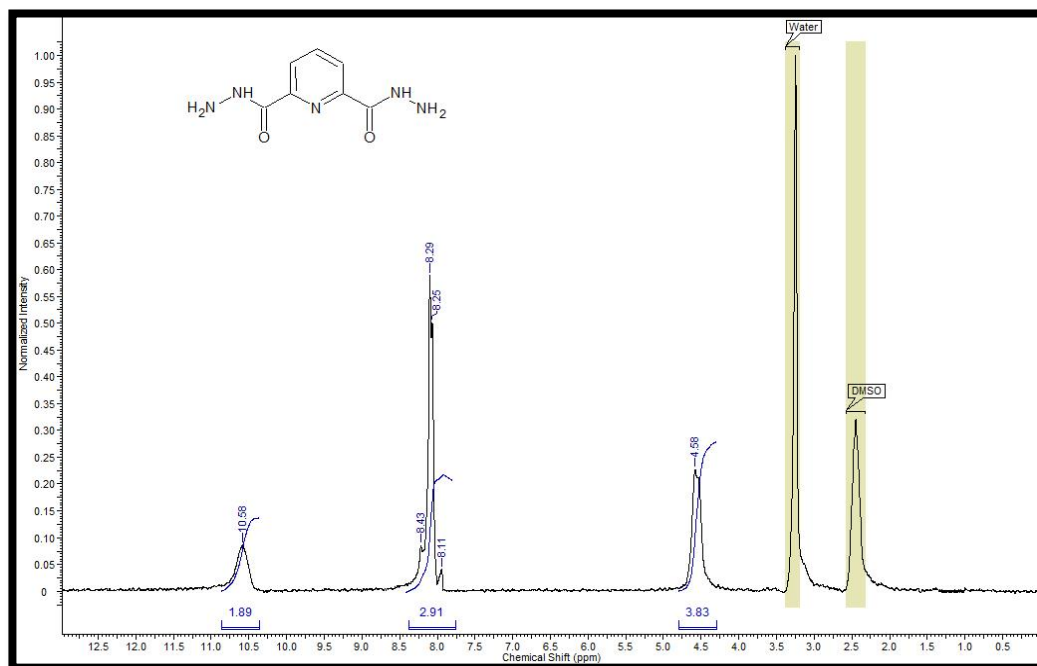
Figure 3–4: ^{1}H-NMR spectrum of comp.2

The CHN element analysis of compound (**2**) was in a good agreement with the proposed structure as listed in Table (3-2).

Table 3-2: CHN Analysis of Comp.2

Compound	Theoretical Value	Practical Value
2	**C**:43.08 **H**:4.56 **N**:35.88	**C**:43.06 **H**:4.61 **N**:35.85

3.3 Synthesis and characterization of P_1

This polymer was synthesized to be starting material for synthesis of Polymer**2**. Reaction of di acid hydrazide (**comp.2**) with oxalyl chloride in equal mill moles at ambient temperature and presence of pyridine as scavenger for chloride ion lead to give **P1.** Meanwhile, heating this reaction for two hours could support the polymerization process. The resulting polymer was characterized by FTIR and ^{1}H-NMR.

The FTIR spectrum of this polymer exhibited at3425 and 3387 cm$^{-1.}$ for two bands of (NH) groups. Furthermore, the spectrum shown one band at 3101 cm^{-1} for (CH) aromatic. The strong band at 1651 cm^{-1} attributed to (C=O) carbonyl group and (C=N) together. The (C=C) aromatic was located at 1538 and 1477 cm^{-1} figure (3-5).
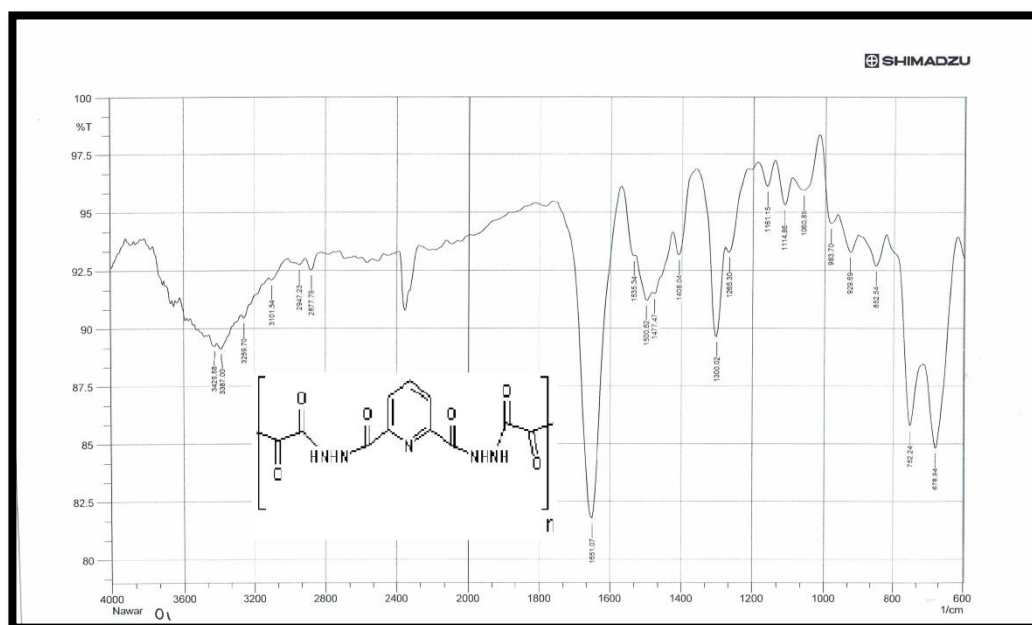
Figure 3–5: FTIR spectrum of P_1

The ^{1}H-NMR spectrum exhibited singlet signal located at 4.55 ppm for NH$_2$ group which is attributed to trace of monomer not polymerized, triplet signal assigned at 7.71-8.03 ppm referred to 3H pyridine ring protons, a broad singlet signal at 10.58 ppm which attributed to NH in (NH-CO-Py) moiety, and a singlet signal at 12.69 ppm referred to NH in (-NH-CO-CO-) moiety, figure (3-6).
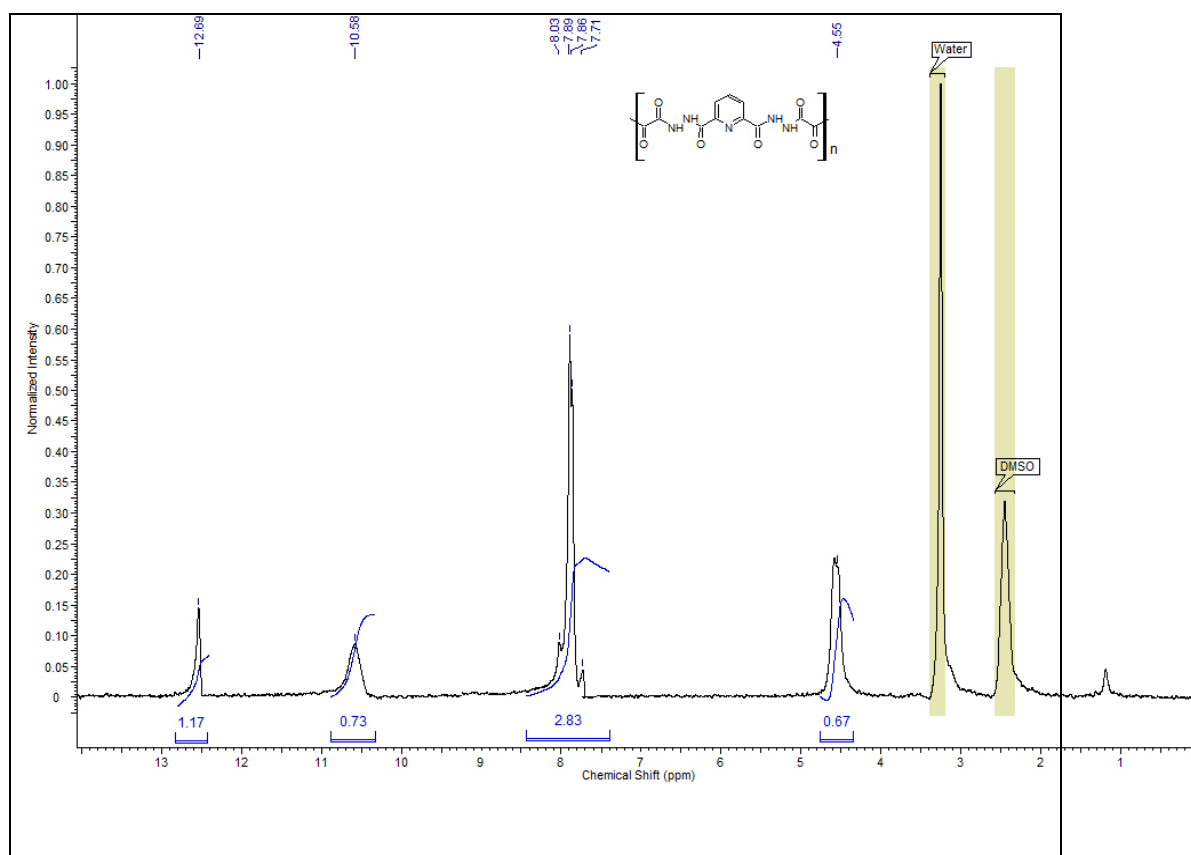
Figure 3–6: ^{1} H-NMR spectrum of P₁

3.4 Synthesis and characterization of P$_2$

Cyclization of **P$_1$** in the presence of PPA as dehydrating agent obtained **P2.**
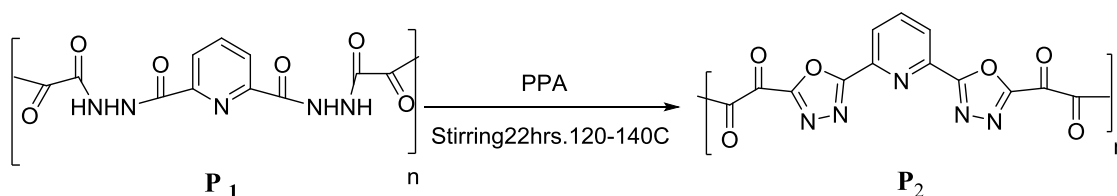
The required   polymer was characterized by FTIR figure (3-7) which shown broad band at 3176 cm^{-1} for (CH) aromatic and shown a band at 1670 cm^{-1} refers to (C=O). Furthermore, the appearance of new band at 1662 cm^{-1} is attributed to cyclized (C=N) of the hydrazide which referred to1,3,4-oxadiazole ring the other two bands at 1500-1442 cm^{-1} belong to the (C=C) of aromatic.
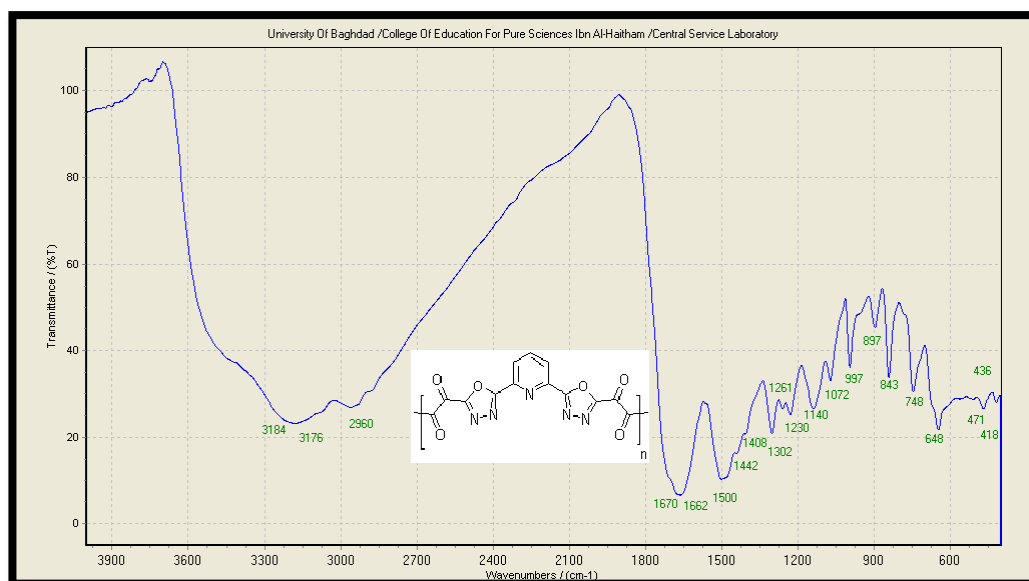
Figure 3–7: FTIR spectrum of P2

3.5 General synthesis and characterization of bis 1,3,4-oxadiazole polymers (P3-P7)

These bis-1,3,4-oxadiazole polymers were synthesized by reaction of the di acid hydrazide (**comp.2**) with five different di acids in the presence of poly phosphoric acid at 120-140°C. The physical properties of these polymers were listed in Table (2-2).

These polymers (P_2-P_7) were characterized by FTIR spectroscopy without ^{1}H-NMR spectrum because they were insoluble in most of known deuterated solvents.

The FTIR spectrum for **P3** exhibited abroad band at 3469 cm^{-1} which refers to traces of (OH) group of carboxylic acid of monomer, also medium band was located at1668 cm^{-1} belong to (C=O). The interested peak for formation 1,3,4-oxadiazole ring was located at 1651 cm^{-1} which attributed to (C=N) and a band at 1369 cm^{-1} attributed to CH$_2$ groups as demonstrated in figure (3-8).
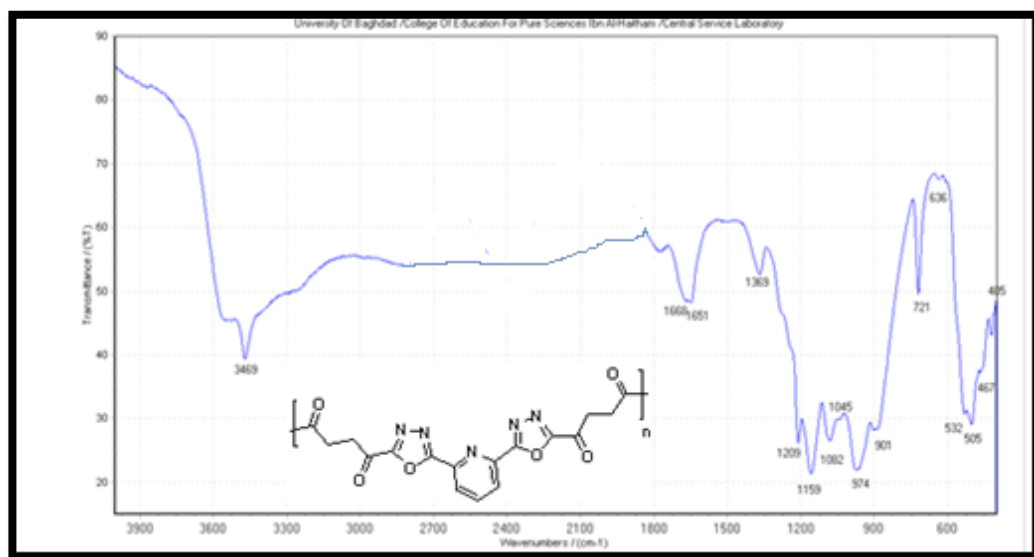
Figure 3-8: FTIR spectrum of P3

Same results have been observed with **P₄** figure (3-9), the broad band referred to (OH) group traces of carboxylic acid and (CO-NHNH₂) group of acid hydrazide of monomer that masked together and not polymerized was assigned at 3396-3275cm⁻¹. The(C=N) group of oxadiazole ring was located at 1631 cm⁻¹ and a single peak at 1579 cm⁻¹ referred to the (C=C) of aromatic.
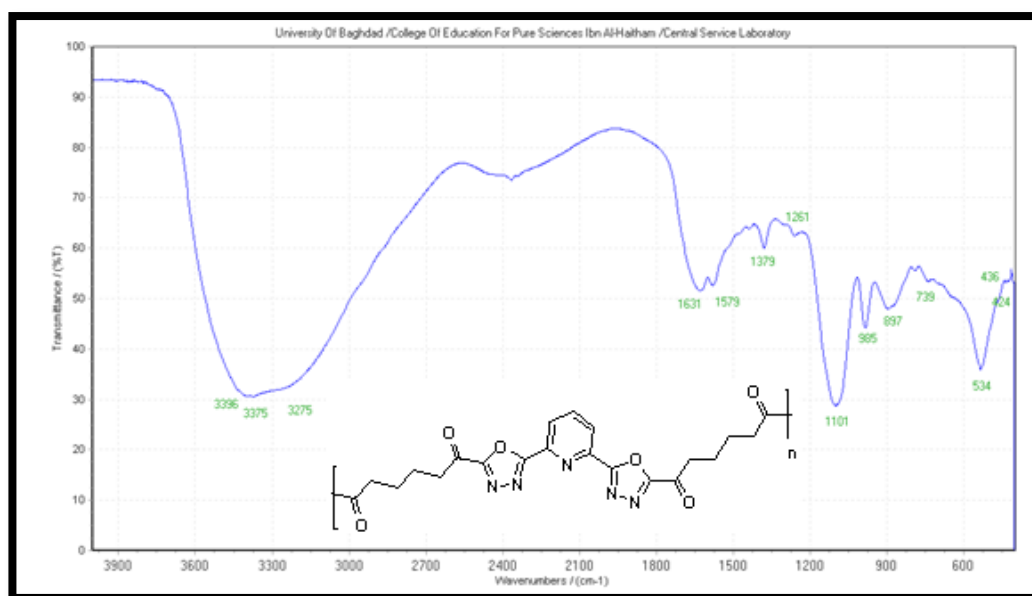
Figure 3–9: FTIR spectrum of P4

The reaction of the acid hydrazide with carboxylic acid to form oxadiazole ring in the presence of PPA is clearly known it take place within two steps.

The first step includes the formation of aryl or acyl hydrazide, while the second step is the cyclization of the acyl or aryl hydrazide to oxadiazole [181-183] as illustrated in scheme (3-1).
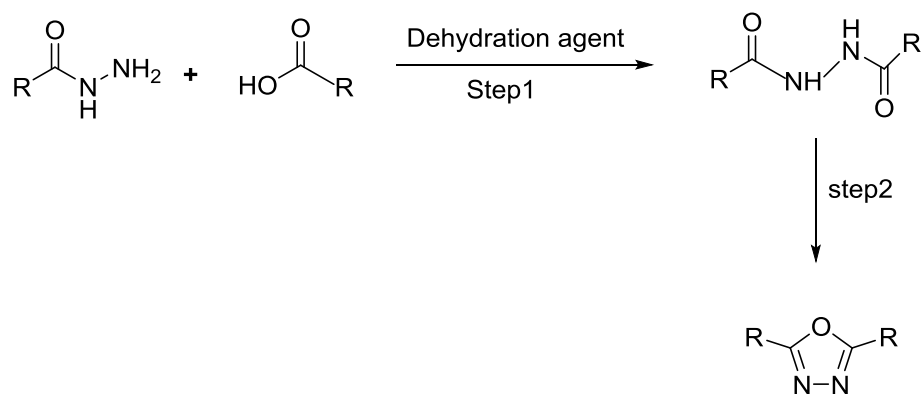
Scheme (3-1): The suggested Reaction of Cyclization

The FTIR spectrum of **P$_5$** figure (3-10) shown a broad band at 3406 cm^{-1} referred to traces of (OH) group for carboxylic acid and the (CO-NHNH$_2$) group of acid hydrazide of monomer that masked together. The weak band at 1670 cm^{-1} attributed to interference between the (C=O) carboxylic group and (C=N) group for oxadiazole ring. The bands of (C=C) aromatic was appeared at 1572 and 1485cm^{-1}. Finally, the bands from (1161-1082) cm^{-1} referred to (C-O) band of oxadiazole ring.
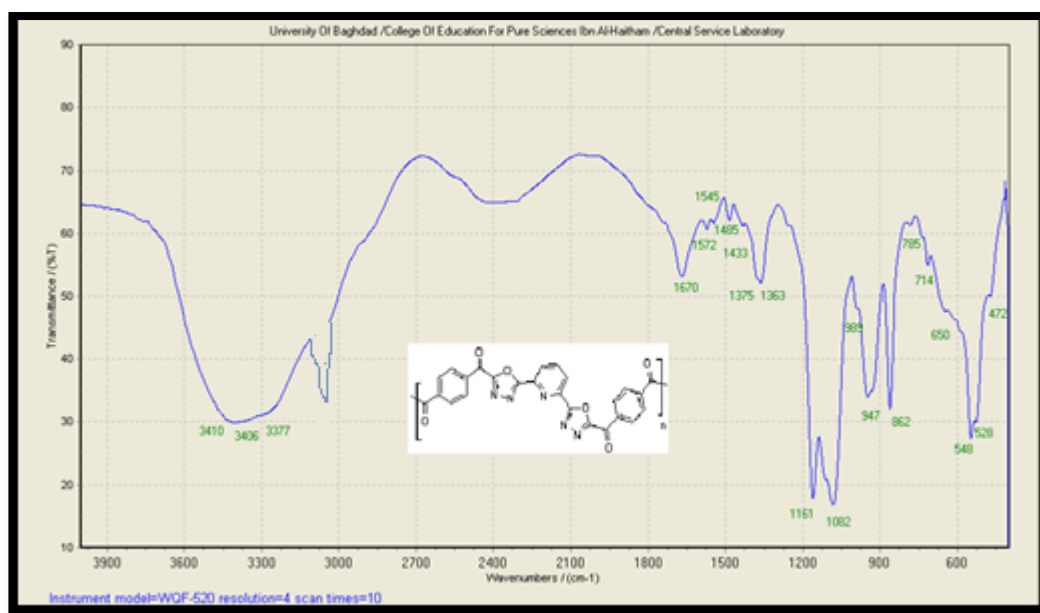
Figure 3–10: FTIR spectrum of P$_5$

 The FTIR spectrum of **P6** shown a new band from (3462-3329) cm^{-1} referred to traces (OH) group of carboxylic acid and the (CONHNH2) group of monomer acid hydrazide that masked with each other, and the band at 3072 cm^{-1} belong to the (CH) of the aromatic. The band of carbonyl amide(C=O) was located at 1658 cm^{-1} , besides, to band at 1616 cm^{-1} for (C=N) , two bands for (C=C) were located at 1541 and 1450 cm^{-1} and the three bands at (823,789,685) cm^{-1} attributed to meta substituted benzene ring as shown in figure (3-11).
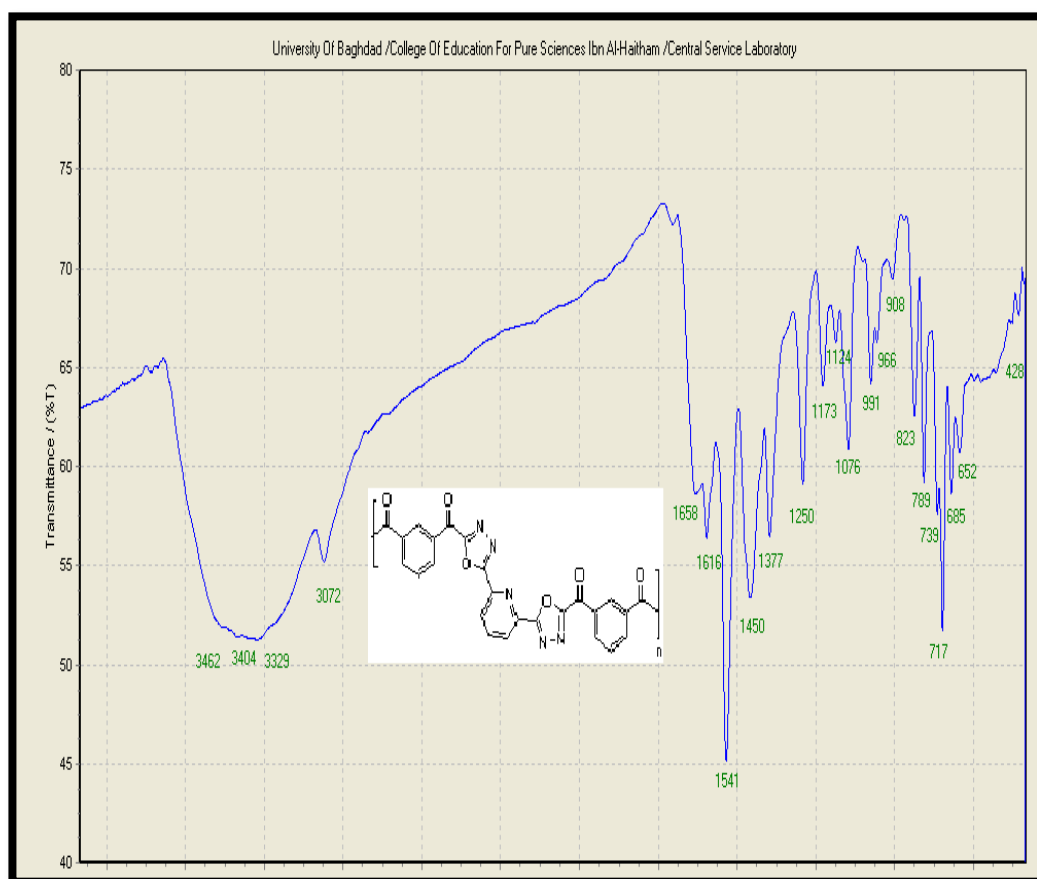
Figure 3–111: FTIR spectrum of P6

The FTIR of **P7** exhibited many medium bands from (3465-3276) cm^{-1} attributed to traces of monomer and (OH) group of carboxylic acid. CH aromatic may be the shoulder with the band at 3126 cm^{-1}. The broad bands in the region from (2447-2374) cm^{-1} represented over tones bands. While, the band at 1691 cm^{-1} attributed to carbonyl group(C=O) besides the band at 1643 cm^{-1} belong to (C=N) group, two bands at 1583 and 1438 cm^{-1} referred to the (C=C) of aromatic, the bands (1211-1068) cm^{-1} referred to (C-O) ester and finally the bands at (868,721,619) cm^{-1} attributed to (CH-Ar.) O.O.P that belongs to meta substituted of benzene ring in figure (3-12).
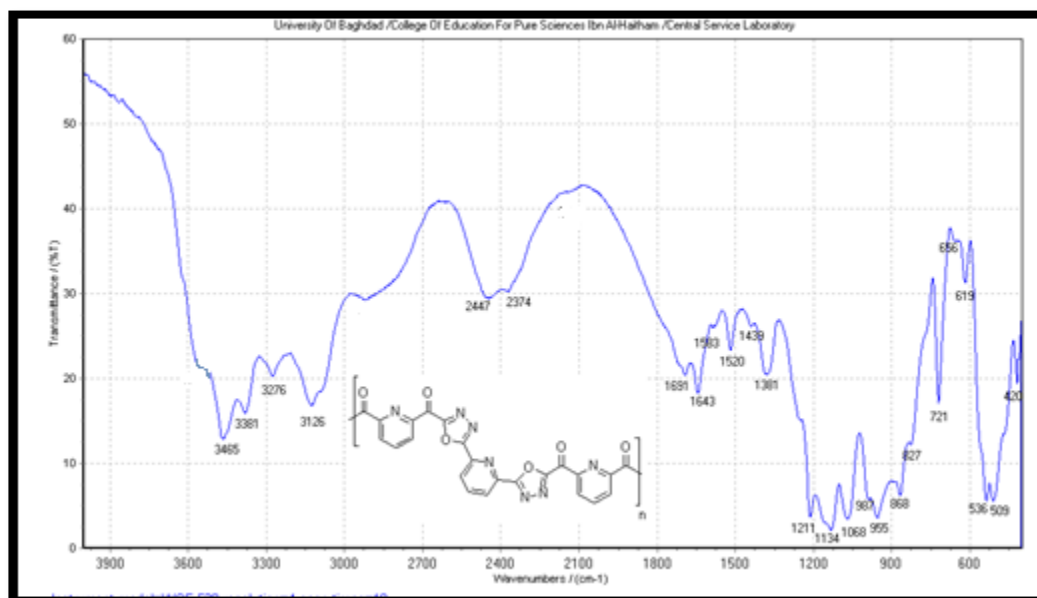
Figure 3–122: FTIR spectrum of P7

3.6 Synthesis and characterization of N'2, N'6-bis(4-hydroxybenzylidene)pyridine-2,6-dicarbohydrazide comp.3

N'2,N'6-bis(4-hydroxybenzylidene)pyridine-2,6-dicarbohydrazide comp.3 was synthesized from reaction of two equivalents of 4-hydroxy benzaldehyde with pyridine 2,6-carbohydrazide in acetic acid. The target compound was identified by FTIR, ^{1}H-NMR spectroscopy and CHN analysis.

The FTIR of this compound revealed a new band at 3425 cm^{-1} for (OH) free group and the band at 3217 cm^{-1} for (NH) of hydrazone group, besides, a band at 3066 cm^{-1} for (CH) aromatic. Moreover, the shifting of the carbonyl peak (C=O) from (1689 to 1658) cm^{-1} considered good evidence for formation of bis hydrazone as shown in figure (3-13).

The band at 1601 cm^{-1} attributed to (C=N) group and another two bands at 1545 - 1510 cm^{-1} for (C=C) aromatic. Finally appearance of the band at 841 cm^{-1} for para substituted of aromatic ring.

The CHN analysis of the compound displayed, that the practical percentage of (C, H, N) elements were in harmony with the theoretical percentage as listed in Table (3-3).

Table 3-3: CHN Analysis of Comp.3

Compound	Theoretical Value	Practical Value
3	**C**:62.53 **H**:4.25 **N**:17.36	**C**:62.55 **H**:4.30 **N**:17.34
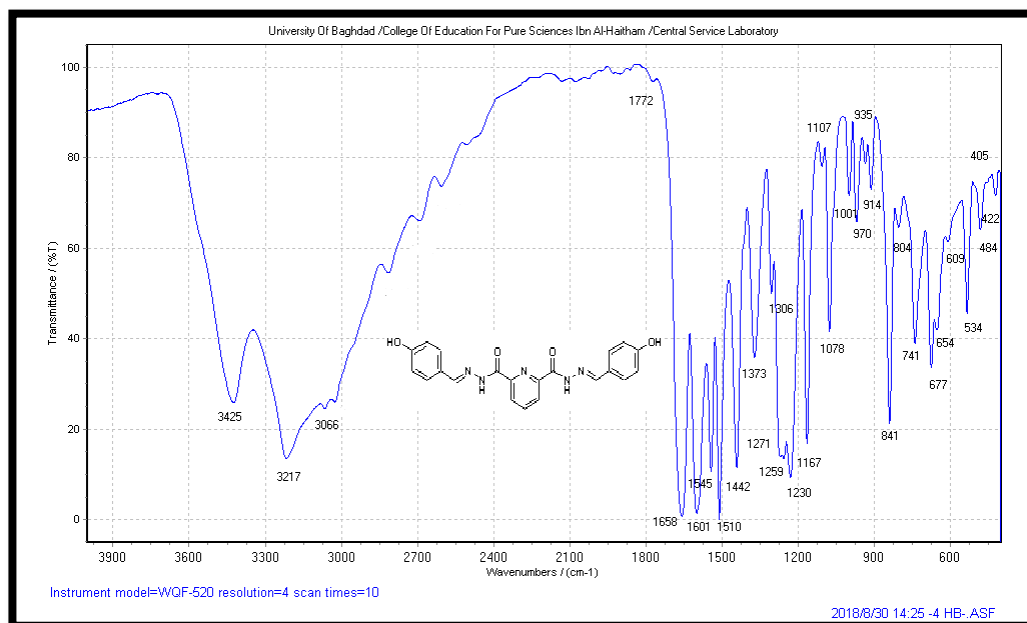
Figure 3–13: FTIR spectrum of comp.3

The ^{1}H-NMR spectrum (figure 3-14) exhibited disappearing of the peak of NH_2 and rising new singlet signal for (s,2H,2CH=N) at 8.62ppm.Furthermore the spectrum shown doublet signal at 6.76-6.90 ppm for (d,4H,Ar-H) and 7.55-7.69 ppm for (d,4H,Ar-H) with coupling constant *J* equal to 8.4Hz, multiplet signal for (m,3H,H$_{pyridine}$) at 8.26ppm, broad singlet signal for (bs,2H,2OH) groups at 9.94 ppm and broad singlet signal at 12.10 ppm for (bs,2H,2NH).
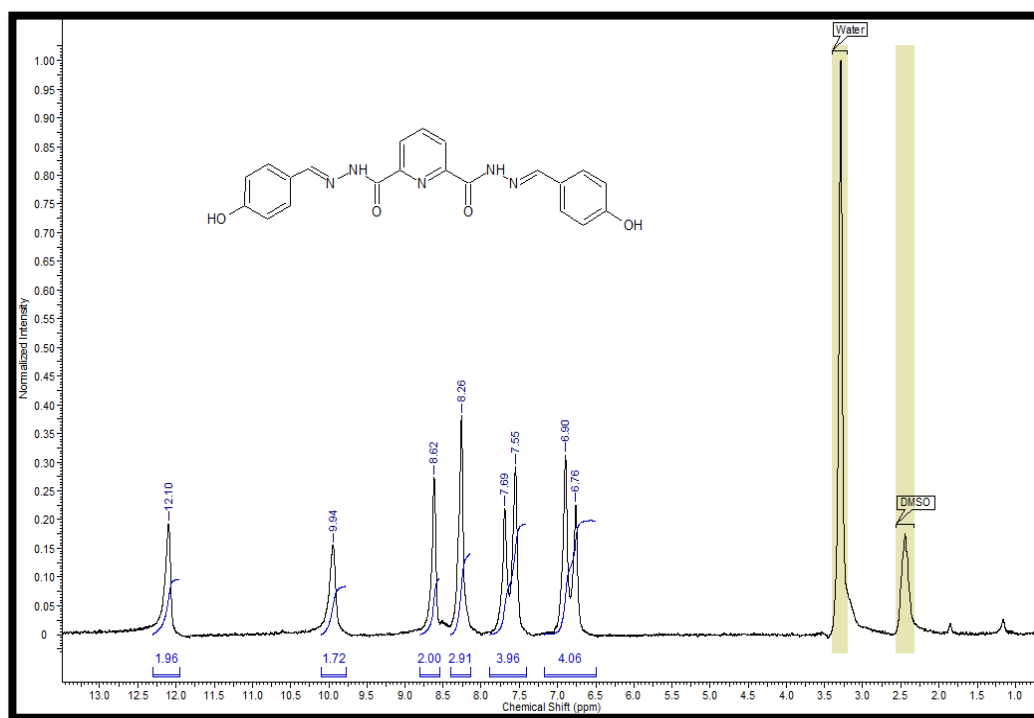
Figure 3-14: ^{1}H-NMR spectrum of comp.3

3.7 Synthesis and characterization of 4,4'-(pyridine-2,6-diylbis(1,3,4-oxadiazole-5,2-diyl))diphenol comp. 4

4,4'-(pyridine-2,6-diylbis(1,3,4-oxadiazole-5,2-diyl))diphenol **comp.4** was synthesized from reaction of bis hydrazone **comp.3** with bromine in the presence of sodium acetate in glacial acetic acid.

The FTIR spectrum indicate the disappearing of the peak of C=O group at 1658 cm^{-1}. The band at 3435 cm^{-1} attributed to free (OH) group, and the band which appeared at 3209 cm^{-1} which referred to trace of NH group of **comp.3**. The band at 3066 cm^{-1} which referred to the (CH) of aromatic. At 1672 cm^{-1} a band attributed to (C=N) for oxadiazole ring and the band at 1587 cm^{-1} for (C=N) of pyridine ring. The (C=C) aromatic bands located at 1539 and 1446

cm^{-1}. Furthermore the band at 1288 and 1082 attributed to (C-O) of oxadiazole rings. Then the band at 839 referred to para substituted ring, while the bands at 814,739,652 referred to out of plane para substituted ring as in figure (3-15).
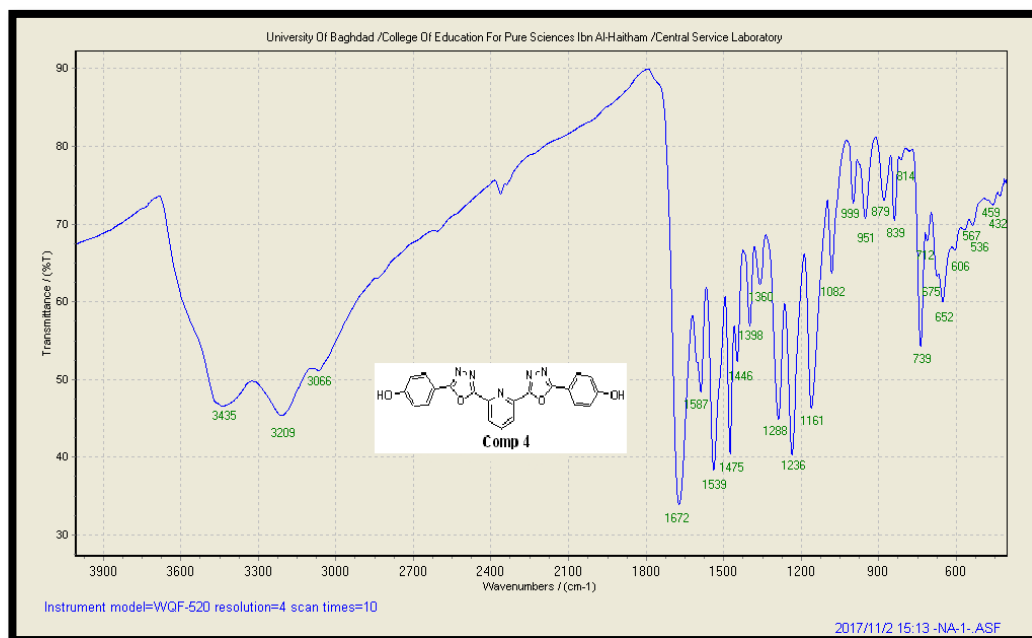
Figure 3-135: FTIR spectrum of comp.4

The ^{1}H-NMR spectrum figure (3-16) of **compound 4** show that all the peaks and their integrations were in agreement with proposed structure of the monomer. Meanwhile, the spectrum shown two signal at 6.90-7.04 ppm (d,4H,Ar-H) with coupling constant *J* equal to 8.4Hz and two signal at 7.69-7.83ppm (d,4H,Ar-H) with coupling constant *J* equal to 8.4Hz, also multiplet signal for (m,3H, H$_{pyridine}$) at 8.27-8.59 ppm and a broad singlet signal for (bs,2H,2OH) at 10.08 ppm.
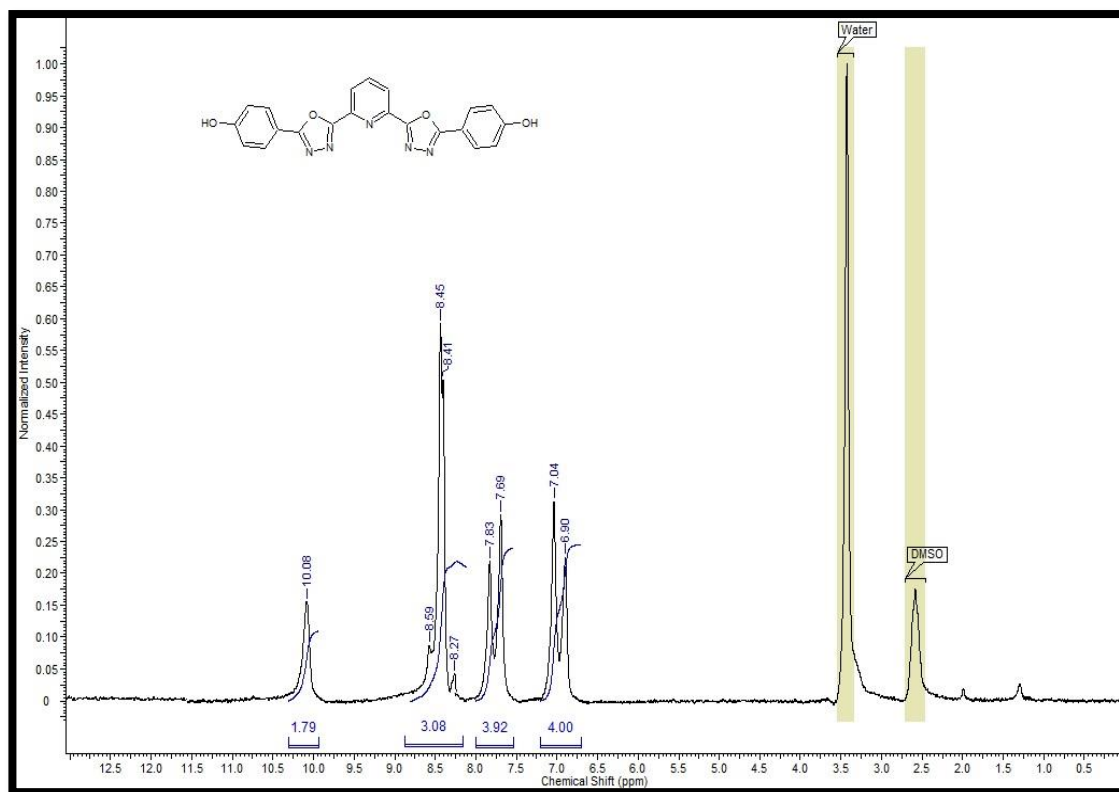
Figure 3-16: ^{1}H-NMR spectrum of comp.4

The CHN analysis of this compound exhibited that the practical percentage was in coordination with the theoretical percentage as listed in Table (3-4).

Table 3-4: CHN Analysis of Comp.4

Compound	Theoretical Value	Practical Value
4	C:63.16 H:3.28 N:17.54	C:63.17 H:3.32 N:17.56

56

3.8. General synthesis and characterization of Bis (1, 3, 4-oxadiazole-2, 5-diyl)-4-hydroxy phenyl P (8-13)

These polymers were synthesized by reaction of 4, 4'-(pyridine-2,6-diylbis (1, 3, 4-oxadiazole-2,5-diyl)) diphenol (**comp.4**) with oxalyl chloride for **P8,** while for (**P9-P13**) were synthesized after converting the di carboxylic acid to their corresponding di carboxylic acid chloride. A mixture of pyridine and NMP was utilized as solvent and scavenger agent. The addition of di acid chloride was occurred at ambient temperature then the mixture was heated to increase the degree of polymerization[184].

The FTIR spectrum of **P8** display deep broad band the attributed to the trace of OH groups of the phenol at 3421 and 3336 cm^{-1}. While the band at 3267 cm^{-1} which attributed to (CH) of aromatic. Assigned band at 1647 cm^{-1} referred to the (C=O) group and the two bands at 1593 and 1477 cm^{-1} attributed to the (C=C) of aromatic figure (3-17), **P8** did not show any ^{1}H-NMR results.
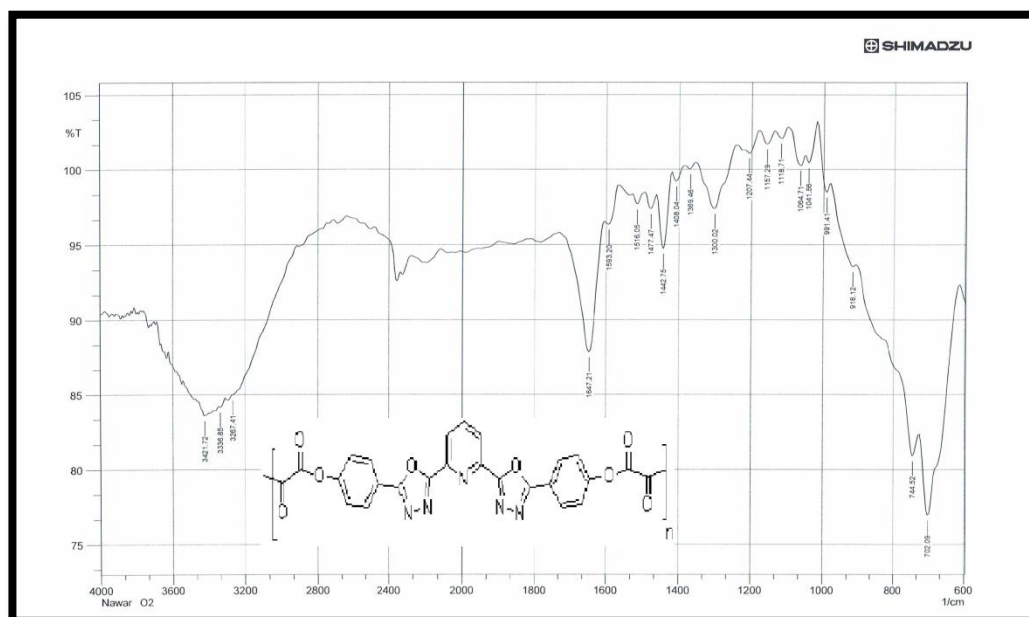
Figure 3–147: FTIR spectrum of P8

The FTIR spectrum of **P$_9$** shown a strong and broad deep bands attributed to the traces of OH groups of phenol and carboxylic acid at 3415 and 3402 cm^{-1}. While the band at 3068 cm^{-1} attributed to (CH) of aromatic, the spectrum exhibited two bands for (CH) aliphatic at 2956 and 2879 cm^{-1}. The band of (C=O) was at 1635 cm^{-1}. Besides to the band at 1618 cm^{-1} for (C=N) group of oxadiazole ring and the band at 1539 cm^{-1} referred to (C=N) group of pyridine ring. The bands of the (C=C) aromatic were located at 1539 and 1487 cm^{-1}. Finally the bands at 1194 cm^{-1} attributed to 1,3,4-oxadiazole ring and the band at 1055 cm^{-1} referred to ester linkage as shown in figure (3-18).
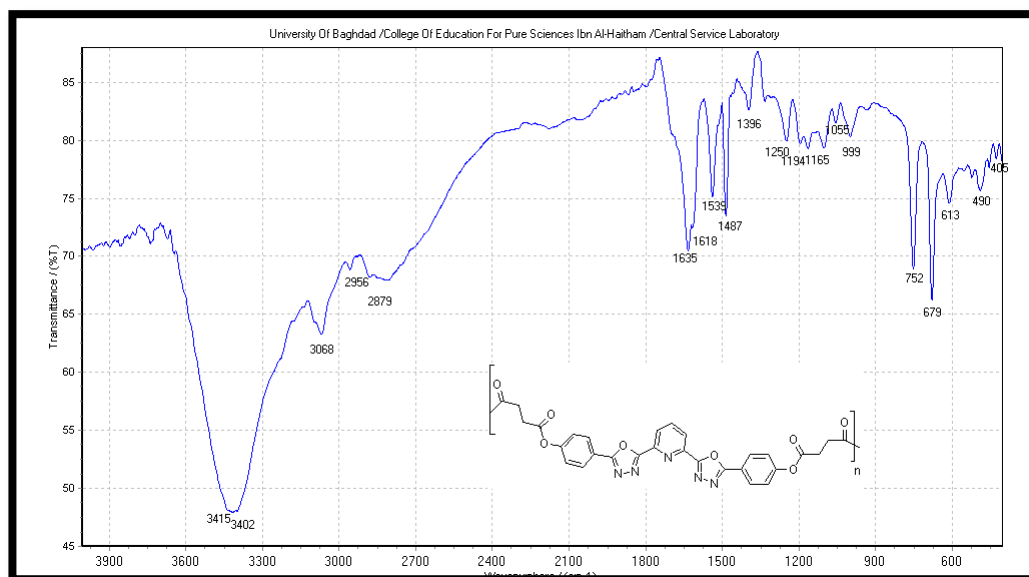
Figure 3-18: FTIR spectrum of P9

The ^{1}H-NMR spectrum figure (3-19) of **P$_9$** displayed multiplet signal attributed to (m,4H,2CH$_2$) at 3.07-3.82 ppm, this peak appeared as a multiplet and could be attributed to the differences in their environment due to the repetition as well their integral support the proposed structure . The doublet signal at 6.68-6.82 ppm for (d, 4H, Ar-H) with coupling constant *J* equal to 8.4 Hz and the doublet signal at 7.47-7.61ppm for (d, 4H, Ar-H). Finally multiplet signal at 8.13-8.44 which attributed to (m, 3H, Hpyridine).
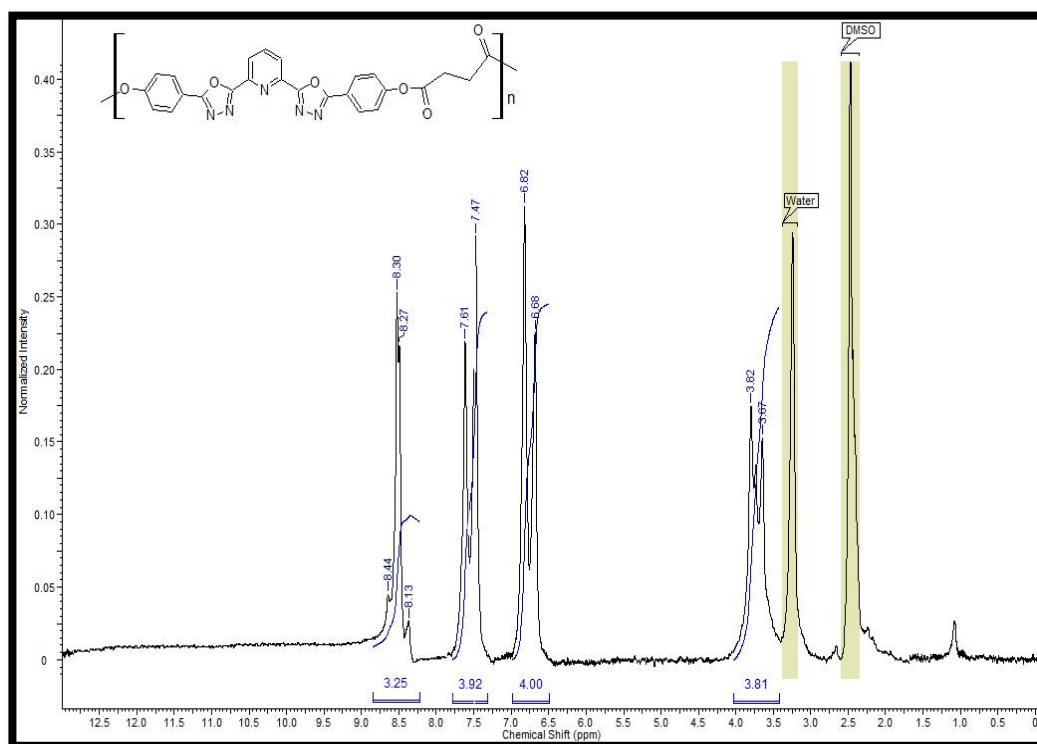
Figure 3–19: ^{1}H-NMR spectrum of P9

The FTIR spectrum of **P$_{10}$** exhibited a strong broad deep band attributed to traces of (OH) group of phenol and carboxylic acid at 3415 cm^{-1}. While a band at 3072 cm^{-1} referred to (CH) aromatic. Then a broad band at 2958-2881 cm^{-1} attributed to (CH) aliphatic. Besides to a band at 1699 cm^{-1} attributed to(C=O) of ester linkage. At 1635 cm^{-1} a band referred to (C=N) and two band at 1539 and 1487 cm^{-1} respectively which attributed to the (C=C) of aromatic. The bands at 1194 cm^{-1} attributed to oxadiazole ring and the band at 1001 cm^{-1} referred to (C-O) of cyclic ester as demonstrated in figure (3-20).
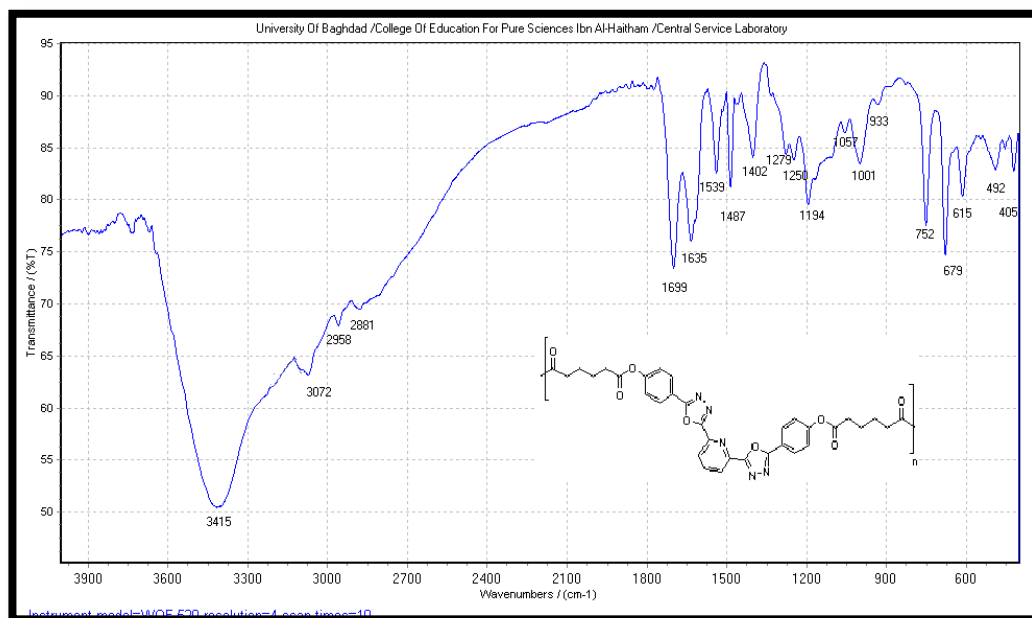
Figure 3-150: FTIR spectrum of P10

The ^{1}H-NMR spectrum figure (3-21) of **P$_{10}$** shown triplet signal at 1.69 ppm for (t, 4H, 2CH$_2$) with coupling constant *J* equal to 7.2Hz and triplet signal at 2.25ppm with coupling constant *J* equal to 7.2Hz for (t, 4H, 2CH$_2$) attributed to different types of CH$_2$ and reflect the repetition of adipyl monomer in addition to their integration support the proposed structure. Besides to doublet signal at 6.36-6.50 ppm for(d,4H,Ar-H) with coupling constant *J* equal to 8.4 Hz, and doublet signal at 7.15-7.29 ppm for (d,4H,Ar-H) with coupling constant *J* equal to 8.4 Hz. Multiplet signal at 8.01-8.33 ppm for (m, 3H, H$_{pyridine}$) and a singlet broad signal at 11.83 ppm attributed to (bs, 1H, OH).
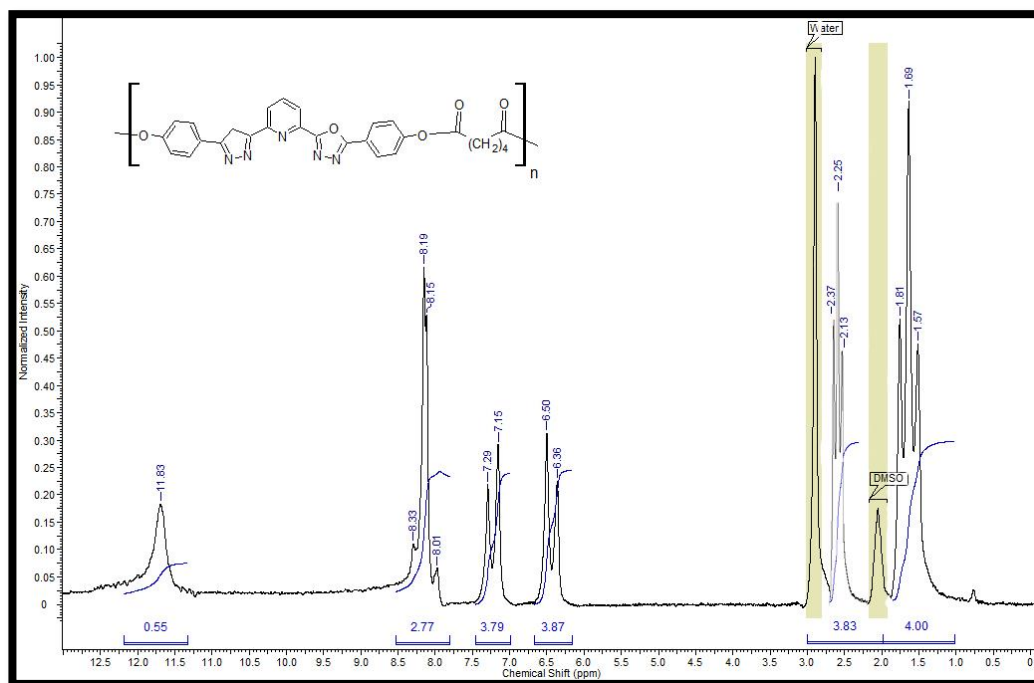
Figure 3-21: ^{1} H-NMR spectrum of P$_{10}$

The FTIR spectrum of **P$_{11}$** shown a strong broad deep band at 3433 cm^{-1} attributed to traces of OH group of phenol and carboxylic acid. The band at 3068 cm^{-1} referred to (CH) aromatic, assigned band at 1691 cm^{-1} attributed to (C=O). The band of (C=N) group of oxadiazole ring was located at 1633 cm^{-1} and the band of (C=N) of pyridine ring was at 1616 cm^{-1}. Then the band of (C=C) aromatic was located at 1539 and 1487 cm^{-1}. Finally the band at 1250 cm^{-1} of (C-O) group referred to 1,3,4-oxadiazole ring and the band at 1003 cm^{-1} of (C-O) attributed to ester linkage as depicted in figure (3-22).
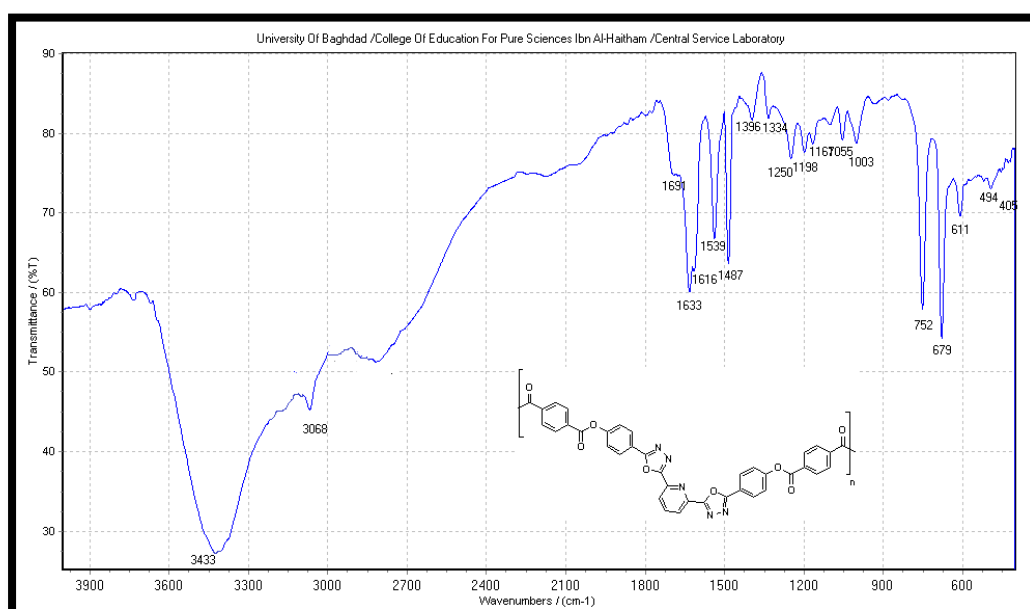
Figure 3-22: FTIR spectrum of P$_{11}$

The ^{1}H-NMR spectrum of **P₁₁** shown a multiplet signal at 7.09-7.73 ppm

for (m, 12H, Ar-H, Hpyridine) ppm and multiplet signal at 8.29 ppm for

(m, 3H, H pyridine) as shown in figure (3-23).
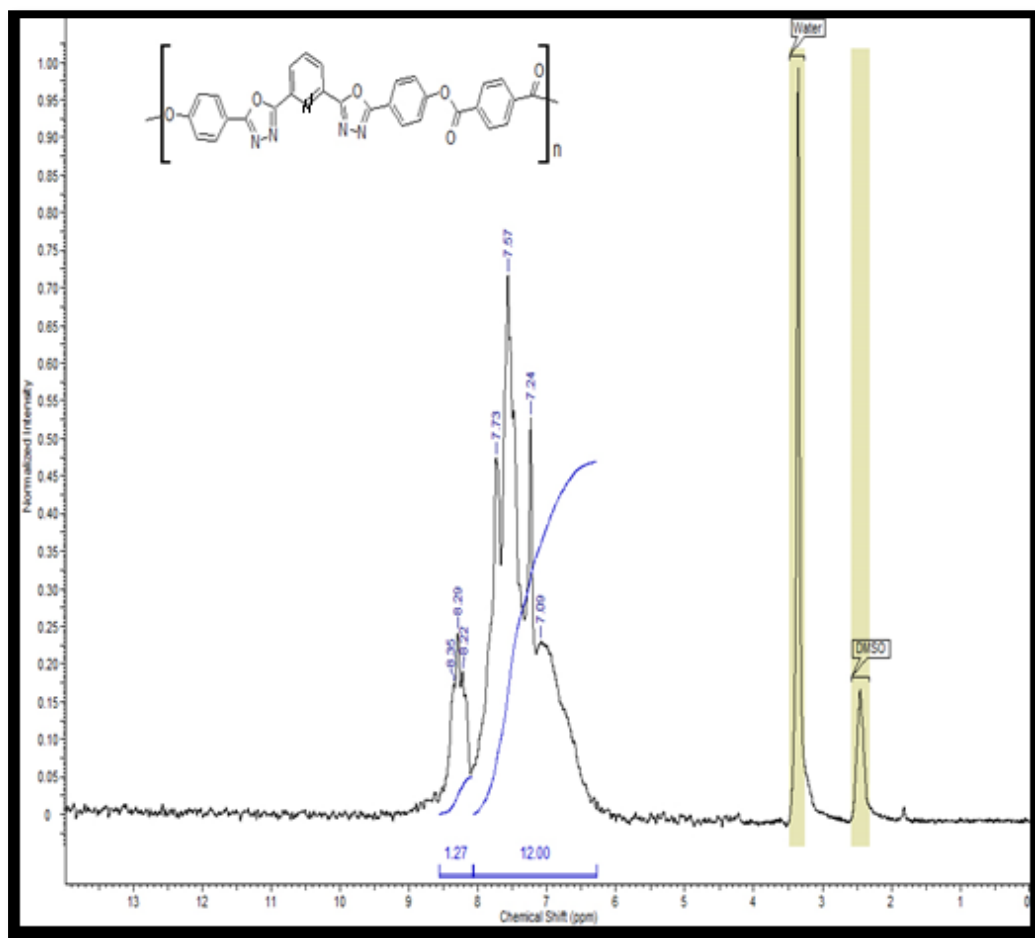
Figure 3-23: ^{1}H-NMR spectrum of P11

The FTIR of **P12** shown Strong deep band at 3433 cm^{-1} attributed to traces of OH group of phenol and carboxylic acid. The band at 3068 cm^{-1} referred to (CH) aromatic, assigned band at 1705 cm^{-1} for(C=O) of ester linkage. Besides to a band located at 1631 cm^{-1} attributed to (C=N) and two bands referred to (C=C) located at 1537 and 1485 cm^{-1}. Finally the bands at 752and 679 cm^{-1} referred to 1,3-di substituted aromatic carboxylic acid as shown in figure (3-24).
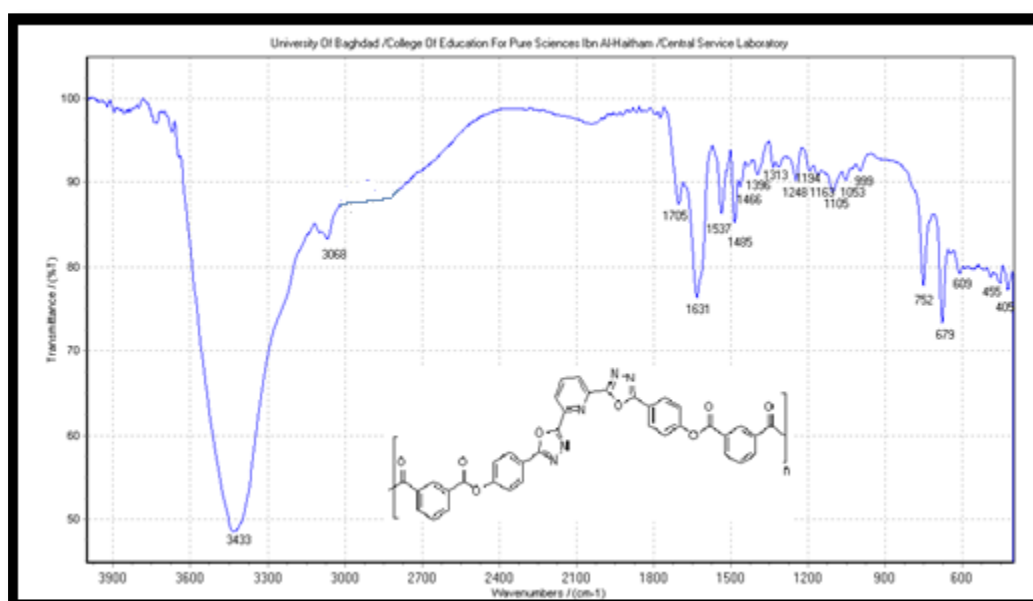
Figure 3-24: FTIR spectrum of P$_{12}$

The ^{1}H-NMR spectrum of **P**12 shown a multiplet signal at 7.02-7.72 ppm for (m, 12H, Ar-H). Then shown multiplet signal at 7.98-8.29 ppm for (m, 3H, H$_{pyridine}$) and a broad singlet signal at 11.83 ppm for (bs, 1H, OH) as demonstrated at figure (3-25).
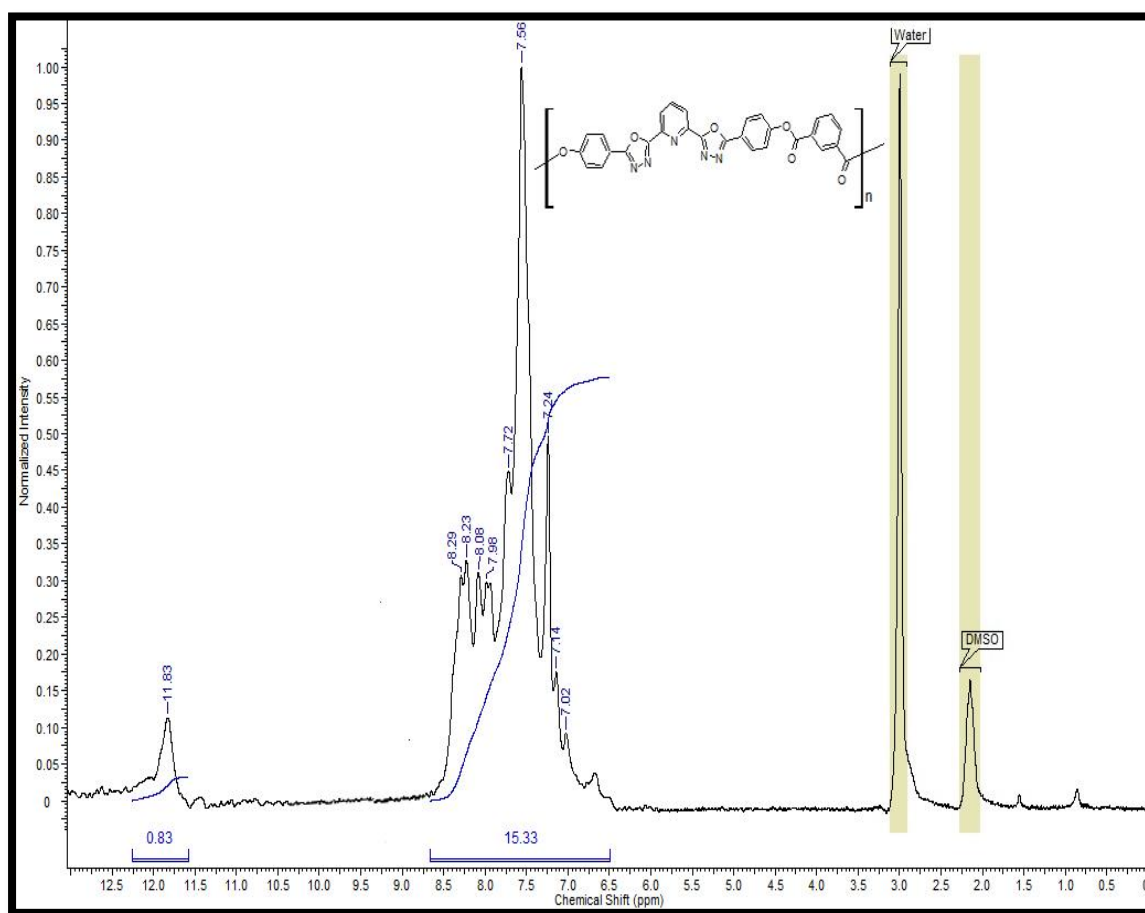
Figure 3-25: ^{1}H-NMR spectrum of P12

The FTIR of **P₁₃** exhibited strong deep band at 3419 cm⁻¹ referred to trace of (OH) group of phenol and carboxylic acid. The band at 3068 cm⁻¹ related to (CH) aromatic, at 1724 cm⁻¹ assigned band referred to(C=O) ,the (C=N) band appeared at 1631 cm⁻¹ which referred to oxadiazole ring and the band at 1539 cm⁻¹ attributed to (C=N) of pyridine ring. While the two bands at 1485 and 1464 cm⁻¹ attributed to (C=C) aromatic. The bands at 1248cm⁻¹ for (C-O) group of oxadiazole ring and the band at 999 cm⁻¹ referred to (C-O) of ester linkage. Furthermore the bands at 752 and 679 cm⁻¹ referred to di substituted ring as shown in figure (3-26).
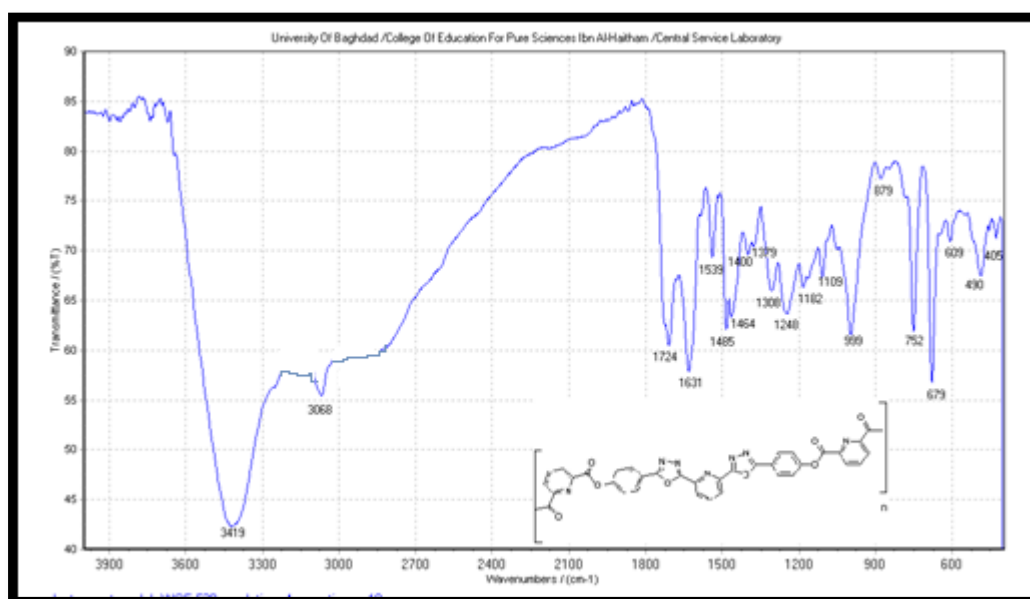
Figure 3–26: FTIR spectrum of P₁₃

The ^{1}H-NMR spectrum of **P₁₃** shown a douplet signal (d, 4H, ArH) at 6.36-6.50 ppm with coupling constant *J* equal to 7.2 Hz. The multiplet Signal (m, 10H, Ar-H, $H_{pyridine}$) at 7.45-8.23 ppm and single signal at 9.87 ppm for (s, 1H, OH) as in Figure (3-27).
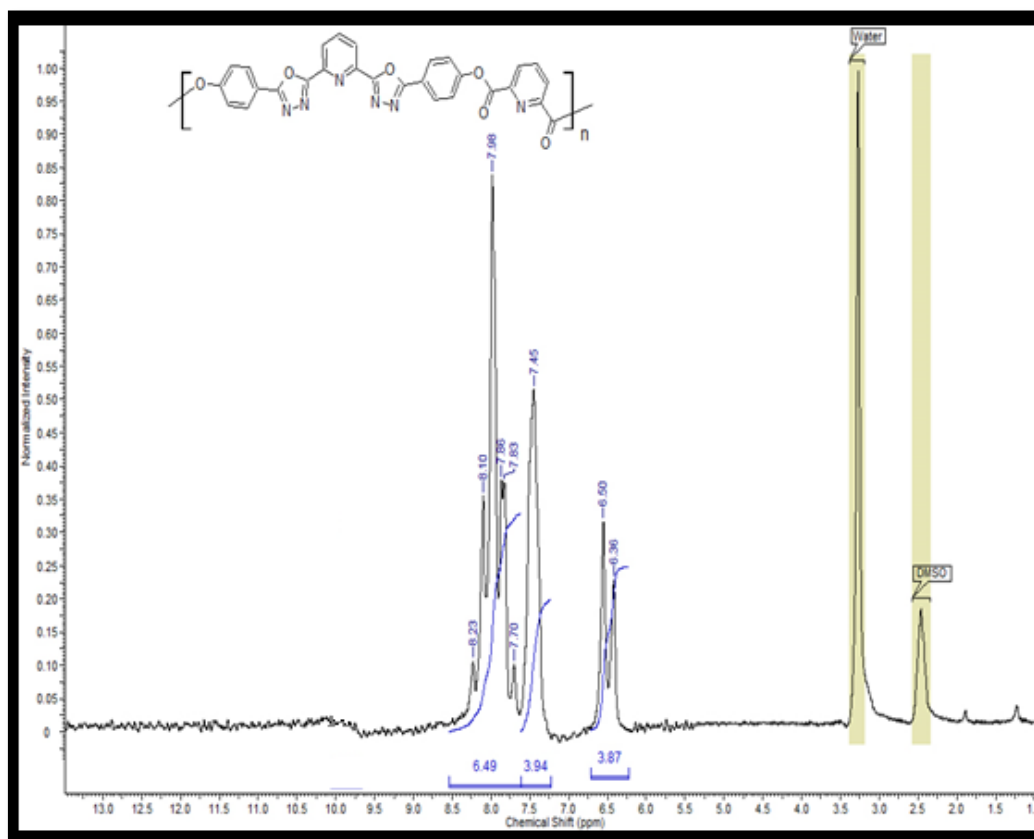
Figure 3–27: [1] H-NMR spectrum of P₁₃

3.9 Thermal Analysis

TGA and DSC were employed to evaluate the thermal properties of oxadiazole-polymer in order to eliminate the effect of absorbed moisture and residual solvent on the thermal transitions.

The TGA analysis shown that polymers are approximately having one to four stages of thermal properties due to the structures of polymers which attributed to aromatic and heterocyclic species which give strength. In addition to the presence of nitrogen atoms in the heterocyclic which generate di polarized bonds that lead to increase the interaction among the chains and verify stability of polymer chains[185].

The first stage is refer to evolution   of(H_2O), (CO_2) and dissociation of small species such as carboxylic groups and amines[186].

The second stage is attributed to the degradation of oligomer and small chains. The third stage of decomposition is related to the thermal degradation of medium polymer chains. The stage of decomposition is classify due to the fragmentation of long covalent macro chains of polymer with active groups which need to high temperature to pass the energy barrier and decomposition the chains[187].

Main while, heterocyclic structure, aromatic species and covalent bonds in polymer structure give less stages of decomposition with continuous heating process, that attributed to the length of chains , structure and molecular weights of the polymer subsequently response of the decomposition of polymer in less stages[188].

The thermo gravimetric curves (TG\DSC) were obtained at the heating rate of 10°C.min^{-1} under argon, and temperature range from (25-600) $^{\circ}$C.
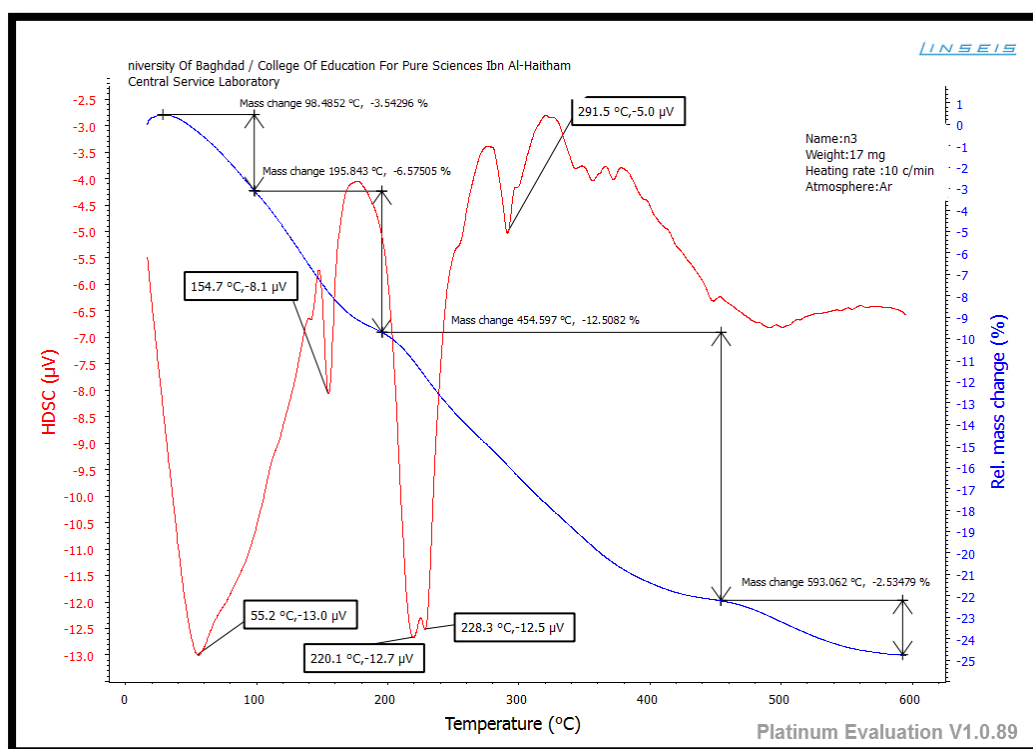
Figure 3–28: TG\DSC Thermogram of P₂

The (TGA) curve of **P₂** figure (3-28) illustrated four stages of a sequences mass loss, the first stage in (40-98.4852) $^{\circ}$C with mass loss (-3.54296%) of water and volatile compounds. The second stage in (98.4852-195.843) $^{\circ}$C with weight loss (-6.57505%), third stage in (195.843-454.597) $^{\circ}$C with mass loss about (-12.5082%), and the fourth stage (454.597-593.062) with mass loss (-2.53479%).

The (DSC) curve in figure (3-28) shown a glass transition temperature (Tg) at (55.2) $^{\circ}$C, an endothermic peak refer to melting point (Tm) at (154.7) $^{\circ}$C, the degradation was began at (220.1) $^{\circ}$C.
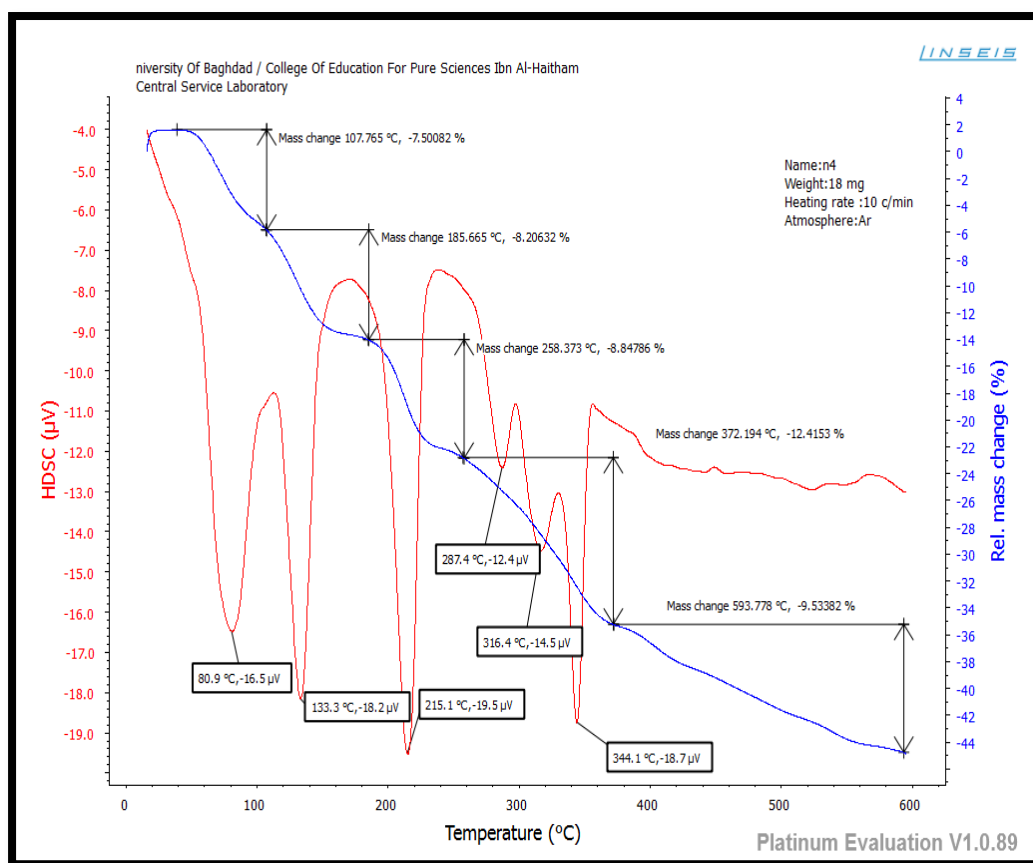
Figure 3-29: TG\DSC Thermogram of P₃

(TGA) curve of **P₃** figure (3-29) characterized by five stages which attributed to decomposition, the first stage (57-107.765) $^\circ$C with mass loss about (-7.50082%).The second stage (107.765-185.665) $^\circ$C with mass loss (-8.20632%), the third stage in (185.665-258.373) $^\circ$C, with mass loss (-8.84786%), fourth stage in (258.373-372.194) $^\circ$C with weight loss (-12.4153%), and the last stage was in (372.194-593.778) $^\circ$C with mass loss about (-9.53382%).

The (DSC) curve figure (3-29) shown (80.9) $^\circ$C glass transition temperature (Tg), (Tm) melting temperature at (133.3) $^\circ$C, and the degradation was began from (215.1-344.1) $^\circ$C.
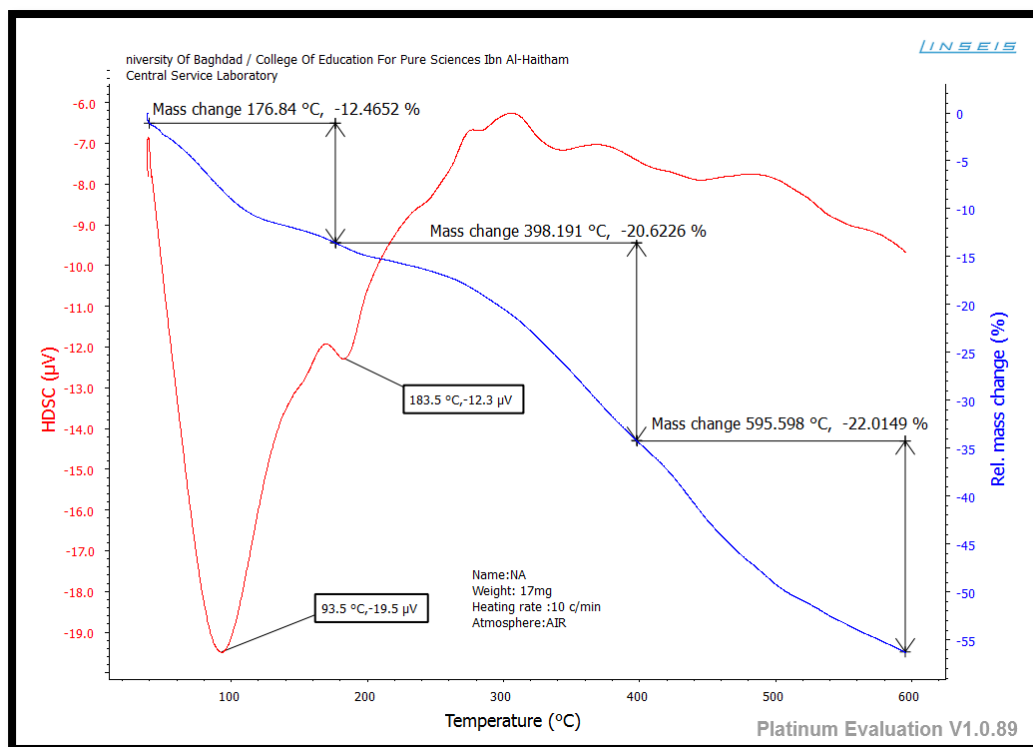
Figure3-30: TG\DSC Thermogram of P4

The (TGA) curve of **P₄** figure (3-30) shown three main stages of weight loss, first (40-176.84) °C referred to evaporation of the volatile compounds such as water, the weight loss about (-12.4652%), the second stage (176.84-398.191%) °C with weight loss about (-20.692%), and the last one was from (398.191-595.598) °C with (-22.0149%) as a weight loss.

The (DSC) curve in figure (3-30) for **P₄** shown glass transition temperature (Tg) at (93.5) °C, an endothermic peak refer to the polymer melting (Tm) at (183) °C, the degradation of polymer (Td) occurs at (275) °C.
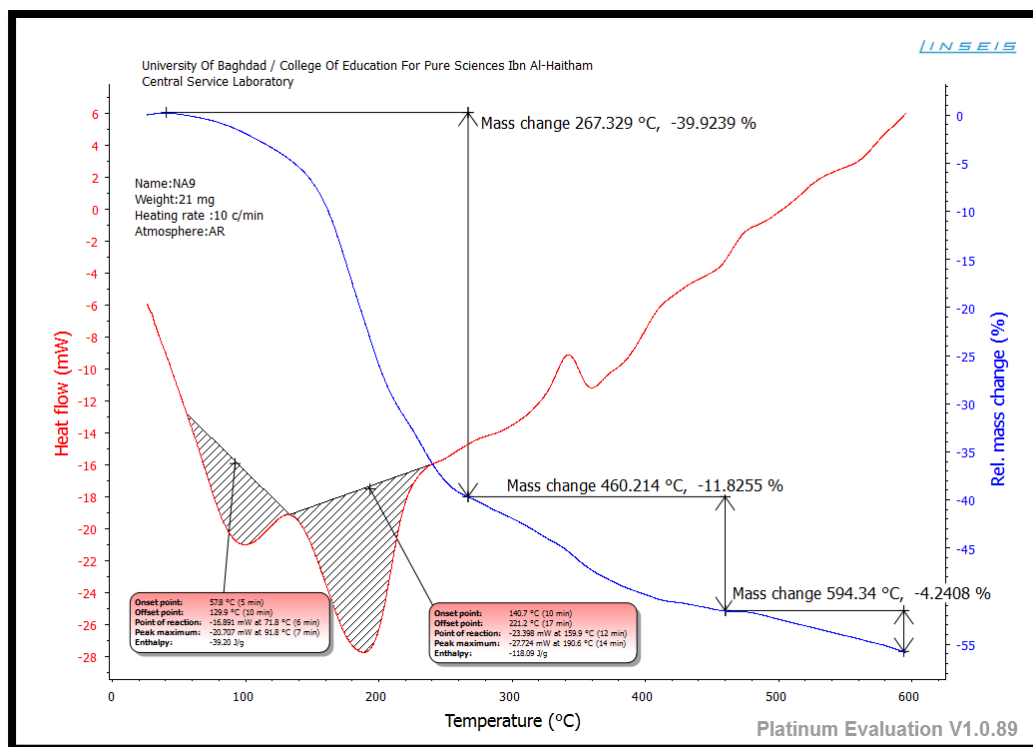
Figure 3-31: TG\DSC Thermogram of P5

(TGA) curve of **P₅** figure (3-31) illustrated that there are three main stages of weight loss, first (45-91.8) °C referred to evaporation of the volatile compounds such as water, the weight loss about (-39.9239 %), the second stage (267.329-460.214) °C with weight loss about (-11.8255%), and the last one was from (460.214-594.34) °C with (-4.2408%) as a weight loss.

While the (DSC) curve figure (3-31), shown a glass transition temperature (Tg) at (91.8) °C, melting point (Tm) at (190.6) °C and the degradation point (Td) was began at (343) °C.
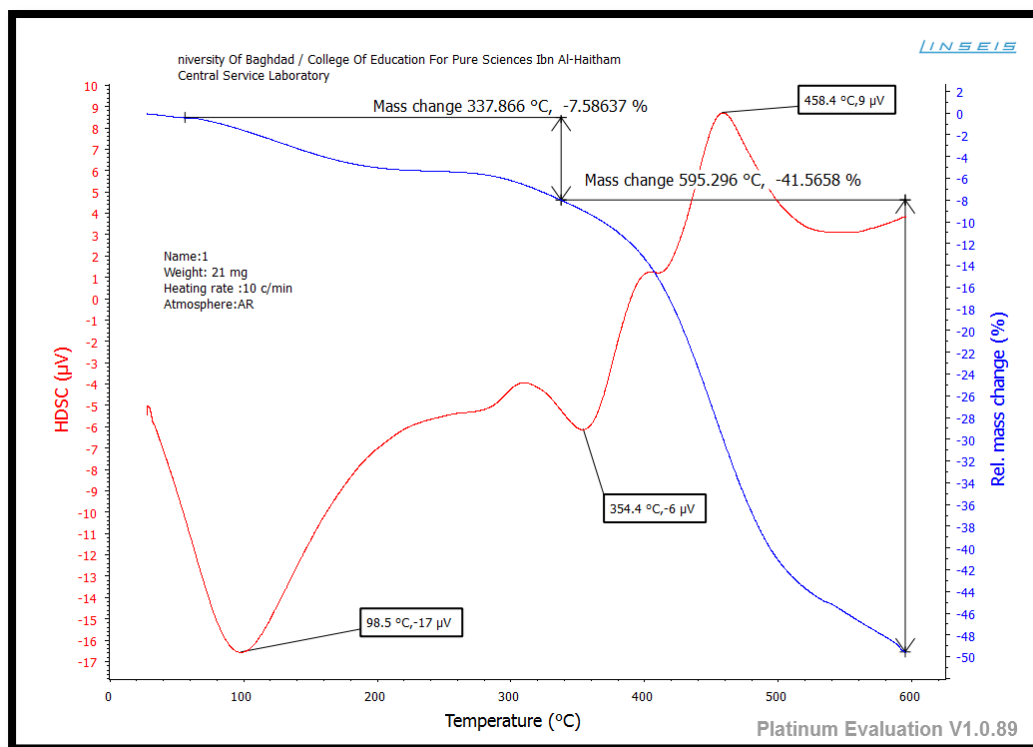
Figure 3–32: TG\DSC Thermogram of P₆

The (TGA) curve of P_6 figure (3-32) presented two stages of weight loss, the first (50-337.866) $^{\circ}$C that is refer to evaporation of volatile compounds mainly water, the weight loss (-7.58637%), the second stage was (337.866-595.296) $^{\circ}$C decomposition with weight loss equal to (-41.5658%).

The (DSC) curve in figure (3-32) for P_6 shown glass transition temperature (Tg) at (98.5) $^{\circ}$C, an endothermic peak refer to the polymer melting (Tm) at (354.4) $^{\circ}$C, and the degradation of polymer was started at (458.4) $^{\circ}$C.
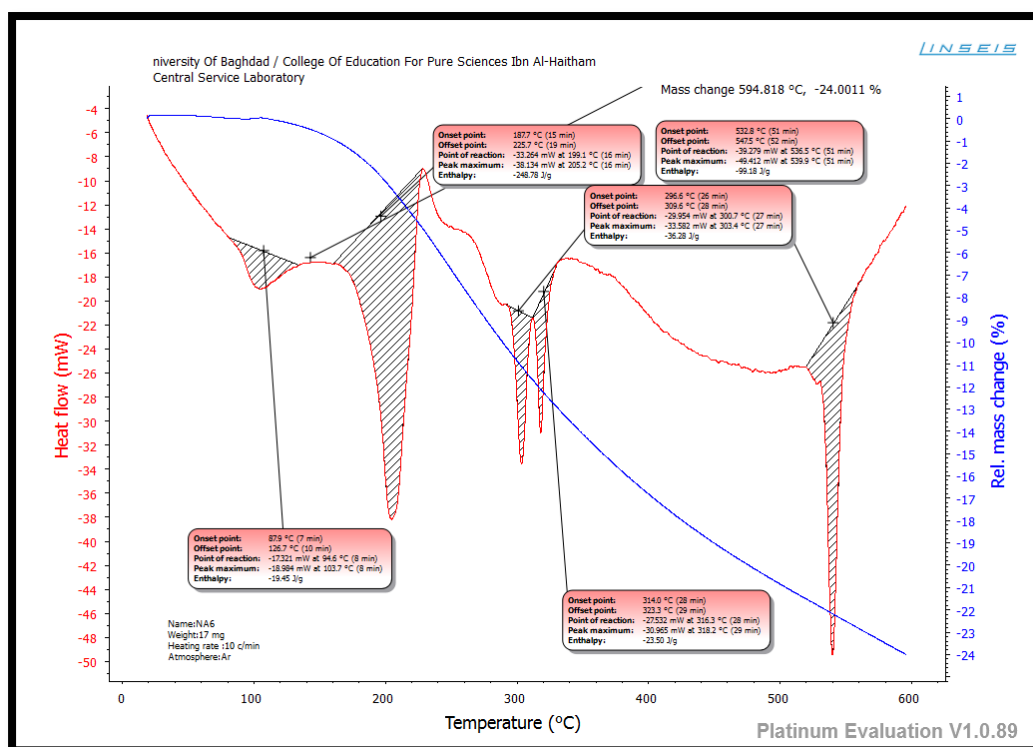
Figure 3–33: TG\DSC Thermogram of P$_7$

The (TG) curve of **P$_7$** figure (3-33) there is only one stage that was beginning from (105-594.818) $^{\circ}$C with weight mass loss about (-24.0011%).

The (DSC) curve in the same figure (3-33) clarify a glass transition temperature (Tg) at (103.7) $^{\circ}$C, melting point (Tm) at (205.2) $^{\circ}$C, and the polymer degradation was started at (303.4) $^{\circ}$C (Td).

Through the all results the observations Tg values were in the range of (80.9-103.7) $^{\circ}$C. That clearly indicate the increase in Tg is approximately constant because of the formation of oxadiazole ring resulted increase chain stiffness[189]. Tg value depending on several factors such as intermolecular forces and chain symmetry but it mainly depends on rigidity of the main chain of polymer[190]

Expect **P₂** which shown lower value of Tg with the respect to those of similar polymers containing methyl and phenyl groups in their structures. The incorporation of aromatic group imparted a significant increase in thermal stability by restricting segmental mobility, so polymers with phenyl moieties shown a good thermal stability in comparison with those contain aliphatic carbon-carbon linkage in the polymer backbone, Moreover shown multi stages of decomposition in (DSC) curve, as shown with **P₅**, **P₆**, **P₇**,Table (3-5).

Table 3-5: Characteristic parameters TG and DSC of the thermal decomposition of some synthesized polymers

polymer	DSC				TGA			
	$Tg\backslash°C$	$Tc\backslash°C$	$Tm\backslash°C$	$Td\backslash°C$	Step	$Ti\backslash°C$	$Tf\backslash°C$	Wt.loss%
P₂	55.2	___	154.7	220.1	1	50	98.4852	3.54296
					2	98.4852	195.843	6.57505
					3	195.843	454.597	12.5082
					4	454.597	593.062	2.53479
P₃	80.9	___	133.3	215.1	1	57	107.765	7.50082
					2	107.765	185.665	8.20632
					3	185.665	258.373	8.84786
					4	258.373	372.194	12.4153
					5	372.194	593.778	9.53382
P₄	93.5	___	183.5	275	1	40	176.84	12.4652
					2	176.84	398.191	20.6226
					3	398.191	595.598	22.0149
P₅	91.8	___	190.6	343	1	45	267.329	39.9239
					2	267.329	460.214	11.8255
					3	460.214	594.34	4.2408
P₆	98.5	___	354.4	458.4	1	50	337.866	7.58637
					2	337.866	595.296	41.5658
P₇	103.7	___	205.2	303.4	1	105	594.818	24.0011

3.10 Thermal Electro conductivity

Now a days the physical materials properties of modern engineering filed, are being highly noticeable.

Modernistic technical products likes vehicles, computers, space craft etc., as well the modern production machines would not be possible without significant improvements on properties of material's or synthesized new materials and explore their physical characteristic[191].

The challenge now is how to make these organic materials perform as a suitable conductor.

Commonly, the lagging have a large energy gap between the valence bands and conduction bands.

Mainly, the conductor polymers have double bonds conjugated or possess heterocyclic ring in their major chain. Newly, there are many references focused on conductive polymers with heterocyclic rings [192, 193].

The reactivates of these materials are very high, and the most lagging compounds have ionic besides to the covalent bands. Meanwhile, when electric field passes across these materials cannot conduct electric current[194].

These materials are very interested for using as dielectric which can turn down electricity transfer as well using as capacitors. Materials which can possess dipoles or ionic polarization or molecular polarization and when electrical field is applied permitting to field across through at definite frequency and definite temperatures[195].

On other hand, it is commonly known that the conductivities of these materials enhances with diminishing the frequency and with enhances the temperature[196].

The thermal conductivity (s/m) [197] of the synthesized materials was screened by LCR meter. The test of thermal conductivity of these materials accorded at 25, 50and 75°C at 50-1 MHz.

The negative conductivity is well known as negative resistance, which is express to enhance in voltage across the device's terminals to outcome diminution in electric current through it [198].

This is in disparity into a regular resistor in which an enhance of applied voltage lead to a proportional increase in current due to Ohm's law, resulting in a positive resistance [199].

Meanwhile, a positive resistance expends the power from current passing through it while, a negative resistance produces power [200].

3.10.1Screening the Electrical Conductivity

The samples of polymers under test were formed by pressing firm weight from the pure polymer to thickness (0.08 cm) and diameter equal (1cm) under 20 MPa. (Mega pascal).

The conductivity was screened by LCR meter at 50 Hz-1MHz at (25- 75)° C. The Electrical capacity and the Tangent of loss angle were determined also, electrical conductivity was determined from the following equations [196].

$Cp = Ɛ0A/d$………………… (1)

$Ɛr' = CP/C0$ $Ɛ0A/d/ C0$ … (2)

$Ɛr'' = Ɛr' \tan (δ) Ɛ0A/d/ C0. \tan (δ)$… (3)

$б_{a.c} = ω Ɛr'' Ɛ0$ ……………… (4)

Where:

Cp = Capacitor of materials (Polymer)   in F

$A = \text{Area}…..πr^2$ in m^2

d = Thickness   in m

C_0 = Capacity in vacuum   in F

$ω$ = Angular frequency…..$2πf$ in f

бa.c = Alternating electrical conductivity   in s/m

$\tan (δ)$ = Tangent of loss angle

$Ɛ_0$ = Permittivity of vacuum $8.85*10\text{-}12$ in F/m

$Ɛr'$ = Permittivity of the material   in F/m

$Ɛr''$ = Relative permittivity   in F

3.10.2 .Electro conductivity of polymer (2-7)

The electro conductivity of **P$_2$** was tasted at 25, 30, 35, 40, 45, 50 and 55° C.
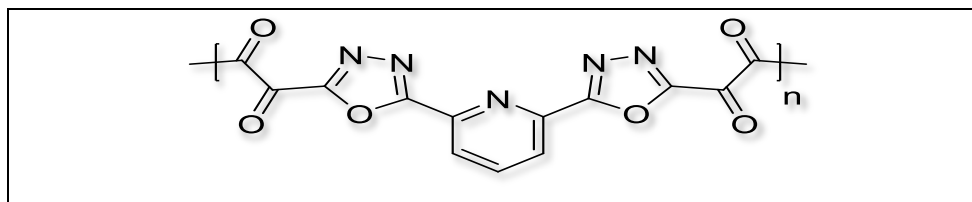
(P$_2$)

The electro conductivity at 25° C exhibited positive electro conductivity equal to 3.30×10^{-5} $(\Omega.m)^1$ at 19596.375 Hz as shown in figure (3-34).
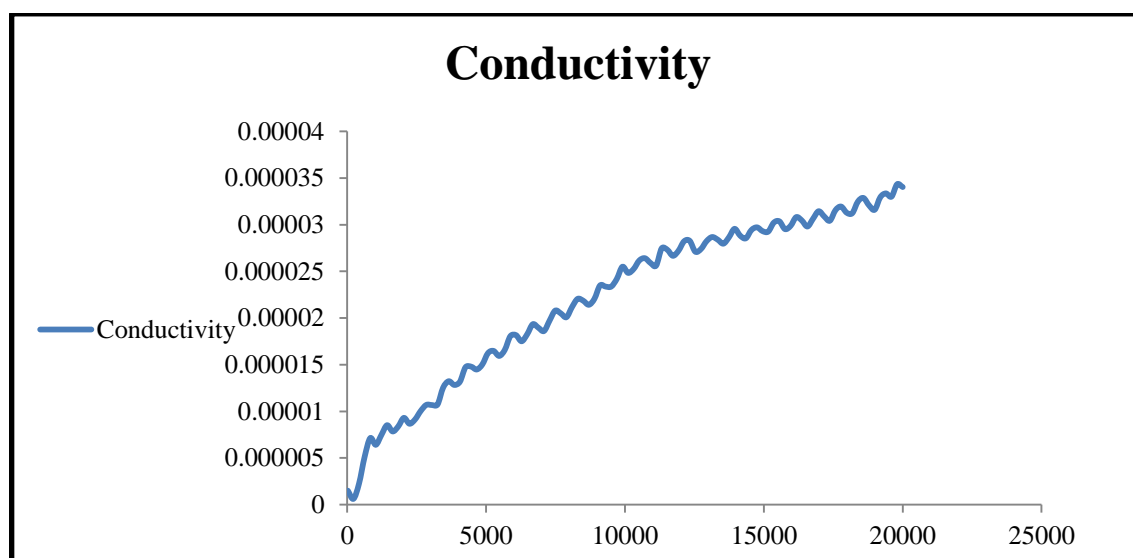
Figure 3-34: Electro conductivity of P$_2$ at 25 $^\circ$C

Figure (3-35) exhibited the electro conductivity of **P$_2$** at 50° C which equal to $2.17644 \times 10^{-5}(\Omega.m)^{-1}$ at 19394.55Hz.
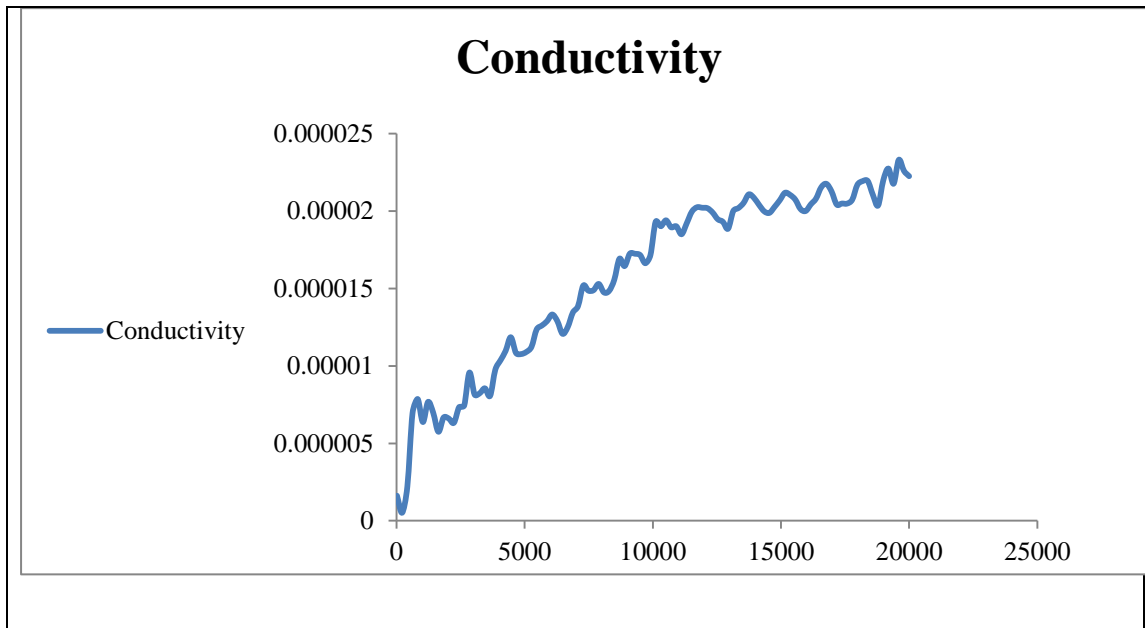
Figure 3–35: Electro conductivity of P$_2$ at 50 ºC

P$_2$ shown interested conductivity equal to 3.6 7$\times10^{-5}$(Ω.m)$^{-1}$ at

30º C and 18789.1 Hz as depicted in figure (3-36) which exhibited increases of electro conductivity with increasing of the frequency at all temperature.
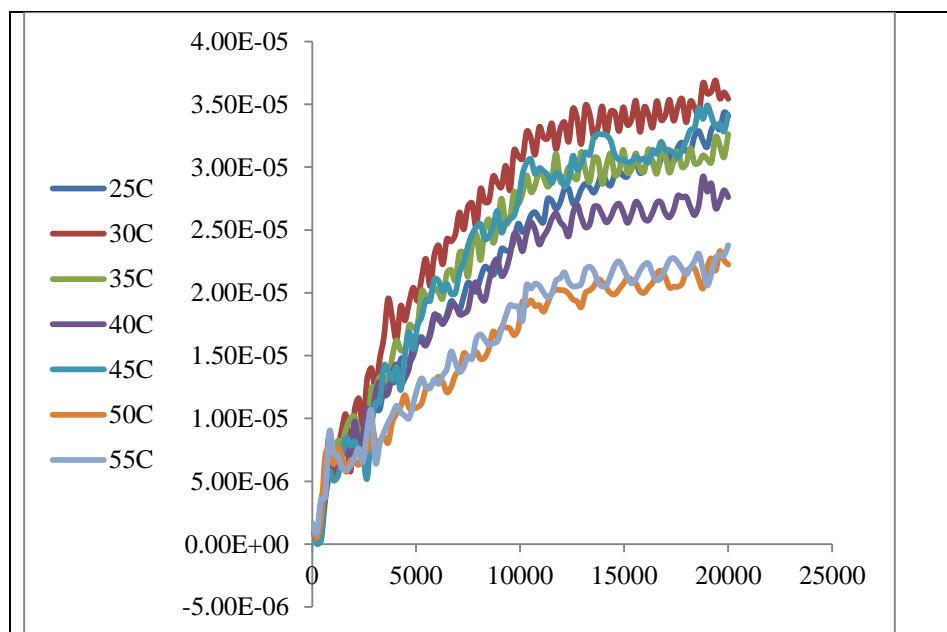
Figure 3-36: Electro conductivity of P$_2$ at all temperature

The electro conductivity of **P**3 was tasted at 25, 50 and 75°C.

(P3)
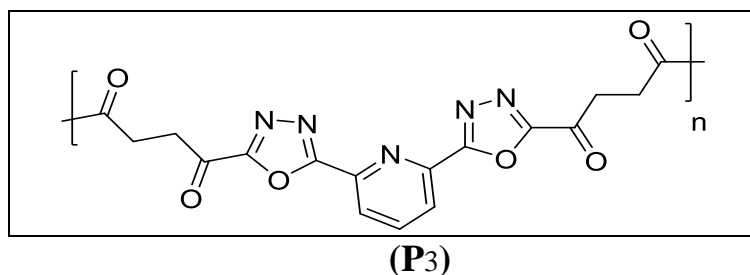
Polymer **3** at 25°C, exhibited electro conductivity equal to 0.092377493 (Ω.m)$^{-1}$ at 5074.874512 Hz, which decreases slightly with increasing in frequency as illustrated in figure (3-37).
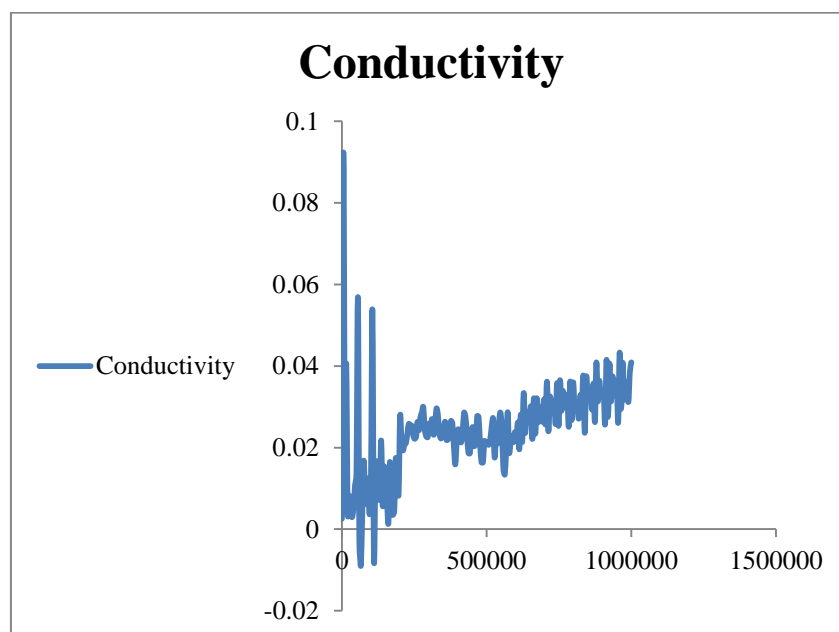
Figure 3-37: Electro conductivity of P3 at 25 °C

At 50°C **P3** shown interested conductivity equal to 0.9799825 (Ω.m)$^{-1}$ at 55323.62109Hz which consider higher electro conductivity in comparison with value of electro conductivity at

25°C as shown in figure (3-38).
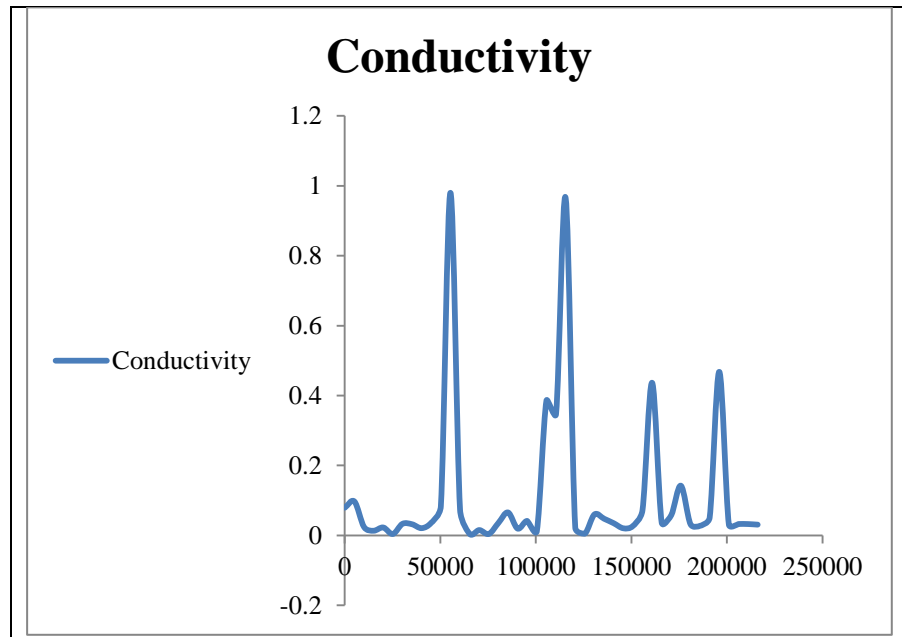
Figure 3-38: Electro conductivity of P3 at 50 ℃

P3 shown at 75° C interested electro conductive which is equal to 0.104589091(Ω.m)$^{-1}$ at 15124.62Hz then decreased gradually after that frequency as depicted in figure (3-39).
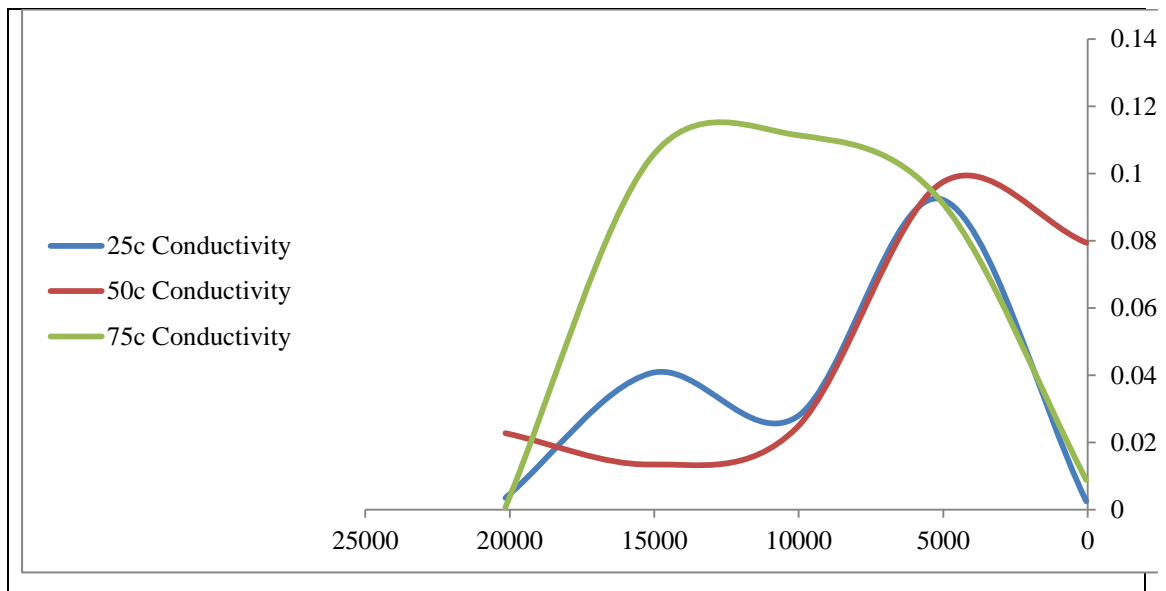
Figure 3–39: Electro Conductivity of P3 at 75 ℃

Figure (3-40) exhibited **P3** attitude at all temperature at frequency of (200000-1000000) Hz which shown good conductive of **P3** at 50°C then began to decrease with the increasing of frequency. While, shown the lowest value at 25 and 75°C.
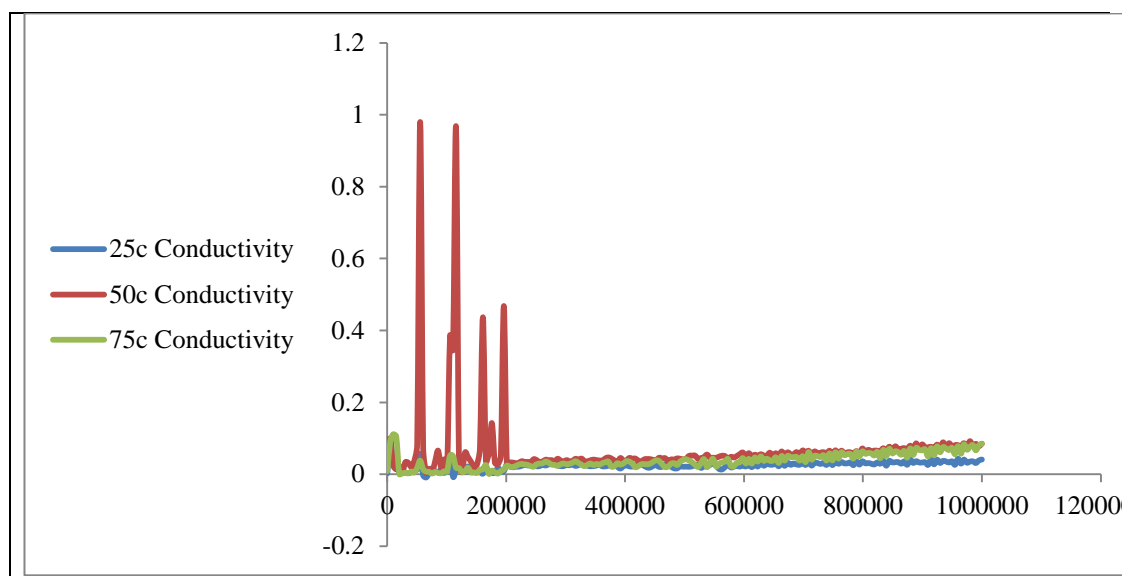
Figure 3–40: Electro conductivity of P3 at all temperature
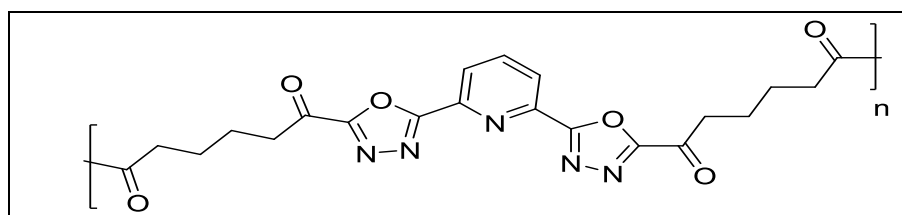
(P4)

P4 at 25°C exhibited conductivity equal to 0.001197628 $(\Omega.m)^{-1}$ at The frequency of 50298.74609 Hz this conductivity decreased rapidly, and then returns to rise at 110597.2422Hz to 0.000913643 Hz. After this frequency the conductivity decreased rapidly as shown in figure (3-41).
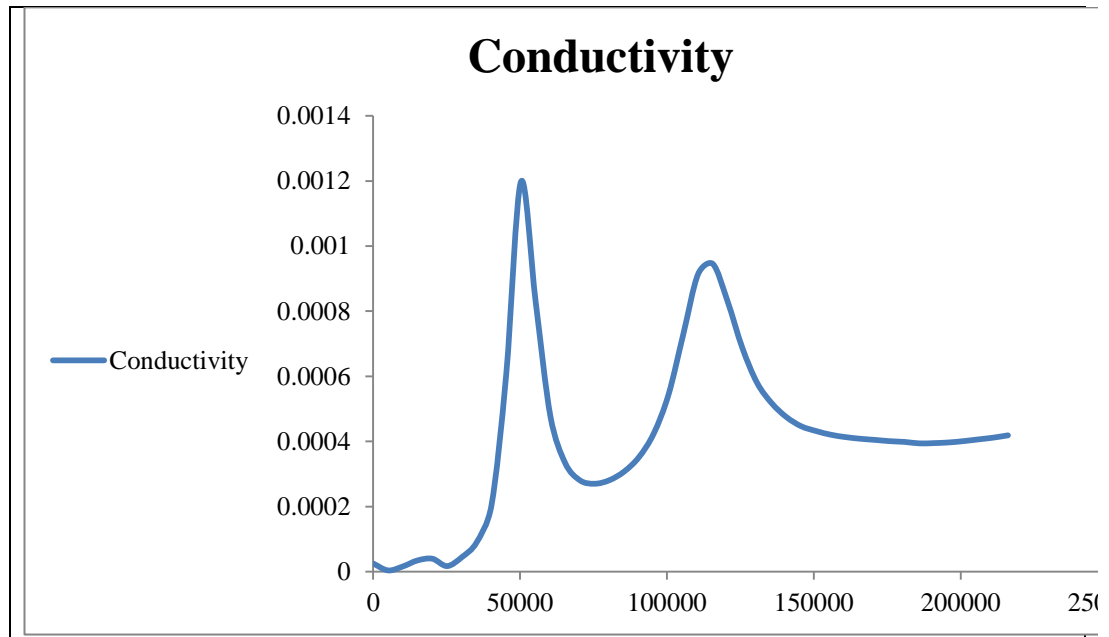
Figure 3-41: Electro conductivity of P4 at 25 ºC

The first range of frequency between (0-65373.37) Hz, the **P**4 shown conductivity equal to $1.20\times10^{-3}(\Omega.m)^{-1}$ at 25ºC, $1.17\times10^{-3}(\Omega.m)^{-1}$ at 50º C and $9.56\times10^{-4}(\Omega.m)^{-1}$ at 75ºC. This conductivity slightly decreased with increasing frequency, then raises partially until reached maximum at the frequency of 110597.2 Hz then returned decreased. However, the conductivity of **P**4 at 25,50 and 75ºC were closed together and they seem to be still steady as shown in figure (3-42).
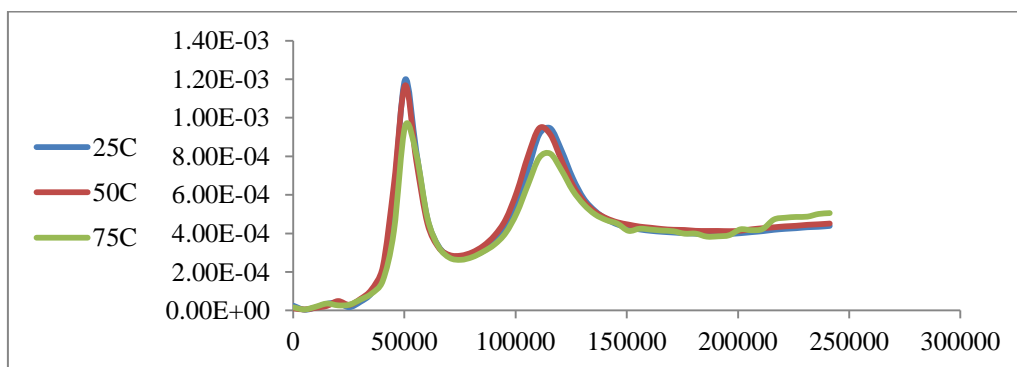
Figure 3-42: Electro conductivity of P4 at all temperature

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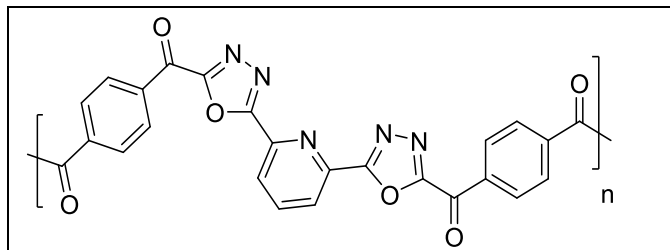
(P5)

Polymer 5 shown linear increases of electro conductivity with the increasing of frequency at all temperature .The highest value was at60°C equal to6.49×10⁻⁵(Ω.m) ⁻¹ with linear increases.
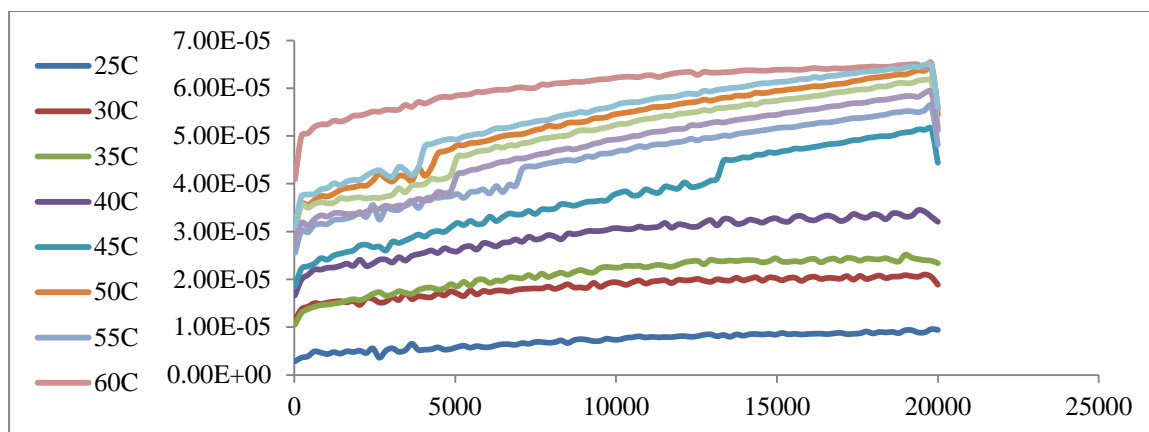
Figure 3-43: Electro conductivity of P5 at all temperature
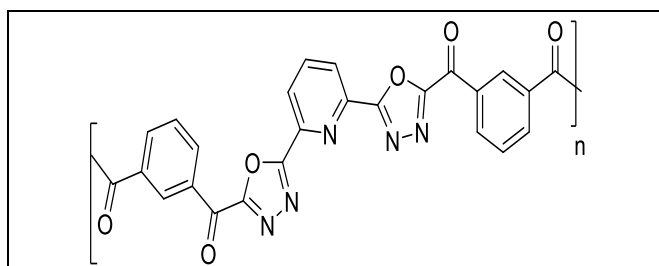
(P6)

P6 at 75° C exhibited conductivity equal 0.35434067(Ω.m)$^{-1}$ at 155821.1094 Hz then began decreased rapidly. After that it seems to be still steady until reached 844228.9375Hz shown interested conductivity equal 1.581568028 (Ω.m)$^{-1}$ then returns to decrease as depicted in figure (3-44).
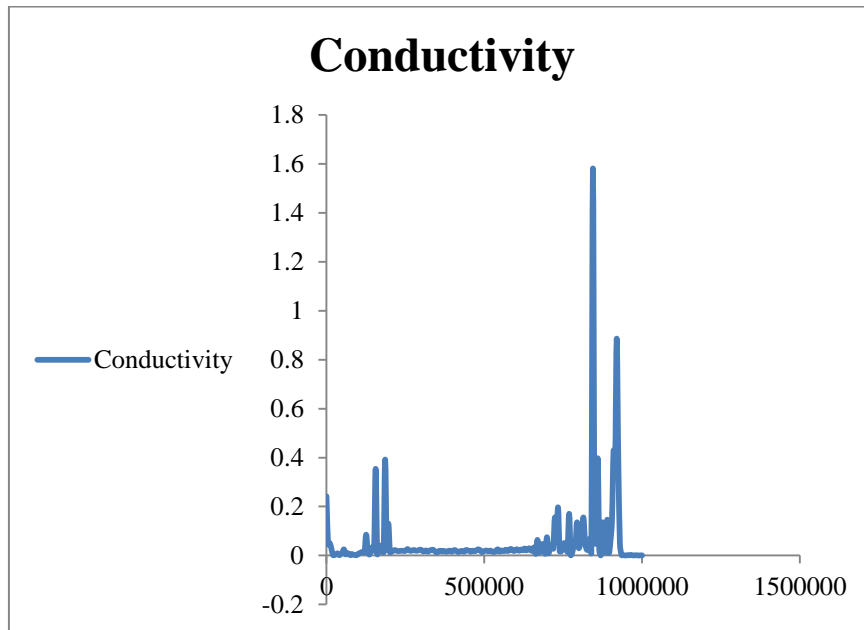
Figure 3-44: Electro conductivity of P6 at 75 ºC

P_6 at 75°C it shown interested electro conductive 0.241896761 (Ω.m)$^{-1}$ at 50Hz then decreased slightly.

At 50°C shown electro conductivity equal 0.077605069(Ω.m)$^{-1}$ at 50 Hz then decreased until reach to minimum value at 10000Hz at which began to rise again.

At 25° C shown electro conductivity equal 0.098808676(Ω.m)$^{-1}$ then fluctuate considerably to reach minimum value of conductivity at 10000Hz then rises slightly at 15124.62Hz to show electro conductivity equal to 0.04122245 (Ω.m)$^{-1}$ as depicted in figure (3-45).
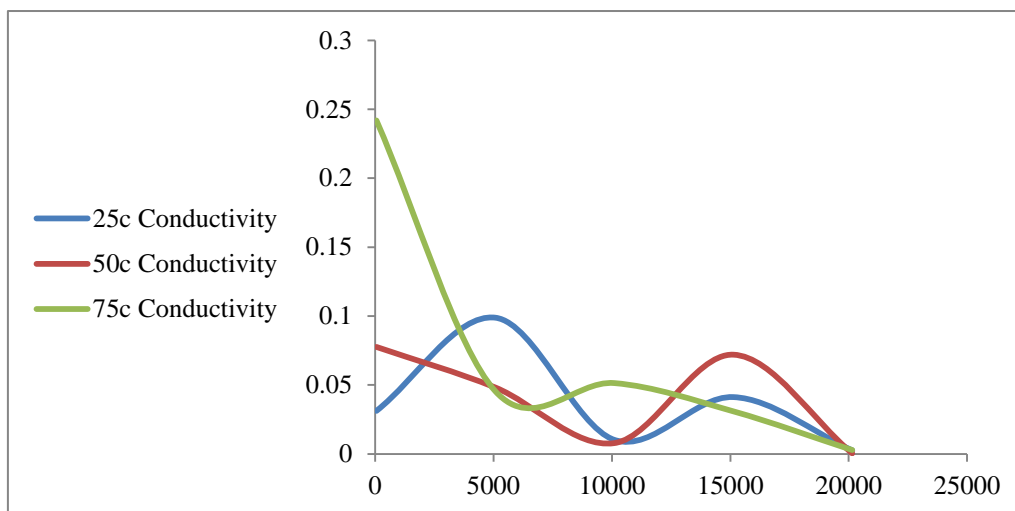
Figure 3-45: Electro conductivity of P$_6$ at all temperature
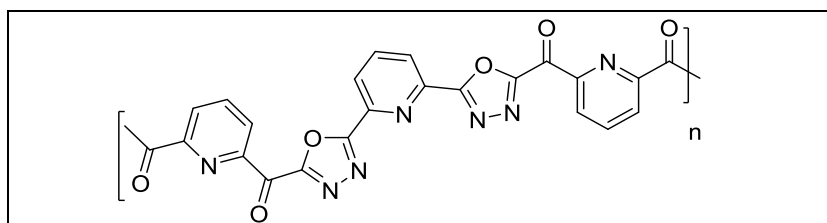
(P$_7$)

Polymer **7** was tested at 25,30,35,40,45,50,55,60,65,70 and 75°C.

The electro conductivities of **P$_7$** take totally different attitude at 25, 60, 70 and 75°C as shown at figure (3-46).

Exhibited at 60°C the highest electro conductivity value equal $2.02×10^{-5}(\Omega.m)^{-1}$ at625.4545 Hz.

At 70° C shown interested electro conductive $1.28×10^{-5}$ $(\Omega.m)^{-1}$ at 625.4545 Hz.

At 25°C the electro conductivity equal to$1.11×10^{-5}$ $(\Omega.m)^{-1}$ at 1230.909 Hz.

While, the electro conductivity of 30,35,40,45,50 and 55° C were too closed together and approximately still steady with increases of frequency.

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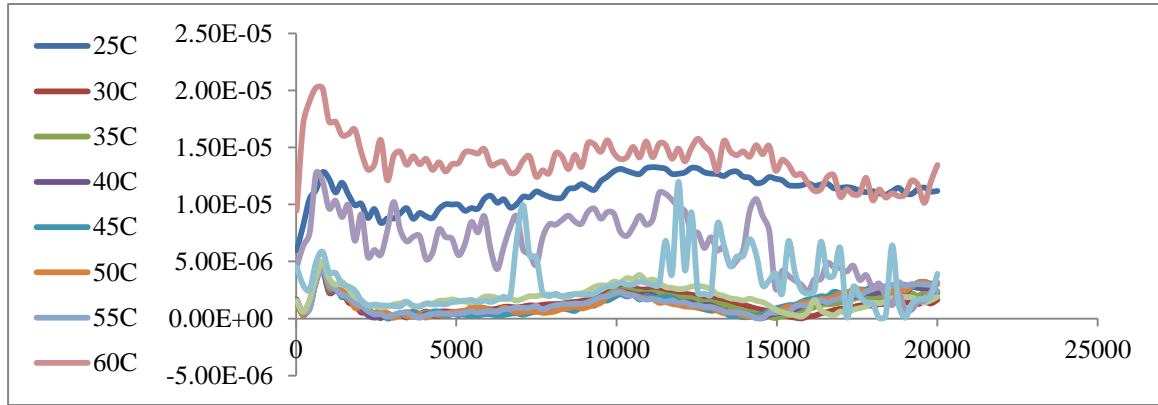
Figure 3-46: Electro conductivity of P₇ at all temperature
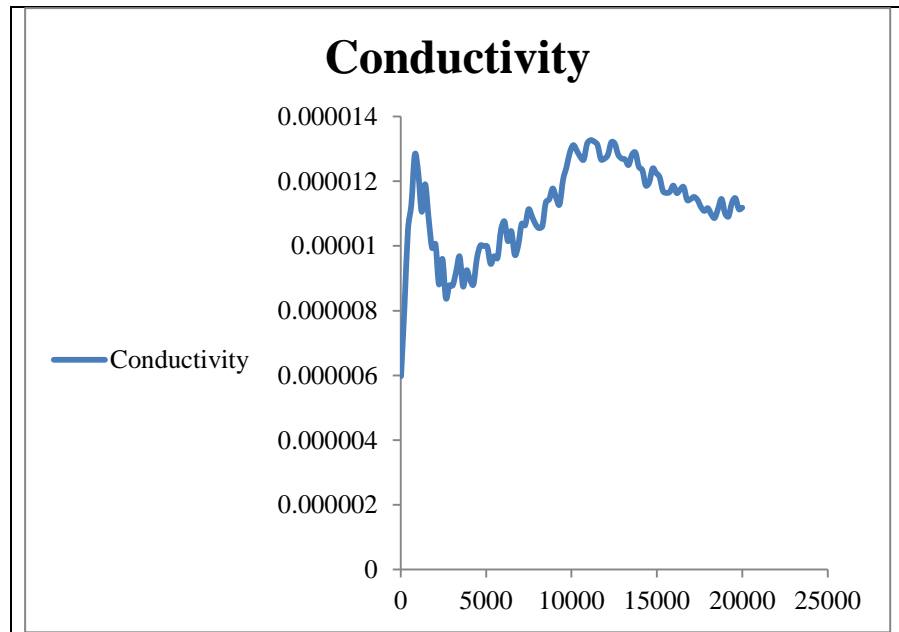
Figure 3-47: Electro conductivity of P7 at 25 ºC
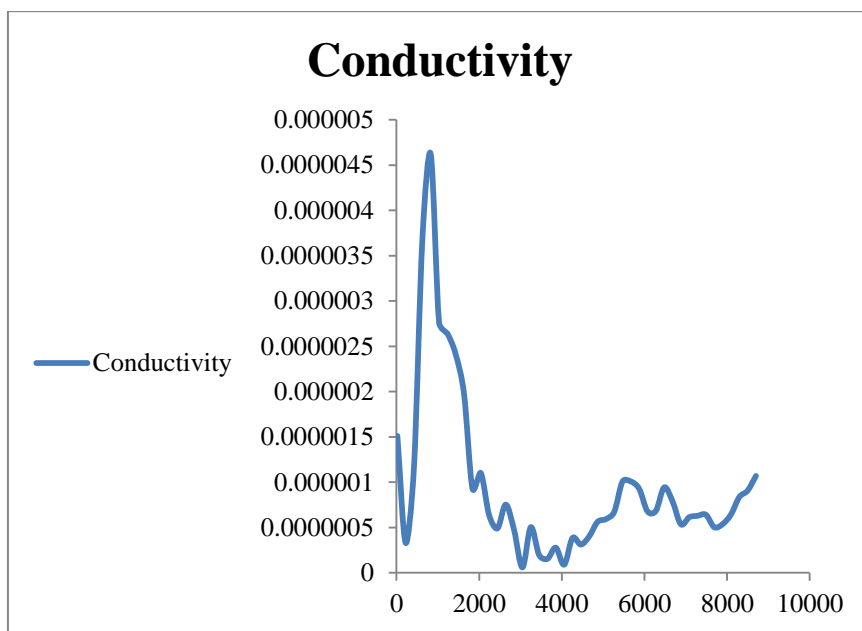
Figure 3-48: Electro conductivity of P₇ at 50 ºC
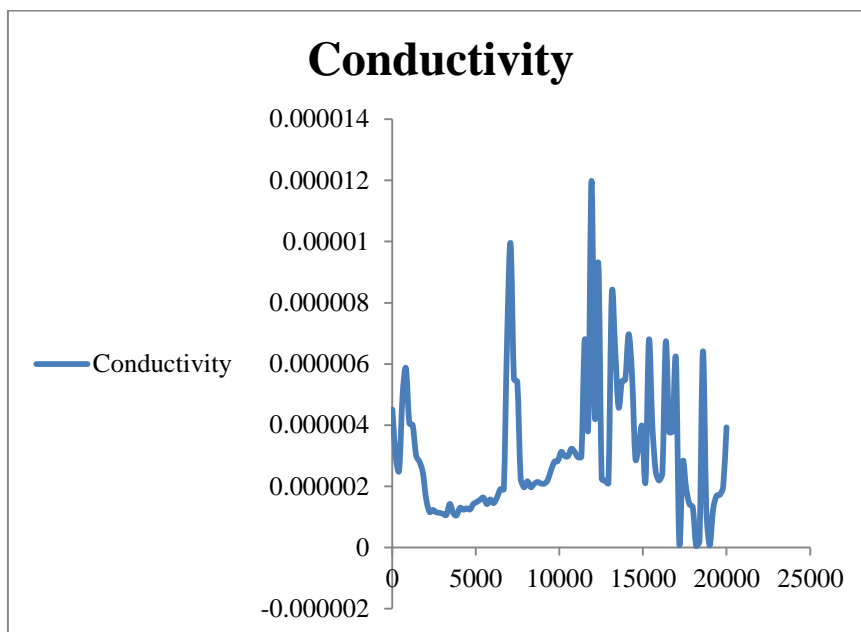
Figure 3-49: Electro conductivity of P 7 at 75 ℃

The polymers under test shown that the existing of doping group like OH and groups with drawing such as C=O, C=C and C=N in the polymers chains exhibited moderate to good electro conductivity, because they act as charge carriers so caused in transfer of electrons and charges along the polymers chains.

In poly conjugated systems, the behavioral properties of the π- electrons such as their delocalization and polarization , play significant roles in determining the electrical properties of the system. Then these amorphous conductive polymers shown variance conductivity and the conductivity was increasing and sometimes decreased because of pronounced disorder in the polymer matrix. Structural and morphological disorder inhibits π-electrons delocalization, thus retarding charge transport [201-210].

3.11 Biological Activity of the Synthesized Polymers

The widespread use of 1,3,4-oxadiazole and their derivatives as a scaffold in medicinal chemistry attributed to a large number of drugs used clinically have oxadiazole rings as a structural building block, also display a wide spectrum of biological activities such as antibacterial, antifungal, anticancer, antimalarial, etc.

The newly synthesized polymers were tested for their inhibitory activity in vitro growth against *Escherichia coli* (gram-negative bacteria), *Bacillus subtilis* and *Staphylococcus aureus* (gram-positive bacteria), and the yeast- like pathogenic fungus *candida albicans*.

The biological activities were carried out using the agar well diffusion method using Mῡller-Hintor agar medium.

The agar plate surface is inoculated by spreading of the microbial inoculum over the entire agar surface. Then, a hole with a diameter of 8mm is punched aseptically with a sterile cork borer or a tip, and was moistened with the polymer solution in dimethyl sulfoxide (DMSO) of specific concentration (50µg\mL) and carefully placed on the agar culture plates, the solution diffuse in the agar medium and inhibits the growth of microbial strain.

The plates were incubated at 37°C, and the diameter of the growth inhibition zone around the hole was measured after 24hrs. in case of bacteria while calculated after 48 hrs. in case of *candida albicans.*

The observations were outlined in Table (3-6) and (3-7).

Table 3-6: Anti-bacterial and anti-fungal zone of inhibition (mm) of synthesized polymers

Polymer	*Esherichia coli*	*Staphylococcus aureus*	*Bacillus subtilis*	*Candida albicans*
P_1	___	___	16	___
P_2	___	19	___	___
P_3	11	___	___	___
P_4	16	___	___	13
P_5	13	14	12	21
P_6	22	15	15	22
P_7	20	16	20	22

(--): inactive polymer against the specified microorganisms.

Polymer (**1**) shown good activity against *Bacillus subtilis*, while was in active against the other microorganisms.**P_2** exhibited good activity against gram positive bacteria *Staphylococcus aureus,* as well shown inactive activity against *Esherichia coli, Bacillus subtilis* and *Candida albicans.*

P_3 exhibited moderate activity against gram negative bacteria *Esherichia coli,* while was inactive against the other microorganisms under test.

P_4 exhibited good to moderate activity against gram negative bacteria *Esherichia coli* and *Candida albicans* respectively.

P_5 shown good to moderate activity against all microorganisms under test.

P_6 and **P_7** shown high activity against all microorganisms as illustrated in Table (3-6).

Table 3-7: Anti-bacterial and anti-fungal zone of inhibition (mm) of synthesized polymers

Polymer	*Esherichia coli*	*Staphylococcus aureus*	*Bacillus subtilis*	*Candida albicans*
P_8	17	12	22	____
P_9	19	22	20	____
P_{10}	25	32	28	17
P_{11}	29	35	28	21
P_{12}	30	38	33	29
P_{13}	32	36	33	30

(--): inactive polymer against the specified microorganisms.

Polymer (**8**) shown good to moderate activity against gram negative and gram positive bacteria but was inactive against *Candida albicans.*

P₉ displayed   good activity against gram negative and gram positive bacteria but also was inactive against *Candida albicans.*

P₁₀ exhibited good activity against all bacterial and fungal under test.

P₁₁, P₁₂ and **P₁₃** exhibited well to high activity against all microorganisms under test.

From the observations polymer (**1,2,3,4)** shown variance activity ranging from low to moderate activity and inactive activity against some microorganisms in some places, then the activity began increase slightly with polymer (**5,6,7,8,9**). The activity increased obviously with polymer (**10, 11, 12, 13)** as illustrated in Table (3-7).

The results indicate that the presence of phenyl group is an important factor for increase the biological activity both in antibacterial and antifungal [211, 212]. So that polymers which afforded from aromatic di carboxylic acid exhibited antibacterial and anti-fungal highest than those which afforded from aliphatic di carboxylic acid.
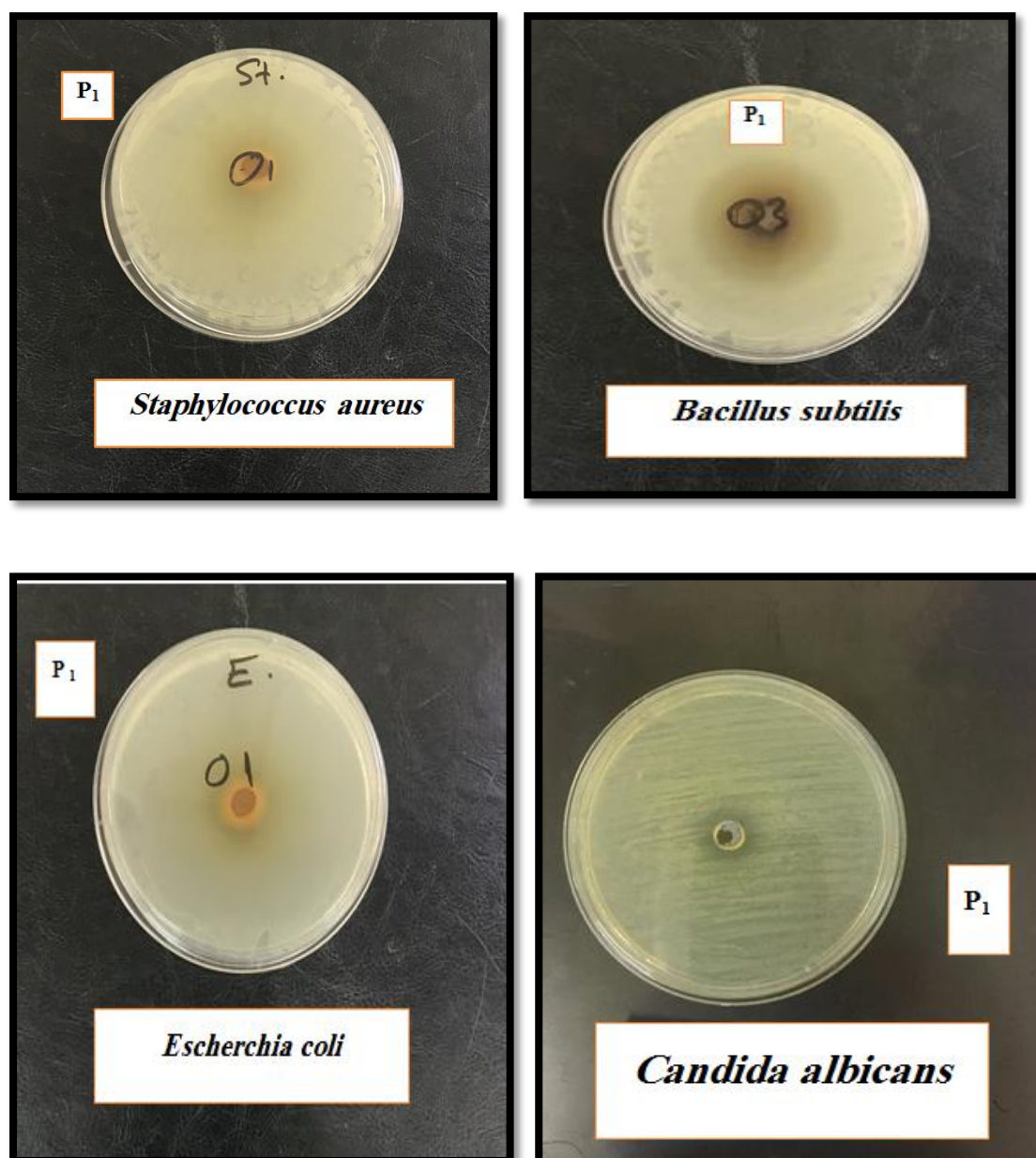
Figure3-50: Inhibition zone of (P₁) against all microorganisms under test
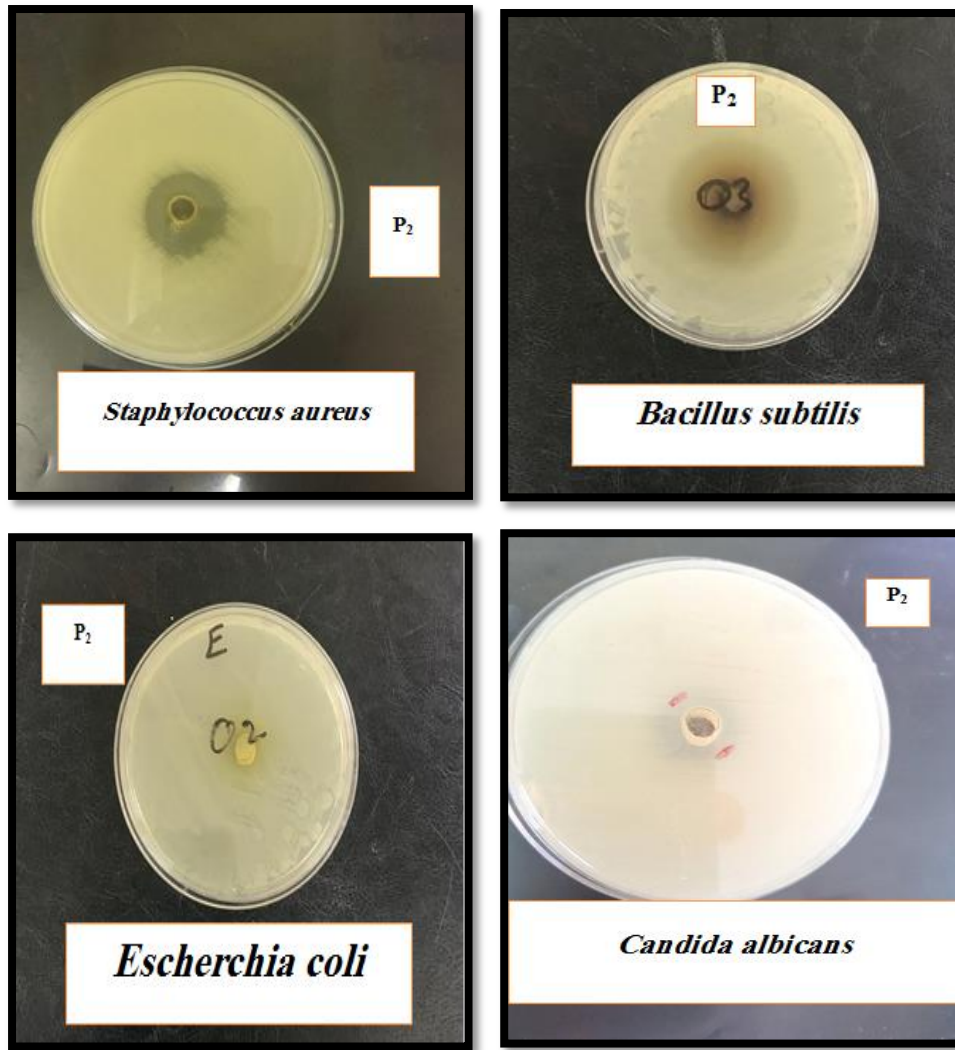
Figure 3–51: Inhibition zone of (P2) against all microorganisms under test
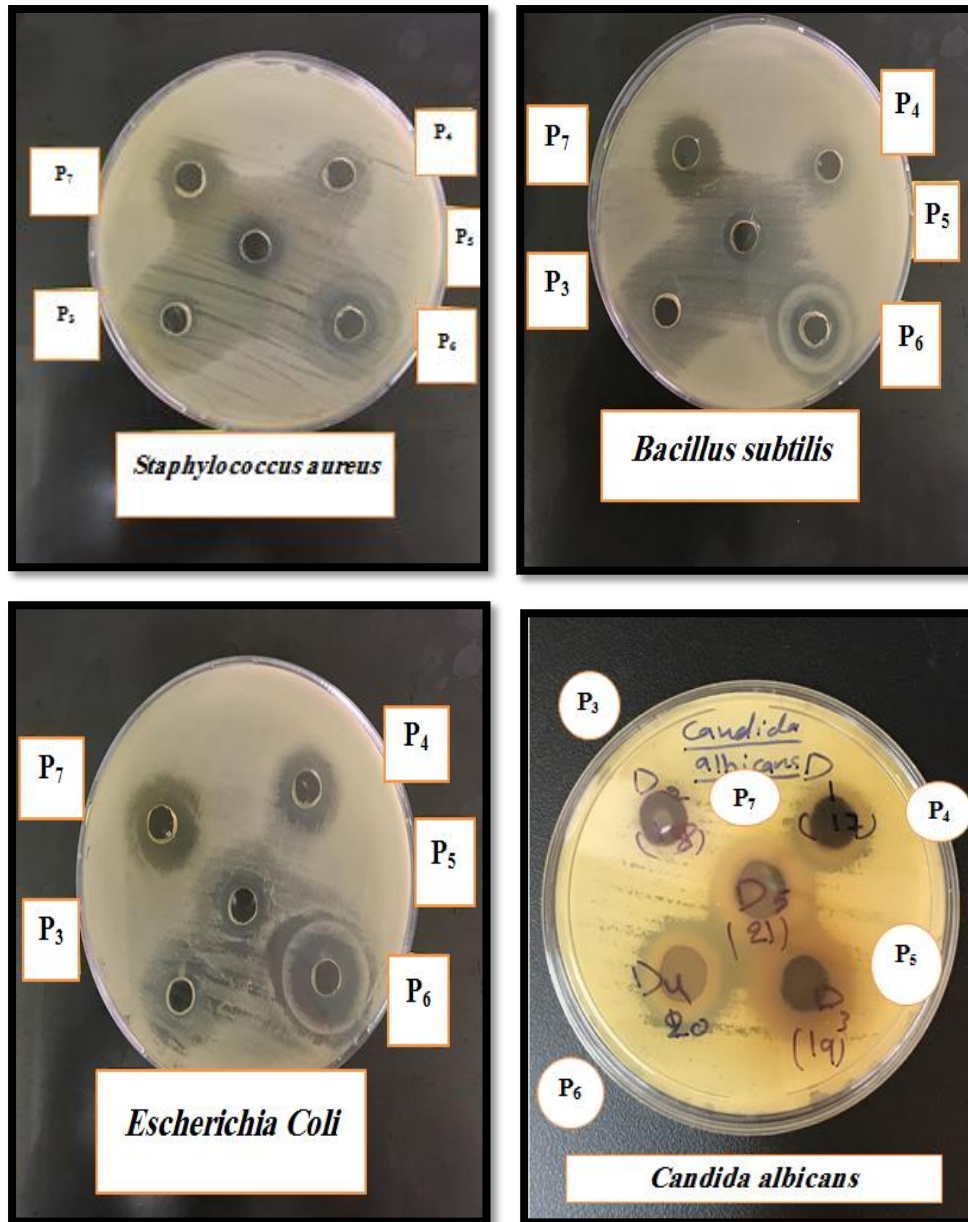
Figure 3-52: Inhibition zone of (P3, P4, P5, P6, P7) against all microorganisms under test
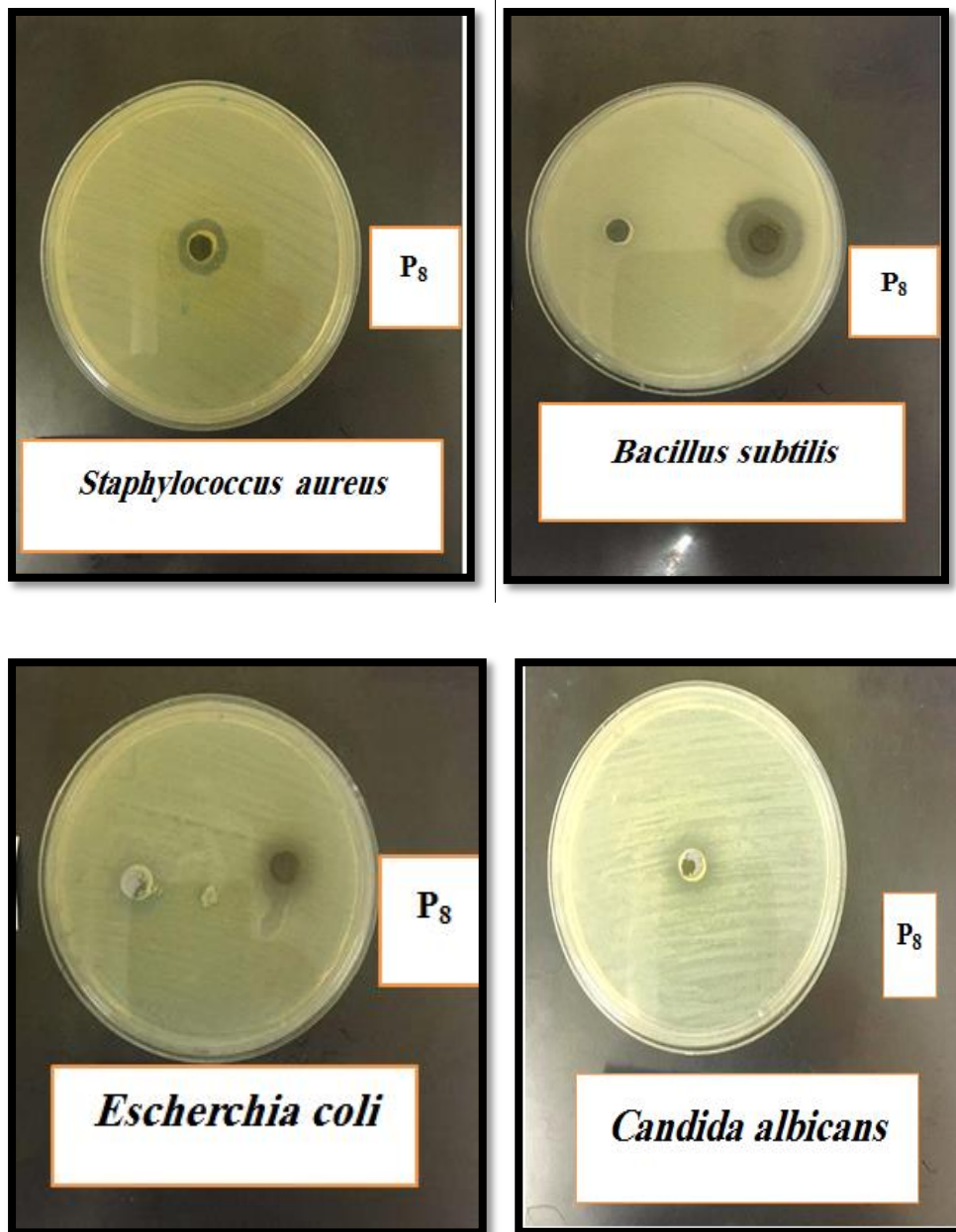
Figure 3-53: Inhibition zone of (P₈) against all microorganisms under test
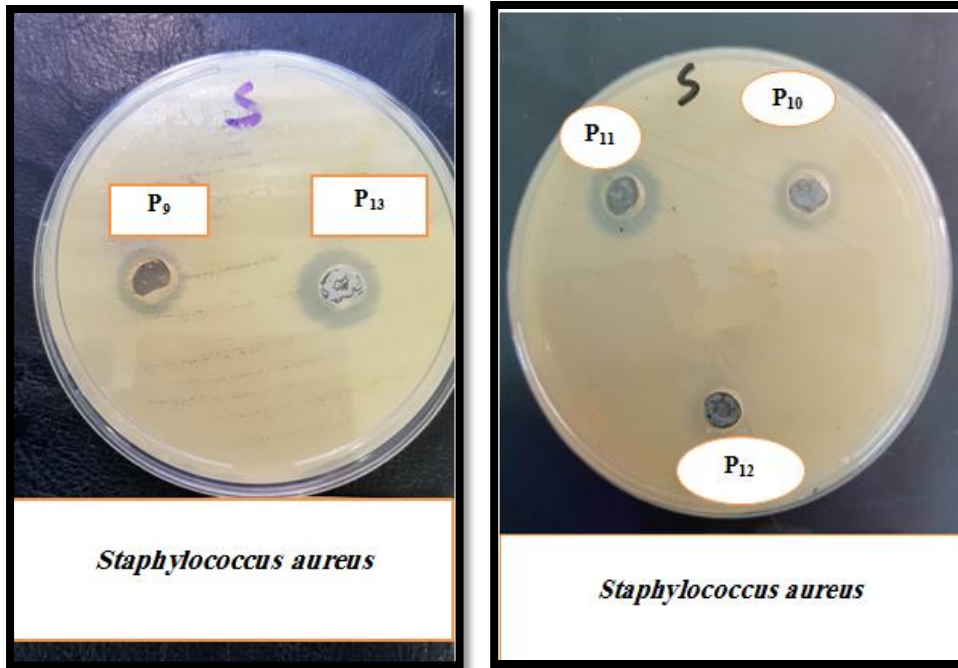
Figure3–54: Inhibition zone of (P9, P10, P11, P12, P13) against *staphylococcus aureus*
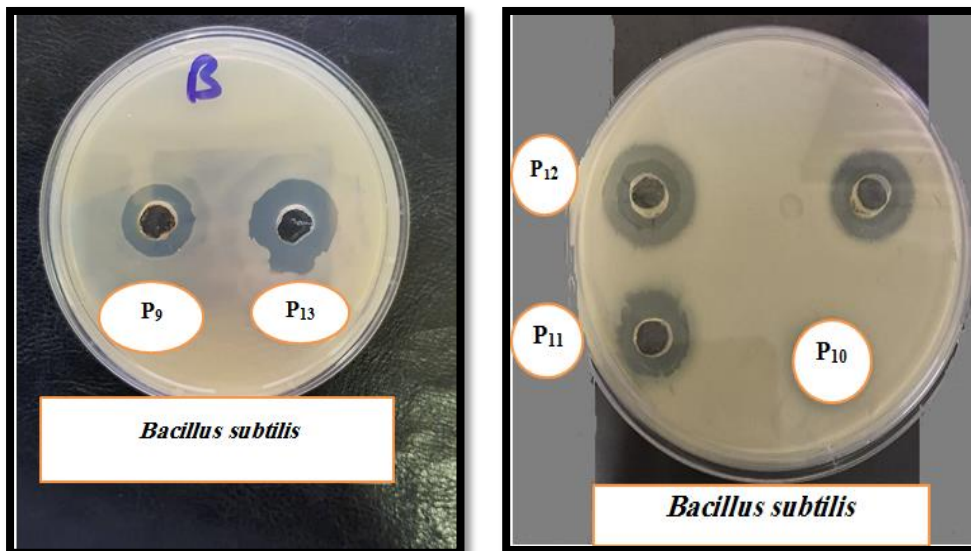
Figure 3-55: Inhibition zone of (P9, P10, P11, P12, P13) against *Bacillus subtilis*
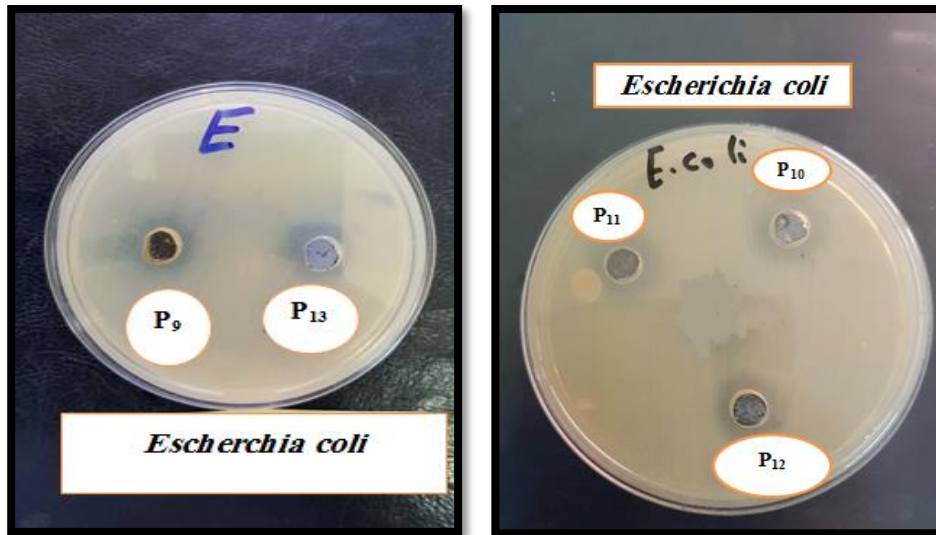
Figure 3-56: Inhibition zone of (P$_{10}$, P$_{11}$, P$_{12}$, P$_{13}$) against *Escherchia coli*
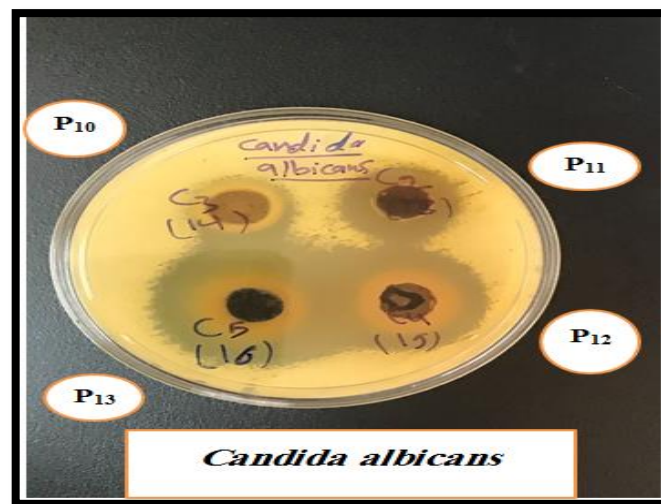
Figure 3-57: Inhibition zone of (P$_{10}$, P$_{11}$, P$_{12}$, P$_{13}$) against *candida albicans*

Figure 3-58: *Bacillus subtillus* **control with DMSO and distilled water**
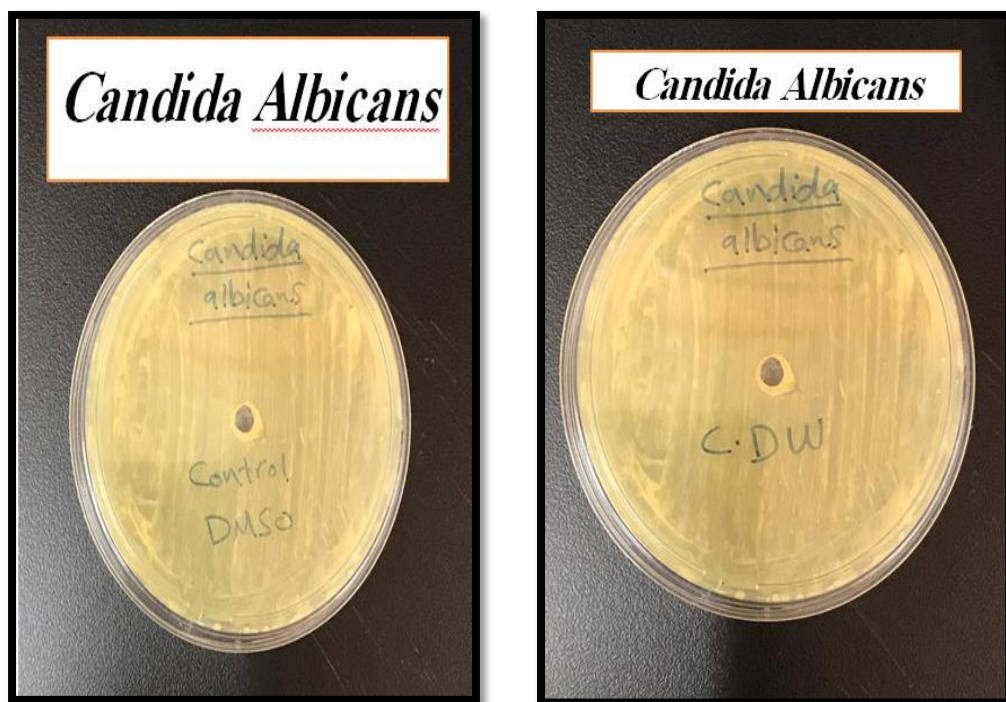
Figure 3-59: *Candida albicans* **control with DMSO and distilled water**

Figure 3-60: *Escherchia coli* **control with DMSO and distilled water**
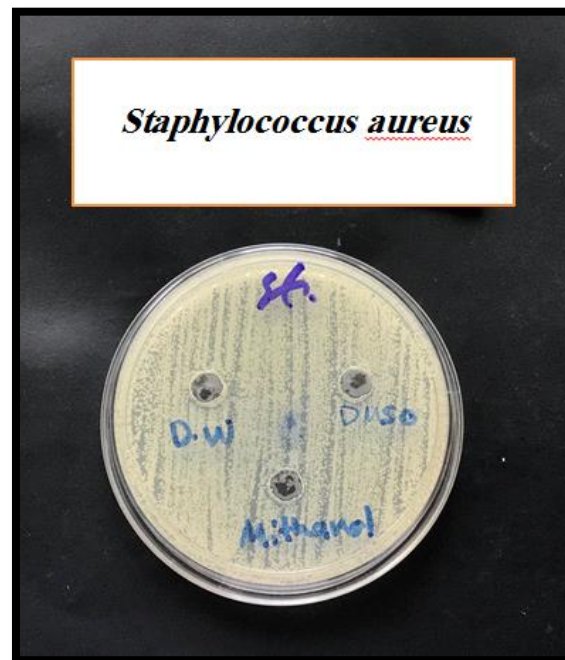
Figure 3-61: *Staphylococcus aureus* **control with DMSO, methanol and distilled**

water

Conclusion

1. The present study targets to achieve synthesis and characterization of some new bis oxadizole polymers. Some of synthesized polymers displayed acceptable FTIR and ^{1}H-NMR, while some of them did not shown ^{1}H-NMR results because they were insoluble in most of deutrated solvents.

2. Thermal stability of Polymers (2-7) were studied and shown good resistance to thermal decomposition especially **P5**, **P6**, **P7** thus shown higher resistance than the other polymers due to their chemical composition.

3. The electro conductivity of P (2-7) was recorded moderate to good conductivity at 50-1MHZ at (25-75°C) so these polymers can act as semiconductors.

4. The biological activity of all synthesized polymers screened and exhibited weak to high biological activity against the microorganisms under tests especially polymers (**5, 6, 7, 11, 12, 13**) which afforded from aromatic di carboxylic acids.

Further work

The following work is going to be carried out in the future:

1. Synthesis metal complexes of bis oxadiazole polymers and study their physical properties and biological activity.
2. Synthesis of new substituted bis oxadiazole polymers and comparison of their conductivity with the current study.
3. Study the chemical stability of the synthesized polymers at different pH and temperature.
4. Study the toxicity of the synthesized polymers derivatives.
5. Pharmaceutical study of synthesized polymers derivatives in vivo.

Further work

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Comp.3

Comp.4

P8

P(9,10,11,12,13)

A=(CH₂)₂, (CH₂)₄,

9 , 10 , 11 , 12 , 13
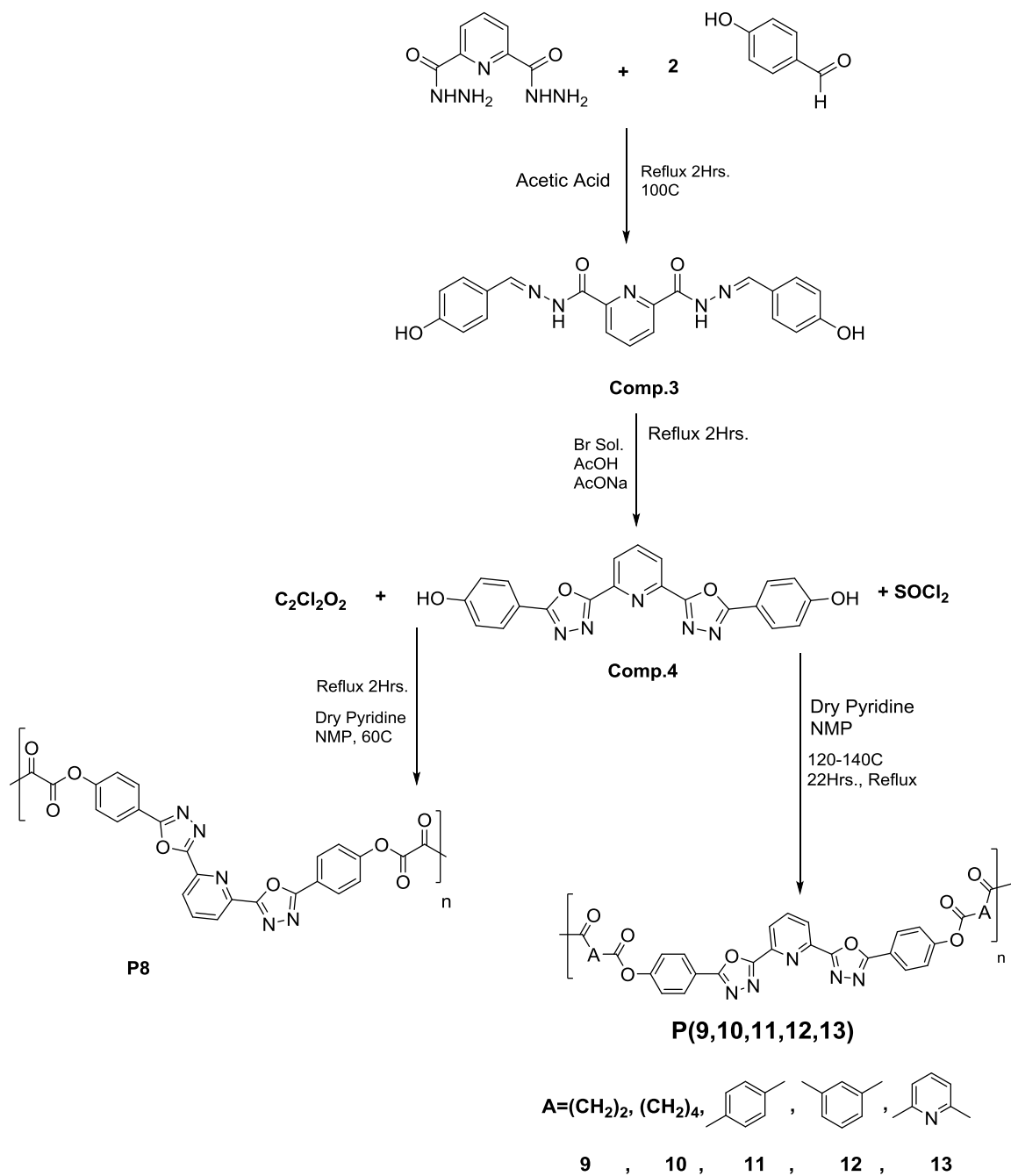
مخطط يوضح تحضير البوليمرات

(13-8)
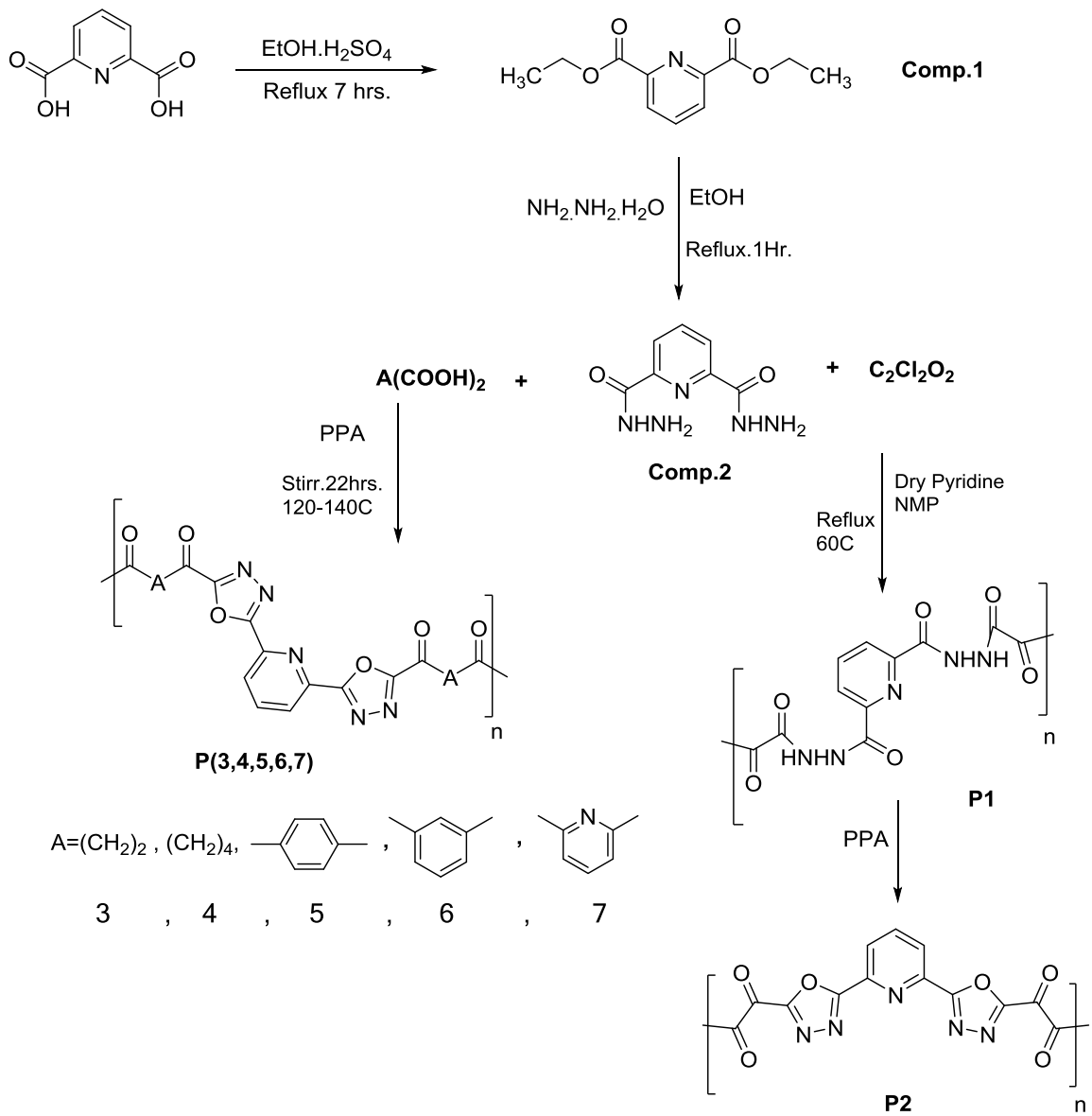
مخطط (1) : يوضح تحضير البوليمرات

(7-1)

تم دراسة التحاليل الحراريه للبوليمرات (2-7) والتي تميزت بثباتيه حراريه عاليه وقد وجد من خلال الدراسه ان البوليمرات التي تحمل في تركيبها حلقات اروماتيه تكون اكثر ثبات من تلك التي تحمل في تركيبها مجاميع اليفاتيه.

كذلك تم دراسة التوصيليه الكهربائيه للبوليمرات(2-7) وقد اعطت نتائج جيده عند درجات حراره تراوحت بين 75-25 درجه سيليزيه وبتردد تراوح بين 50 الى 1 ميغاهيرتزاغلب تلك البوليمرات اظهرت نتائج توصيليه تراوحت بين متوسطه الى جيده

كما تم دراسة الفعاليه البايولوجيه لجميع البوليمرات المحضره تجاه بعض البكتريا سالبة الغرام وبكتريا موجبة الغرام والفطريات , واظهرت نتائج جيده مع اغلب البوليمرات المحضره فيما لوحظ كفاءه بايلوجيه عاليه مع البوليمرات (13,12,11,7,6,5) و ذلك لوجود حلقات اروماتيه في تركيبها.

الخلاصه

تم تحضير سلسلتين من بوليمرات الاوكسادايازول . السلسله الاولى تمثلت بتحويل محلول حامض 2,6- بريدين ثنائي الكابوكسيل بوجود حامض الكبريتيك المركز والايثانول الى داي اثيل 2,6- داي كاربوكسيلات (مركب 1) والذي يتحول بوجودالهايدرازين الى المركب الثاني المقابل له (مركب2) .

ثم تمت مفاعلة (مركب 2) مع ثنائي اوكزاليل كلورايد وبوجود البريدين ومركب ن-مثيل -2- بيروليدونين كي يعطي البوليمر الاول والذي سيتحول بدوره للبوليمر الثاني, بوساطة عملية الغلق و بوجود حامض البولي فسفوريك .

اما البوليمرات من (3-7) فيتم تحضيرها بتفاعل(مركب 2) مع5 حوامض ثنائية الكاربوكسيل مختلفه وبوجود حامض البولي فسفوريك وكما موضح في المخطط رقم 1.

هذه البوليمرات تم فحصها وتشخيصها بوساطةمطيافية الاشعه تحت الحمراء وقداعطت نتائج جيده .

في حين تعذر الفحص لنفس النماذج بمطيافية الرنين النووي المغناطيسي وذلك بسبب عدم ذوبان تلك البوليمرات في اغلب المذيبات المعروفه عدا البوليمر الاول.

اما السلسله الثانيه فقدتم تحضيرها من تفاعل المركب الثاني مع مركب 4-هيدروكسي بنزالديهايد وبوجود كميه مناسبه من حامض الخليك لينتج المركب 3.

ثم يحول المركب 3 الى (مركب رابع) بوجود محلول البرومين وحامض الخليك الثلجي بوجود خلات الصوديوم اللامائيه , بعدها يدخل(مركب 4) الى مسارين للتفاعل .

الاول يتمثل بتفاعل (مركب 4) مع اوكزاليل كلورايد كي ينتج بوليمر 8 .

اما المسار الثاني للتفاعل فيتمثل بالحصول على البوليمرات (13-9) و ذلك بمفاعلة (مركب4) مع خمسة احماض مختلفه ثنائيةالكاربوكسيل لكن بعد تحويلها الى كلوريد الحامض المقابله له وكما موضح في المخطط رقم 2 المرفق.

هذه البوليمرات تم تشخيصها بوساطة مطيافيتي الاشعه تحت الحمراء و الرنين النووي المغناطيسي

تحضيروتشخيص بوليمرات جديده ذات حلقات غيرمتجانسه تحتوي على مشتقات ٦,٢ ـ بريدين ودراسة بعض تطبيقاتها

اطروحه مقدمة الى

كلية التربية للعلوم الصرفة ـابن الهيثم ـجامعة بغداد

وهي جزء من متطلبات نيل درجة الدكتوراه علوم في الكيمياء

من قبل

نوار جمال عبد الرضا

بكالوريوس علوم كيمياء (2001)

ماجستير علوم كيمياء(2014)

كلية التربية ـ ابن الهيثم للعلوم الصرفةـ جامعة بغداد

باشراف

أ.م.د.ضحى فاروق حسين

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