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# Preparation of polymers containing oxadiazole and study the anti-bacterial activity for some of them

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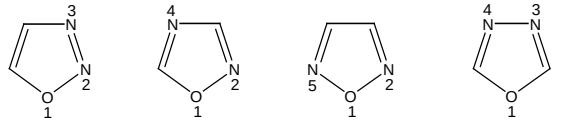
**Abstract:**
This work involves synthesis of 1,3,4-oxadiazol derived from p-hydroxy benzaldehyde and glutaryl chloride, which polymerized with acid chloride ,the compounds got to be polymers having ( amide , imine and ester) . The structures of these compounds and polymers were identified by H-NMR, FT-IR, Uv-Vis spectroscopy and checked by TLC and study the anti-bacterial activities for some of the synthesized compounds and polymers. These activities were determined in vitro using well diffusion method against three types pathogenic strains bacteria staphylococcus aureus(G+), E.coli and proteus vulgaris.The results revealed that some of these compounds showed measurable activity.
**Key words:** preparation, polymer, oxadiazole, antibacterial activity.

## 1. Introduction

Heterocyclic systems are widespread in nature, especially in such natural products as plant alkaloids , nucleic acids and chlorophyll [(1)].Heterocyclic compounds are the most important types of organic compounds due to their use in industrial studies and drugs . at least one element other than carbon, such as sulfur, oxygen or nitrogen within a ring structure[(2)].

### 1.1 The Oxadiazoles

The oxadiazole are five-membered ring compounds with three hetero atoms one oxygen atom ,two nitrogen. The oxadiazole ring has four [(3)] isomers with the formula $C_2H_2N_2O$ as shown below.




### 1.2 Heterocyclic Polymers

They are linear high polymers comprising, heterocyclic rings, or groups of rings, linked together by one or more covalent bonds. As a group such polymers are often both mechanically rigid and inherently resistant to thermal degradation. Some of these polymers from molecules in which the rings are fused together[(4)].

## 2. Materials and Methods:

Absolute ethanol, Acetic acid\ Glacial acetic acid Bromine [$Br_2$], Cinnamic acid, Dimethy sulfoxoamide[DMSO] ,Dimethyl formamide[DMF], Dry pyridine, Glutaric acid , Hydrochloric acid , Phosphoryl chloride [$POCl_3$], ***p***-Hydroxy benzaldehyde, Semicarbazide hydrochlorid, Sodium acetate, Sodium or Potassium hydroxide, Terephthalic acid, Thionyl chloride [$SOCl_2$], Vanilline. All chemicals and solvents used were of highest purity from (BDH, Fluka, Aldrich, GCC, Merck, Riedel-DeHaen).

### 2.1 Instrumentation

FTIR spectra were recorded on:-

A. A SHIMADZU FTIR-8400 Fourier transform infrared spectrophotometer in College of Education for pure Science Ibn Al-Haitham , University of Baghdad
B. In [The Central Service Laboratory] College of Education For Pure Science Ibn AL-Haitham, University of Baghdad
C. In [The Central Service Laboratory] College of Science , University of Baghdad UV/Vis spectra of the polymers were recorded on a (Shimadzu UV-Vis 160A) Ultraviolet spectrophotometer by using quartz cell in the wave length range (200-1100) nm, in Ibn Sina State Company, Melting points were recorded by using (Gallenkamp) melting point apparatus, Thin layer chromatography (TLC) was carried by using Alumina plates precoated with silica-gel, compound was detected by Iodine vapor, X-Ray measurements were made at Kashan University - Islamic republic of Iran$^1$H-NMR spectra were registered on a BRUKER-400 MHz operating at 400 MHZ with tetra methyl silane as internal standard in DMSO-d6 as a solvent, measurements were made at Kashan University - Islamic republic of Iran, The biological activity was performed in University of Baghdad, College of Science, Biology Department, Advisory Office \ The Central Laboratory

### 2.2 synthises of compound and polymer

#### 2.2.1 Synthises of bis(4-formylphenyl) glutarate comp.[1]

***p***-hydroxy benzaldehyde (0.057mole,7g) was dissolve in dry pyridine and cooled The glutaryl chloride was added dropwise in cooling with stirring . The reaction was monitened by TLC .Then the reaction mixture is poured in crushed ice with diluted HCL . By filtration the precipitate was collected ,then dried and re-crystallized by ethanol.[(5)]

#### 2.2.2 Synthesis of bis(4-((E)-(2-carbamoylhydrazineylidene)methyl)phenyl) glutarate comp.[2]

bis(4-formylphenyl) glutarate (0.011mole, 3.9 gm) , semcarbazide hydro chloride (0.021mole, 2.4gm) with ethanol and sodium acetate, the mixture was refluxed for 6 hrs The reaction was checked by TLC .The reaction was poured into ice-cold water to give solid and the precipitate was filtered ,washed and dried. [(6)]

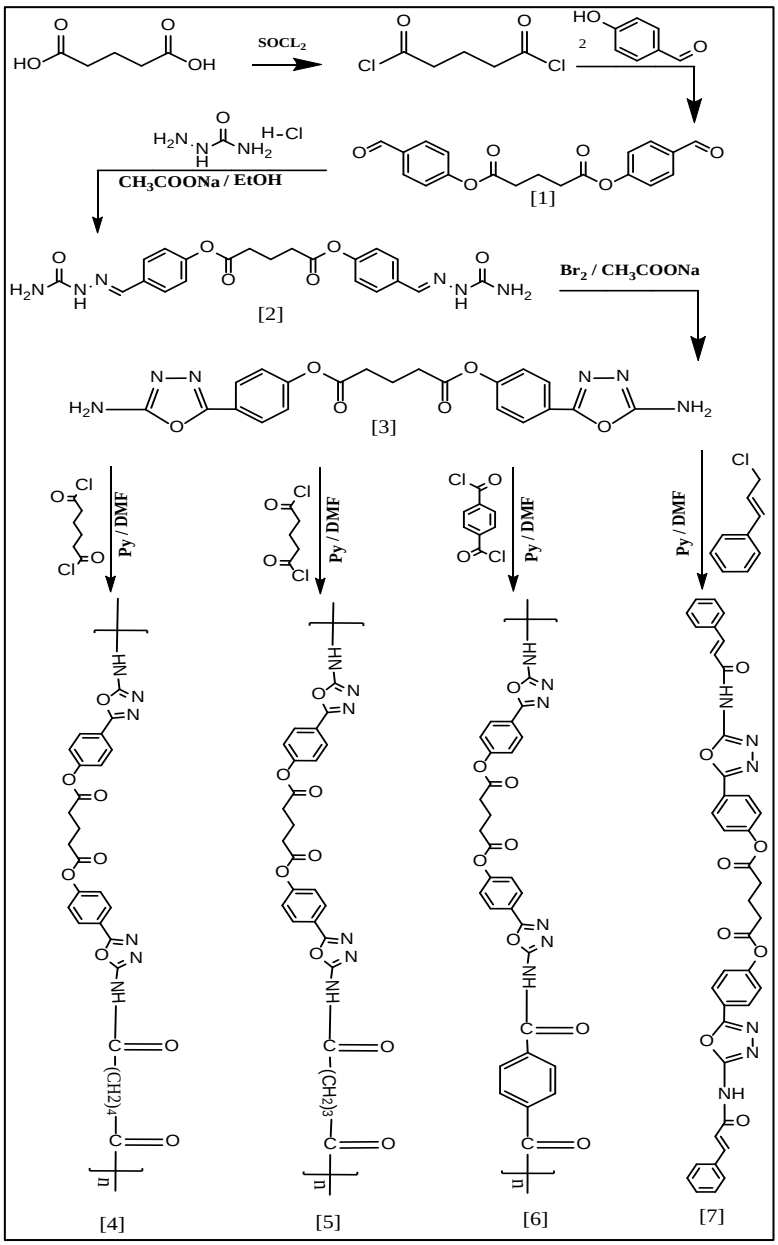
#### 2.2.3 Synthesis of bis(4-(.5-amino-1,3,4-oxadiazo-2-yl),phenyl) glutarate comp.[3]

bis(4-((E)-(2-carbamoylhydrazineylidene)methyl)phenyl) glutarate (0.008mole, 3gm) , (0.5ml) bromine solution , sodium acetate (0.029 mole, 1.2 gm) in glacial acetic acid

(15 ml) were stirred in ice bath .The product was poured in ice water and neutralized with NaOH The precipitate was filtered , recrystallized from ethanol and dried. [6]

### 2.2.4 Synthesis of polymers [4-6&mono.7]

The polymers [4-6 and monomer 7] were prepared by condensation polymerization of a mixture of (0.002mole ,1.2gm) of compounds [3] which dissolved in dry pyridine and (1- 3) drops of DMF were added with (0.5 ml) of acid chloride [Adipoyl chloride or Glutaryl chloride or terephthaloyl chloride or cinnamoyl chloride] in ice water bath with continues stirring for (5 hrs) . The reaction was continuous until checked by TLC. Then cooled the mixture was refluxed for (1 hrs) (96-100)ºC ,poured into ice distilled water which acidified with diluted (HCl), then filtered and dried to produce the precipitate. [7]




### 2.3 Physical properties of compounds and polymers

| No.of Comp. | *Molecular formula* | *Reaction time (hr)* | $R_f$ | *Yield(%)* | Colour | *M.P.(°C)* |
|---|---|---|---|---|---|---|
| 1 | $C_{19}H_{16}O_6$ | 4 | 0.83 | 90 | Dark brown | 74-76 |
| 2 | $C_{21}H_{22}N_6O_6$ | 1 | 0.72 | 87 | Brown | 199-200 |
| 3 | $C_{21}H_{18}N_6O_6$ | 7 | 0.77 | 79 | Gray | 194-195 |
| 4 | $[C_{29}H_{30}N_6O_8]_n$ | 6 | 0.69 | 82 | Yellow | UP 250 |
| 5 | $[C_{28}H_{28}N_6O_8]_n$ | 6 | 0.8 | 81 | Brown | 233-235 |
| 6 | $[C_{31}H_{26}N_6O_8]_n$ | 6 | 0.71 | 81 | Brown | 248-250 |
| 7 | $C_{39}H_{30}N_6O_8$ | 6 | 0.62 | 80 | Brown | 193-195 |

Table (l) :FT-IR spectral data of polymer [5,6 ,monomer 7].

| | υ(NH) amide | υ(CH) aromatic | υ(CH) aliphatic | υ(C=O) ester | υ(C= O) amide | υ(C=C) | υ(C=N) | υ(C-N) | υ(C-O) |
|---|---|---|---|---|---|---|---|---|---|
| 5 | 3327 | 3078 | 2926 | 1749 | 1654 | 1575 | 1606 | 1269 | 1134 |
| 6 | 3200 | 3070 | 2926 | 1740 | 1645 | 1571 | 1608 | 1234 | 1166 |
| 7 | 3269 | 3059 | 2931 | 1751 | 1631 | 1575 | 1602 | 1201 | 1124 |

## 3. Results and Discussion

### 3.1 Characterization of compound [1]

This compound was prepared from reaction between glutaryl chloride and two mole of ***p***-hydroxy benzaldehyde in presence of pyridine. The structural assignment of product was based on its melting point (other physical properties) and spectral FT-IR. The FT-IR spectrum exhibited significant bands at:- at (3074) $cm^{-1}$ for υ (CH) aromatic , at (2960,2890 $cm^{-1}$) may attributed to (CH) aliphatic ,and a strong at(1758 $cm^{-1}$) for υ (C=O) ester group,at (1685 $cm^{-1}$) for υ (C=O) aldehyde group besides the band at (1124-1207) for υ (C-O).

### 3.2 Characterization of compound [2]

This compound was prepared by the reaction of bis(4-formylphenyl) glutarate and semcarbazide hydro chloride. The prepared compound [2] was characterized by checking it's physical properties besides spectral data . The FT-IR spectrum of show the disappearance of (C=O) aldehyde group and appearance of ($NH_2$) at (3477,3388) $cm^{-1}$ ,at (3191 $cm^{-1}$) due to υ(NH) ,at (3060 $cm^{-1}$) to υ (CH) aromatic , at (2935, 2895 $cm^{-1}$) due to υ(CH) aliphatic, at (1753) forυ (C=O) ester group besides the band at (1689 $cm^{-1}$) for υ (C=O) amide group , at (1130 $cm^{-1}$) back toυ (C-O) , at (1409 $cm^{-1}$) due to υ(C-N) , at (1604 $cm^{-1}$) due to υ(C=N), at (1583 $cm^{-1}$) back to υ(C=C).

### 3.3 Characterization of compound [3]

This compound prepared from the reaction between bis(4-((E)-(2 carbamoylhydrazineylidene)methyl)phenyl) glutarate with bromine solution.The prepared compound [3] was characterized by checking its physical properties and spectral (FT-IR , $^1$H-NMR) .The FT-IR spectrum show the disappearance of amino group and appearance of ($NH_2$) group at (3454-3321) $cm^{-1}$ and υ (CH) aromatic at (3090) $cm^{-1}$ also υ (C-H) aliphatic at (2966-2890) $cm^{-1}$ υ (C=O) group, at(1755) $cm^{-1}$ ester group , at due to υ (C=O) ester group .besides band at (1660 $cm^{-1}$) for υ (C=N) , at (1554 $cm^{-1}$) for υ (C=C) aromatic,at (1136-1271)$cm^{-1}$ for υ (C-O-C) and finally at (1047 $cm^{-1}$) for υ (C-N) group .The $^1$H-NMR spectrum show the characteristic chemical shift (DMSO-$d_6$) ppm , protons ($NH_2$) at δ (4.3) ppm , aromatic protons ring of phenyl appeared at (δ 7-8) ppm aliphatic protons appeared at δ (3.9-2.2).

### 3.4 Characterization of polymer [4-5-6 and monomer 7]

These polymers and monomer were prepared from the reaction of compound [3] with di acid chloride in dry pyridine .The structures of these polymers were identified by their M.P. and FT-IR ,UV-vis spectral data and they checked by T.L.C. The FT-IR spectrum of polymer [4] , show the appearance of band at (3120 $cm^1$) due to (NH) starching and disappearance of two absorption bands assigned to (3454-3321) $cm^{-1}$ ($NH_2$) group ,besides the appearance of (CH) aromatic proton at (3061 $cm^{-1}$) , (CH) aliphatic at (2976,2877 $cm^{-1}$) ,(C=O) ester at (1753 $cm^{-1}$) and (C=O) amide at (1678 $cm^{-1}$) ,also (C=C) aromatic at (1578 $cm^{-1}$),at (1610 $cm^{-1}$) for (C=N), at (1201 $cm^{-1}$) due to (C-N) and finally (1280 $cm^{-1}$) for (C-O-C). All the spectral data for the others [5,6,mono.7] are listed in table (1) .

**3.5 The UV-vis spectrum :-** The UV-vis spectrum of (polymer 4,5,6and monomer7), showed the absorption band that listed in table (2)

Table (2): Spectral data UV λ max for (polymer 4,5,6and monomer7)

| No. of Poly.& Mono. | Wavelength | Description |
|---|---|---|
| P[4] | 285 nm | (π → π*) and (n- π*) transitions |
| P[5] | 280nm | (π → π*) and (n- π*) transitions |
| P[6] | 278nm | (π → π*) and (n- π*) transitions |
| M[7] | 271,360 | (π → π*) and (n- π*) transitions |

### 3.6 The X-ray diffraction

The X-ray for some of polymers The results of the analysis show that the polymers owns different crystalline forms in which the polymer (4) is crystalline while polymer (5) is amorphous.

### 3.8 Biological activity

The results of the preliminary screening tests are listed in Table (3) compound (5,),(5,7)and (2,7) showed high activity to ***Staphylococcus aurous, Escherichia Coli and Pseudomonas*** respectively .

**Table 3: Show Biological activity for compounds & polymers(1-7)**

| Comp.&Poly. No. | *Staphylococcus aurous* | *Escherichia Coli* | *Pseudomonas* | Simple |
|---|---|---|---|---|
| **1** | 8 | *7* | *12* | *A* |
| **2** | *12* | *7* | *20* | *B* |
| **3** | *6* | *6* | *14* | *C* |
| **4** | *10* | *8* | *6* | *C3* |
| **5** | *16* | *18* | *10* | *C2* |
| **6** | *10* | *10* | *12* | *C1* |
| **7** | *13* | *15* | *15* | *C4* |

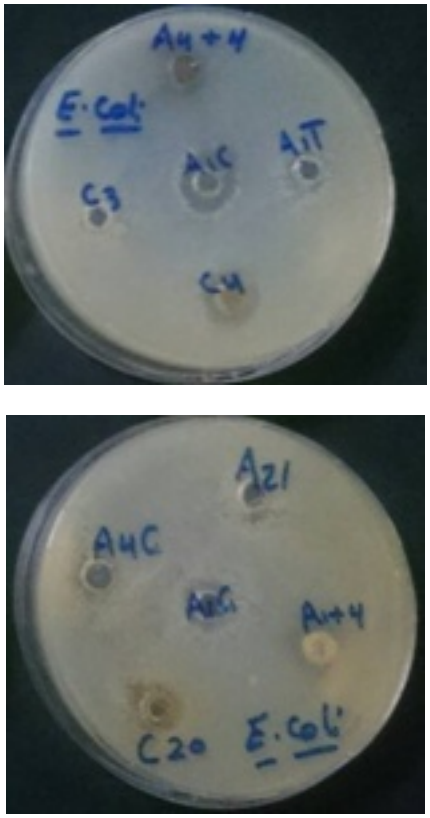



**Figure (7):Inhibition ability of polymers (4,5,7) on Escherichia coli**

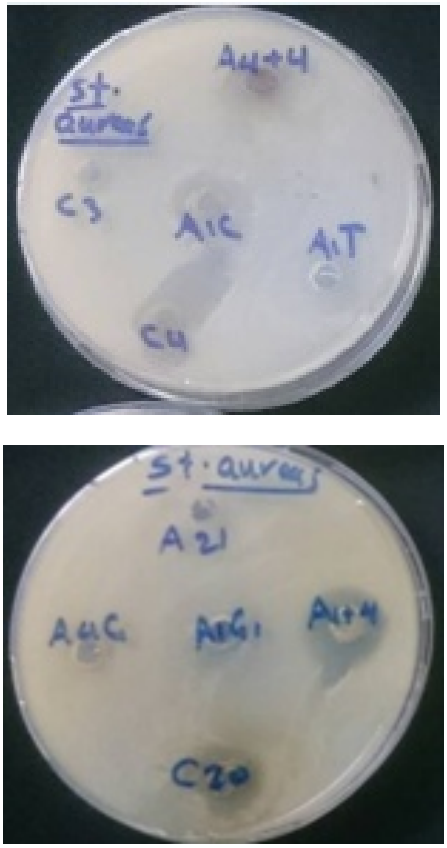



**Figure (8):Inhibition ability of polymers (4,5,7) on staphylococcus aurous**

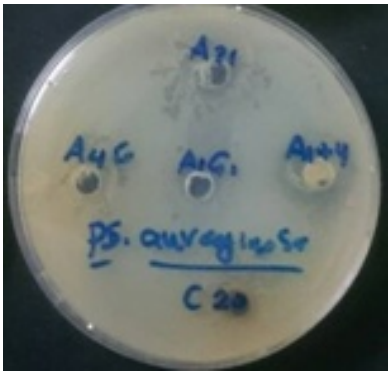




**Figure (9):Inhibition ability of polymers (4,5,7) on pseudomonas aeruginosa**

## CONCLUSIONS:

Through this work, we have succeeded in building monomer with heterocyclic ring (Oxadiazole) with characterization :

1- The presence of heterocyclic rings give good solubility for the prepared polymers.
2- Analytical and spectral data (FTIR, UV-Vis. , $^{1}$H-NMR, X-Ray diffraction and Solubility) of synthesized monomers and polymers were in agreement with proposed structure.
3- The prepared polymers have highly melting point comparable with homo polymers.
4- The presence of heterocyclic rings in some of prepared monomers and polymers exhibited (high or low) biological activity.

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