Synthesis of anti-corrosion polymers from thia diazole

Ibtisam Kalifa Jassim¹, Intisar Yahiya Mohammed*² and Sara Salman³

¹,³ College of Education for Pure Sciences, Ibn Al-Haitham, University of Baghdad, BGD 00964, Iraq
² Department of Materials Research, Ministry of Science and Technology, BGD 00964, Iraq

*Correspondence: nasorayouo@yahoo.com

Abstract. One of the biggest problems facing many industries particularly oil, is the problem of corrosion, where the metal parts under the influence of the vital factors are eroded during use and storage, therefore, to lift the metal's ability and to protect it against corrosion, corrosion inhibitors are used. For the first time in this research, polymers which contain sulfur - heterocyclic ring with a thia diazole base were made. Anti- corrosion polymers were made on two stages, in the first stage, thia diazole was made from hydrazine hydrate reaction to carbon disulfide, afterwards the first product was reacted with an excess of hydrazine. In the second stage, polymers were prepared by the reaction of the monomer produced from benzaldehyde reaction with [dichloro methane, dichloro ethane or vanillin] and the reactions progress were monitored using thin layer chromatography technique. Prepared compounds were characterized using FT-IR, ¹HNMR spectra, TLC, DSC, m.p measurements and weight loss measurement. More than one type of polymers prepared with different concentrations (0.5, 1.0%) was tested as a weight loss inhibitor and the results were very good.

1. Introduction
A corrosion inhibitor is a chemical compound that, when added to a liquid or gas, decreases the corrosion rate of a material, typically a metal or an alloy[1]. The effectiveness of a corrosion inhibitors depend on fluid composition, quantity of water, and flow regime. A common mechanism for inhibiting corrosion involves the formation of a coating, often a passivation layer, which prevents access of the corrosive substance to the metal. Corrosion is an electrochemical process by which metallic structures are destroyed gradually through anodic dissolution [2]. This phenomenon necessitates the continuous search for better corrosion inhibitors, due to vast differences in the media encountered in industry which remains a focal point in corrosion control as inhibitors slowdown the corrosion process on metals. Corrosion is one of the main concerns in the durability of materials and structures; as a result, studies are continually carried out to develop an effective means of corrosion control.

Selection of an appropriate inhibitor for a particular system is actually complicated, due to their specificity and great variety of corrosion-related applications [3]. The use of organic compounds to inhibitor corrosion has assumed great significance due to their applications in preventing corrosion under various corrosive environments [4]. The inhibiting action of organic compounds is attributed to interactions with metallic surfaces by adsorption. The molecular structure of organic compounds exerts a major influence on the extent of inhibition, thus the effect of the functional atom in the adsorption processes varies due to highly different situation created by changing various factors such as medium and inhibitor in the system [5]. Thia diazole as five-member heterocyclic compounds; particularly nitrogen and sulfur heterocyclic; have been successfully used as anti-corrosion [6].
Thiadiazole and their derivatives can be considered as simple five membered heterocyclic possessing one sulfur and two nitrogen atoms. Thiadiazole exist in different isomeric forms such as 1,2,4-, 1,2,5-, 1,2,3- and 1,3,4-thiadiazoles[7]. Utilized thiadiazole in a variety of other applications including synthesizing polymers and heavy metal and basic salts in cross linking halogenated polymers; as an additive in lubricating oils and greases; in electrode compositions; as an intermediate or starting material for anti-corrosion, pharmaceuticals, dyes and extreme pressure agent in compositions of finished greases, lubricating oils, as a sulfur deactivator, antioxidant in gasoline, heating oil, and liquefied petroleum gas [8].

2. Experimental Part

2.1 Materials and Instruments

- Hydrazine hydrate 85% / Merck, Carbon disulfide 99% / Fluka, p-hydroxy benzaldehyde 85% / Merck, Vanillin(4-hydroxy-3-methoxy benzaldehyde) 75% / Fluka, Dichloro ethane 95% / GCC, Dichloro methane 95% / GCC, Absolute ethanol 99.9% / BDH, NaOH, KOH 90% / BDH, Hydrochloric acid 99% / BDH, tap water, which has the physical properties shown in table 1.

| Properties | Requirements maximum allowed | Test Method |
|------------|-----------------------------|-------------|
| Conductivity | 667-732 ms/cm | D756 |
| pH | 6.5 – 8.5 | D692 |
| Turbid | 5 units | D726 |
| Color | 10 units | D746 |

- Thin layer chromatography (TLC) was carried out using fertigfollen precoated sheets type Polygram silica-gel as stationary phase ethyl acetate as eluent, and the plates were developed with iodine vapor.
- Melting points were recorded using hot stage Gallenkamp melting point apparatus and were uncorrected.
- Infrared spectra were recorded using Fourier transform infrared SHIMADZU (8300) (FTIR) infrared spectrophotometer, KBr disc.
- 1H-NMR spectra were recorded on a BRUKER-400 MHz operating at 400 MHZ with tetra methyl silane as internal standard in (CHCl3) as a solvent.
- Differential Scanning Calorimetry (DSC) analysis was carried out using LINSEIS DSC, equipped with an internal cooler 2P-cooling accessory.
- X-Ray Diffraction spectrum was carried out using - 6000, SHIMADZU \ JAPAN, 220V-50HZ.
- Iron sheet (Fe), length 3cm, width 2cm, thickens 0.5cm and weight 38.3gm, the X-Ray Diffraction spectrum represent its composition shown in the figure 1.
2.2 Methods

2.2.1 Synthesis of 1, 3, 4-thiadiazole 2, 5-dithiol (1)

A known and previously prepared compound [9].

2.2.2 Synthesis of 2, 5-dihydrazinyl 1, 3, 4-thiadiazole (2)

A known and previously prepared compound [10].

2.2.3 Synthesis of compounds (3, 4, 5)

A mixture of substituted aldehyde (0.5gm), chloro alkane (2mL) and potassium hydroxide (1.0gm) were dissolved in (10mL) absolute ethanol and refluxed at (80-85)°C with stirring for (5 hrs.). The mixture was cooled and the precipitate was filtered then dried to produce precipitate (3, 4, 5) [11].

2.2.4 Synthesis of Poly derivative of thiadiazole (3a, 4a, 5a, 6a, b)

A mixture of compound [2] (0.23gm) was reacted with compounds [3, 4, 5] (0.21gm) in (15mL) absolute ethanol and added few drops of glacial acetic acid and refluxed at 80°C for (15hrs). The product was poured into ice water. The precipitate was filtered and dried to obtain polymers (3a, 4a, 5a and 6a, b) [12]. Scheme 3 and 4.
2.2.5 Corrosion test by weight loss method

This test was carried out to evaluate the corrosion of metals in tap water. The first tap water sample was prepared without inhibitor while the second contained an inhibitor at the following concentrations [0.5 or 1] % at room temperature. An Iron sheet (Fe) with a weight of (38.3gm) was immersed into the tested solutions, for different amounts of time [24, 48, and 72] hours.

The weight loss test was conducted in a weight loss manner in accordance with the ASTM G31 [13] criteria and it was calculated by using the following equation:

\[ mdd = \frac{\Delta w}{A \cdot t} \]

Where
- \( mdd \) = corrosion rate
- \( \Delta w = w_0 - w \) (mg)
- \( \Delta w \) is weight loss by mg\( \cdot \)dcm\(^2\)
- \( A = \) area (dcm\(^2\))
- \( t = \) time by days

3. Results and Discussion

All characteristic physical properties of synthesis compounds are listed in table (2). The completions of all synthesized compounds were characterized by TLC, melting point.
Table 2. Physical Properties for Prepared compounds

| Name of prepared compounds | Structure of prepared compounds | Molecular Formula | Yield % | RF | m.p | Color |
|----------------------------|---------------------------------|-------------------|---------|----|-----|-------|
| [1] 1,3,4-thiadiazole 2,5-dithiol | ![Structure](image1) | C$_7$H$_3$N$_2$S$_3$ | 80      | 0.88 | 182-184 | Light yellow |
| [2] 2,5-dihyrazinyl 1,3,4 thiaadiazole | ![Structure](image2) | C$_7$H$_8$N$_6$S | 73      | 0.9  | 207-209 | White |
| [3] 4,4-ethane-1,2diyl bis (oxy) dibenzaldehyde | ![Structure](image3) | C$_{16}$H$_{10}$O$_4$ | 75      | 0.85 | 107-109 | Red brown |
| [3a]Poly-2-(2-methylene hydrazinyl)-5-(2-(4-(2-(4-vinylphenoxy)ethoxy) benzylidene)hydrazinyl)-1,3,4-thiadiazole | ![Structure](image4) | ----- | -- | 0.88 | 76-78 | Brown |
| [4] 4,4-(ethane-1,2-diyl bis(oxy)bis(3-methoxy benzaldehyde) | ![Structure](image5) | C$_{18}$H$_{16}$O$_6$ | 75      | 0.87 | 117-119 | Dark brown |
| [4a]Poly-2-(2-(3-methoxy-4-vinylphenoxy)ethoxy) benzylidenehydrazinyl)-5-(2-methylenehydrazinyl)-1,3,4-thiadiazole | ![Structure](image6) | ----- | -- | 0.87 | 103-105 | Red brown |
| [5] 4,4-methylene bis (oxy) di benzaldehyde | ![Structure](image7) | C$_{15}$H$_{12}$O$_4$ | 72      | 0.87 | 113-115 | Earthy |
| [5a]Poly-2-(2-methylene hydrazinyl)-5-(2-(4-(2-(4-vinylphenoxy)methoxy)benzylidene)hydrazinyl)-1,3,4-thiadiazole | ![Structure](image8) | ----- | -- | 0.89 | 256Dec | Earthy |
| [6a]Poly2-(2-methyl hydrazinyl)-5-(2-propyl hydrazinyl)-1,3,4-thiadiazole | ![Structure](image9) | ----- | -- | 0.88 | 102-104 | Dark brown |
| [6b] Poly2-(2-ethyl hydrazinyl)-5-(2-methyl hydrazinyl)-1,3,4-thiadiazole | ![Structure](image10) | ----- | -- | 0.86 | 99-101 | Brown |

3.1 Characterization of 1, 3, 4-thiadiazole 2, 5-dithiol (1)
Compound (1) was prepared through the reaction of hydrazine hydrate with carbon disulfide in the presence of sodium hydroxide in absolute ethanol. Compound (1) was identified by TLC, m.p and FT-IR spectroscopy [14]. The FTIR spectrum of compound (1), Figure 2. showed different bands, the (-SH) stretching band found as very weak shoulder at (2665) cm$^{-1}$, a band (1643) cm$^{-1}$ were due to (C=N) of the thiadiazole ring moiety stretching. The sharp bands (1415) cm$^{-1}$ is due to the (N-N) bending and (952) cm$^{-1}$ (C-S) stretching vibration respectively [15].
3.2 Characterization of 2, 5-dihydrazinyl 1, 3, 4-thiadiazole (2)

The condensation reactions of compound (1) with excess of hydrazine hydrate (NH₂NH₂·H₂O) in ethanol absolute gave compound (2) as a final product. The FTIR spectrum Figure 3, for compound (2) showed the band (3417- 3466) cm⁻¹ of the (−NH₂) confirming the reaction of compound (1) and excess of hydrazine had occurred, (C-N) band identified as a medium band (1381) cm⁻¹, and absorption band (3263) cm⁻¹ reflected the (N-H) stretching [16].

3.3 Characterization of 4,4- ethane-1,2 diyl bis (oxy) dibenzaldehyde(3)

The FTIR spectrum for compound (3), Figure 4, showed the characteristic bands, (3066) cm⁻¹ for υ (C-H) aromatic, (2902-2835) cm⁻¹ for asymmetric and symmetric stretching vibration of υ(C-H) aliphatic, (2584)cm⁻¹ for υ(H-C=O) aldehyde group, (1593)cm⁻¹ for υ (C=C) aromatic ring group, and (1165-1103)cm⁻¹ for υ(C-O) ether group.
The $^1$H-NMR spectrum of compound (3), Figure 5, showed the following signals $\delta$: (3.45) ppm (4H, H aliphatic), (6.0506) ppm (2H aromatic), (7.25) ppm (2H, aromatic), (9.19) ppm (H, H aldehyde), and (2.49) ppm was due to CHCl₃.

3.4 Characterization of Poly 2-(2-metylnehydrazinyl)-5-(2-(4-(2-(4-vinylphenoxy)ethoxy) benzylidene) hydrazinyl)-1,3,4-thiadiazole (3ₐ)

Compound (3ₐ) was prepared from the reaction of compound (2) with compound (3), potassium hydroxide in absolute ethanol. FTIR spectrum of compound (3ₐ), Figure 6, identified the characteristic bands (3099) cm⁻¹ for $\nu$ (C-H) aromatic, (2924) cm⁻¹ for stretching vibration of $\nu$ (C-H) aliphatic, (3217-3267)cm⁻¹ for $\nu$ (NH-) groups, (1593)cm⁻¹ for $\nu$ (C=C) aromatic ring group, (1157-1087)cm⁻¹ for $\nu$ (C-O) ether group, (1643)cm⁻¹for $\nu$ (C=N), and (1415)cm⁻¹for $\nu$ (N-N).
Figure 6. FTIR spectrum of Poly 2-(2-methylenehydrazinyl)-5-(2-(4-(4-vinylphenoxy)ethoxy) benzylidene) hydrazinyl)-1,3,4-thiadiazole (3a)

3.5 Characterization of 4,4-(ethane-1,2-diyl bis(oxy) bis(3-methoxybenzaldehyde)) (4)

Compound (4) was prepared from the reaction of vanillin and dichloroethane (DCE) and potassium hydroxide in absolute ethanol.

The FTIR spectrum of compound (4), Figure 7, showed the characteristic bands, (3070) cm\(^{-1}\) for \(\nu\) (C-H) aromatic, (2978-2927) cm\(^{-1}\) for asymmetric and symmetric stretching vibration of \(\nu\) (C-H) aliphatic, (2769) cm\(^{-1}\) for \(\nu\) (H-C=O) aldehyde group, (1597) cm\(^{-1}\) for \(\nu\) (C=C) aromatic ring group, (1165-1107) cm\(^{-1}\) for \(\nu\) (C-O) ether group and (1033) cm\(^{-1}\) for \(\nu\) (C-O) methoxy group.

Figure 7. FTIR spectrum of 4,4-(ethane-1,2-diyl bis(oxy) bis(3-methoxybenzaldehyde)) (4)

3.6 Characterization of poly 2-(2-(3-methoxy-4-(2-(2-methoxy-4-vinylphenoxy)ethoxy)benzylidenehydrazinyl)-5-(2-methylenehydrazinyl)-1,3,4-thiadiazole (4a)

Polymer (4a) was prepared from the reaction of compound (2) with compound (4) and potassium hydroxide in absolute ethanol. The FTIR spectrum of compound (4a), Figure 8, showed the characteristic bands, (3050) cm\(^{-1}\) for \(\nu\) (C-H) aromatic, (2942-2937) cm\(^{-1}\) for asymmetric and symmetric stretching vibration of \(\nu\) (C-H) aliphatic, (2769) cm\(^{-1}\) for \(\nu\) (H-C=O) aldehyde group, (1595) cm\(^{-1}\) for \(\nu\) (C=C) aromatic ring group, (1163-1118) cm\(^{-1}\) for \(\nu\) (C-O) ether group and (1029) cm\(^{-1}\) for \(\nu\) (C-O) methoxy group.
3.7 Characterization of 4, 4-methylene bis (oxy) di benzaldehyde (5)

Compound (5) was prepared from the reaction of \( p \)-Hydroxy benzaldehyde and 1, 2 dichloromethane (DCM) and potassium hydroxide in absolute ethanol.

FTIR spectrum of compound (5), Figure 9, identified the characteristic bands (3066) cm\(^{-1}\) for \( \nu (C-H) \) aromatic, (2835) cm\(^{-1}\) for stretching vibration of \( \nu (C-H) \) aliphatic, (2762-2746) cm\(^{-1}\) for \( \nu (H-C=O) \) groups, (1593) cm\(^{-1}\) for \( \nu (C=C) \) aromatic ring group, and (1165-1103) cm\(^{-1}\) for \( \nu (C-O) \) ether group.

The \(^1\)H-NMR spectrum of compound (5), Figure 10, showed the following signals at \( \delta: \)
- 3.47 ppm (H,H aliphatic),
- 6.35 ppm (2H aromatic),
- 6.62 ppm (2H aromatic),
- 7.51 ppm (H,H aldehyde),
- 2.49 ppm was due to CHCl\(_3\).
3.8 Characterization of Poly 2-(2-methylenehydrazinyl)-5-(2-(4-(2-(4-vinylphenoxy)methoxy)benzylidene)hydrazinyl)-1,3,4-thiadiazole (5a)
Polymer (5a) was prepared from the reaction of compound (2) with compound (5) and potassium hydroxide in absolute ethanol.

FTIR spectrum of compound (5a), Figure 11. identified the characteristic bands (3070) cm\(^{-1}\) for \(\nu (C-H)\) aromatic, (2927) cm\(^{-1}\) for stretching vibration of \(\nu (C-H)\) aliphatic, (2762-2746) cm\(^{-1}\), (1590) cm\(^{-1}\) for \(\nu (C=C)\) aromatic ring group, and (1176-1153) cm\(^{-1}\) for \(\nu (C-O)\) ether group.

3.9 Characterization of poly 2-(2-methylhydrazinyl)-5-(2-propylhydrazinyl)-1,3,4-thiadiazole (6a), - poly 2-(2-ethylhydrazinyl)-5-(2-methylhydrazinyl)-1,3,4-thiadiazole (6b)
Polymers (6a, 6b) were prepared from the reaction of compound (2) with DCE and DCM respectively and potassium hydroxide in absolute ethanol [2].

FTIR spectrum of compound (6a), Figure 12. identified the characteristic bands (3089) cm\(^{-1}\) for \(\nu (C-H)\) aromatic, (2924) cm\(^{-1}\) for stretching vibration of \(\nu (C-H)\) aliphatic, (2732-2665) cm\(^{-1}\) for \(\nu (-CH\_\_2)\), (1590) cm\(^{-1}\) for \(\nu (C=C)\) aromatic ring group, and (3263) cm\(^{-1}\) for \(\nu (NH\_)\).
3.10 A stack plot of DSC thermogram depicted in figures 13, 14, and table 3. Clear sole endothermic transition appeared at both plots represent the Tg of the products [17].

Table 3. Thermal data of the prepared polymers (3, 5a)

| Curve Information | Polymer [3a] | Polymer [5a] |
|-------------------|--------------|--------------|
| Onset             | 100.6°C (13min) | 160.1°C (13min) |
| Offset            | 116.4°C (16min) | 174.4°C (14min) |
| Point of reaction | -7.524 mW at 105.5°C (14min) | -42.680 mW at 165.3°C (13min) |
| Peak maximum      | -7.868 mW at 112.0°C (15min) | -55.848 mW at 167.9°C (13min) |
| Enthalpy          | -6.11 J/g | - 130.63 J/g |
3.11 Study the effect of the addition of the prepared polymers as corrosion inhibitor

One of the most widely used techniques to reduce or prevent metal wear is the use of inhibitors, for the purpose of evaluating the performance of the polymer inhibitor. The results showed that the sample in the tap water containing inhibitor was remained intact throughout the immersion period.

The iron sheet in the tap water containing the inhibitor showed no loss in weight, which confirms the efficiency of the polymer that works to cover the surface of the sample and protected from corrosion, all data of the immersion test of anti-corrosion prepared polymers listed in table 4.

| Sample No. | Compounds                  | Loss of weight % |          |          |          |          |
|------------|----------------------------|------------------|----------|----------|----------|----------|
|            |                            | Con. 0.5% polymer | Con. 1.0% polymer |          |          |          |
|            |                            | CR\ mdd mg\ cm² | CR\ mdd mg\ cm² |          |          |          |
| 1          | tab water without          | 0.78             | 1.7       | 2.9       | 0.79     | 1.9       | 3.2       |
|            | inhibitor addition         |                  |           |           |          |          |           |
| 2          | tab water with inhibitor    | 0.0004           | 0.0017    | 0.0019    | 0.0006   | 0.0021    | 0.0036    |
|            | addition [3a]              |                  |           |           |          |          |           |
| 3          | tab water with inhibitor    | 0.0003           | 0.0018    | 0.0021    | 0.0007   | 0.0023    | 0.0027    |
|            | addition [5a]              |                  |           |           |          |          |           |

4. Conclusions

Through this work, we have succeeded to synthesis heterocyclic compounds as monomers to be polymerized. Spectral data (FTIR and ¹HNMR) of synthesis monomers were in full agreement with the proposed structure. Corrosion test by immersion method indicated that prepared polymer as a good inhibitor.
5. References

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