



ISSN: 0067-2904

Synthesis and Characterization of New Polymers Bearing Tetrazole and Triazole Moieties with Studying their Corrosion Protection of Stainless Steel Surface in Hydrochloric Acid

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Received: 9/4/2020

Accepted: 2/6/2020

Abstract

A series of polymers containing 1,2,4-triazole and tetrazole groups in their main chains were synthesized through several steps. Poly(acryloyl hydrazide) was first prepared and then subjected to a hydrazide reaction with phenyl isothiocyanate to give a 1,2,4-triazole ring (2). This polymer was introduced into a reaction with chloro acetylchloride to yield polymer (3), which was refluxed with sodium azide to give polymer (4). Polymer (5) was synthesized by the reaction of polymer (4) with acrylonitrile in the presence of NH₄Cl as a catalyst. Finally, polymer (6) was synthesized by the electrochemical polymerization of polymer (5) using 316L stainless steel as an anti-corrosion coating. Polymer-coated and uncoated stainless steel was tested for corrosion safety in a solution of 0.1 M HCl, followed by Tafel and Potentiostatic procedures at a temperature of 293 K. Nano materials such as ZnO were applied to the monomer solution at different concentrations to enhance the corrosion resistance of the 316L stainless steel surface. The results showed that the performance values of corrosion protection for the polymer coating were increased with the introduction of the nano materials. Furthermore, ¹³C-NMR, ¹H-NMR, and FTIR were recorded to confirm the structures of the polymers, while their physical properties were tested using atomic force microscope (AFM) and scanning electron microscope (SEM).

Keywords: Polymer, Electropolymerization, Corrosion, Tetrazole, Triazole,

تحضير وتشخيص بوليمرات جديدة حاملة لحلقة التترازول والتريازول، ودراسة حماية التآكل على سطح الفولاذ في محلول حامض الهيدروكلوريك باستعمال البلمرة الكهربية

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الخلاصة

من خلال عدة خطوات تم تحضير سلاسل بوليمر تحتوي على حلقات (1,2,4-تريازول) و(التترازول)، أولاً تحضير (بولي اكريلول هيدرازيد) (1) من تفاعل البولي اكريلول كلورايد مع الهيدرازين. بعدها يتم التفاعل مع الفينيل ايزو سيانيد ليعطي حلقة (1,2,4-تريازول) (2). البوليمر الناتج يتفاعل مع الكلورو اسيتايل كلورايد لتحضير البوليمر (3). يتم اضافة صوديوم ازيد الى بوليمر (3) مع التصعيد للحصول على بوليمر (4). يحضر

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البوليمر (5) من تفاعل بوليمر (4) مع اكريلوناتريل بوجود NH_4Cl كعامل مساعد. في النهاية يتم الحصول على البوليمر (6) من خلال البلمرة الكهربية للبوليمر (5) على سطح الفولاذ المقاوم نوع 316 كعامل مقاوم للتآكل. تم دراسة قياسات التآكل للمعينات الغير مطلية والمطلية بالطبقة البوليمرية في محلول حامض الهيدروكلوريك المخفف بتركز 0.2 مولاري عند درجة حرارة 293 كلفن . تم استخدام نانو ZnO بتركيز مختلفة لتحسين مقاومة التآكل للفولاذ اثبتت التجارب زيادة كفاءة الحماية من التآكل بزيادة تركيز المادة النانوية . تم تشخيص المركبات باستعمال اطياف [^{13}C -NMR, ^1H -NMR, FTIR, والخصائص الفيزيائية, كذلك قياس جهاز القوة الذرية ومجهر المسح الالكتروني.

1. INTRODUCTION

Five-membered heterocyclic chains are one of the most common heterocycles. After the triazole synthesis by Fischer in 1878, the synthesis of substituted triazole derivatives showed a significant numerical increase. Triazoles were shown to have certain desirable characteristics, such as high acid / base hydrolysis stability, metabolic degradation / resistance, and reduction conditions [1]. Triazoles is currently regarded as a significant moiety in the design and synthesis of bioactive compounds associated with a broad variety of biological activities [2], including antifungal, antibacterial [3], anti-inflammatory[4], anti-HIV[5] and anti-tumor activities [6]. Additionally, analysis studies showed that 1,2,4-triazoles has distinctive roles in the fields of medicinal and pharmaceutical chemistry [7] as well as in agricultural and polymer applications [8, 9]. Tetrazoles are heterocyclic compounds with a ring four nitrogen atoms and one carbon atom [10]. The development of tetrazole chemistry has been largely associated with the widespread use of these compounds in medicine, biochemistry, agriculture, material sciences, etc.[11-16]. Also, tetrazole possesses a unique combination of properties of substantial thermal stability along with high positive enthalpy rates of formation and the highest nitrogen content among organic compounds with relatively high stability [17]. The development of a new generation of polymers has drawn a large deal of attention of researchers [18]. Many conductive polymers have been synthesized by electropolymerization methods[19], an approach which allows uniform coating on the surface of the electrode, whose thickness can be easily changed by reaction conditions. Additionally, the approach of electro-polymerisation is simple to apply and has the ability to better control the resulting polymer properties [20]. The use of polymers to protect metals from corrosion has been explored in several studies. These polymers are electrically conductive due to their widely π -conjugated backbone which allows the flow of layer metal current to suppress the corrosion reactions due to their reversible redox activity [21]. More recently, the emphasis has been on the manufacture of nanostructured polymers, as these polymer nanostructures do not only retain their unique properties but also have the characteristics of nanomaterials, such as large surface area and quantum effect. The fascinating properties of these nanostructured polymer films have been used in a variety of applications [22]. They enhance electrical, mechanical, magnetic, optical, and corrosion properties far better than their individual components, because of their electro-active and conductive nature [23]). Nano-material polymers are the best candidates for minimizing the risk of corrosion on steel structures [24]. Via new methods, we synthesize new polymers in the main chain that include 1,2,4-triazole and tetrazole rings. We then investigate the corrosion behavior of uncoated and coated (316L) stainless steel with and without nanomaterials, using the Potentiostatic technique in 0.2 M HCl solution with different concentrations of Nano ZnO.

2. EXPERIMENTAL PART

2.1. Materials and Measurements

All starting materials and solvents were obtained from Fluka and Sigma-Aldrich) and applied without further purification. The reaction was completed on aluminum-coated TLC plates of 60 F245 (E. Merck). The purity of all compounds was tested using ethyl acetate and hexane as the mobile phase and examined under iodine vapor. Softening points were measured using Kofler method with a thermal microscope. Reichert thermovar SP. 10.25, 160. with Shimadzu model (FTIR-8400S) was employed. Spectra (^1H NMR and ^{13}C NMR) were obtained with the Bruker ultra-shield spectrophotometer at 400 MHz in DMSO solution with the TMS as internal standard. Zeiss / Sigma (SEM), Germany. AA3000/220V, Angstrom Advanced Inc. (AFM) U.S.A.

2.2. Synthesis of poly acryloyl hydrazide (1) [25].

A mixture of polyacryloyl chloride (0.1 mole) and hydrazine hydrate (0.1 mole, 99 %) was refluxed for 7 hours in 15 ml of dimethyl formamide (DMF). The solvent was then evaporated, cooled and filtered. Dissolving the separate precipitate in DMSO and reprecipitating from acetone removed it. The physical properties of the synthesized compound are given in Table-1.

2.3. Synthesis of Poly(3-thio-4-phenyl-5-vinyl)-1,2,4-triazole (2) [26]

A mixture of polymer (1) 0.01mol and phenyl isothiocyanate in 20 ml DMSO was prepared and refluxed for three hours. Then, 10 ml of 5% NaOH was added and refluxed for one hour. The reaction mixture was allowed to cool and then adjusted to pH 6 with hydrochloric acid. The formed precipitate was filtered and the separated precipitate was purified by dissolving in DMSO and reprecipitating to remove acetone, ethanol, and water. The physical properties of the synthetic substance are introduced in Table-1.

2.4. Synthesis of Poly[{3-(2-chloro ethanethioate)4-phenyl-5-vinyl}-1,2,4-triazole](3) [27]

Triethyl amine (2-3 drops) was applied to a solution of polymer (2) (0.005 mol) in dry DMSO (25 ml) and then cooled at (0-5) °C. Chloroacetyl chloride (0.005 mol) in dry DMSO (5 ml) was applied with continuous stirring at room temperature. The substance obtained was washed with ether and the separated precipitate was purified by dissolving in DMF and recycled from acetone, ethanol, and water. The physical properties of the synthetic substance are introduced in Table-1.

2.5. Synthesis of Poly[{3-(2-azido ethanethioate)4-phenyl-5-vinyl}-1,2,4-Triazole](4) [28]

Sodium azide (0.003 mol) was added to polymer (3) solution (0.003 mol) in 15 mL DMF. The reaction mixture was refluxed for 12 hrs. The solvent was evaporated and the off-white product was precipitated, filtered, dried, and then purified by dissolving in DMF and DMF and precipitating from acetone and water. The physical properties of the synthesized compound are given in Table-1

2.6. Synthesis of Poly[{3-(2-(5-vinyl-tetrazolo-2-yl)ethanethioate-4-phenyl-5-vinyl)-1,2,3-triazole] (5) [29]

In a round-bottomed , a mixture of 0.002 mol of polymer (4) and 30 mL of DMF was applied to a solution of 0.002 mol of acrylonitrile and 0.004 mol of NH_4Cl , with continuous stirring at room temperature. The round was heated immediately to 120 °C for 14 h. and then cooled to room temperature. The final blend of reactions was evaporated. The brown precipitates were left to dry in air at room temperature, purified by DMF, and then precipitated from ethanol. The physical properties of the synthesized compound are introduced in Table-1.

3. Electrochemical polymerization

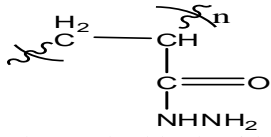
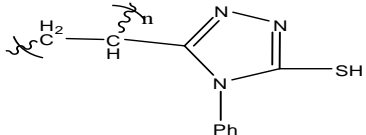
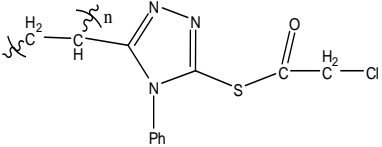
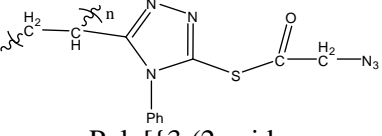
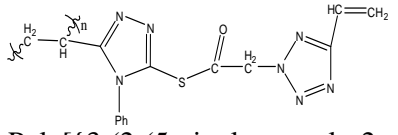
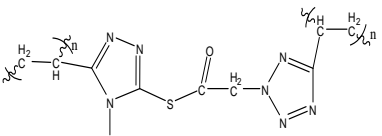
3.1 Electrochemical polymerization of polymer (5) [30]

Electrochemical polymerization of polymer (5) was performed on the surface of S.S working electrode using a DC power supply. The electrode was polished with an abrasive paper (2000 mesh) and washed with acetone and deionized water. The preparation of the electro-polymerization solution involved dissolving 0.1 g of compound (5) in 100 ml of H_2O , with three drops of 95 % H_2SO_4 . The polymer film was mounted on the electrode surface of the anode at 293 K. In addition, nanomaterials involving Nano ZnO (0.02 and 0.04 g) were combined with the monomer solution after dispersion and applied to the monomer solution to improve the corrosion protection performance of the film coating.

3.2 Electrochemical corrosion measurement

The corrosion cell test, with all the instruments that included the cell, electrodes and a working electrode holder, was performed using the advanced potentiostat method. The polarization curves were measured starting from an open circuit potential of -200 and reaching to + 200 mv and the corrosion current i_{corr} respectively. Corrosion potentials (E_{corr}) was tested for polarization curves at two concentrations using extrapolation of the cathodic and anodic Tafel axes. A temperature solution of 0.2 M HCl (293 K) was studied for corrosion measurements of the S.S.

Table1-The physical properties of all compounds

No. of comp.	Structure and names of polymers	Chemical formula	Color	Molecular weight	Softing Point C ⁰	Yield %
1	 Poly(acryloyl hydrazide)	C ₃ H ₆ N ₂ O	White	86.086	257-272	90
2	 Poly(3-thio-4-phenyl-5-vinyl)-1,2,4-triazole	C ₉ H ₉ N ₃ S	yellow	203.256	210-214	69
3	 Poly[3-(2-chloro ethanethioate) 4-phenyl-5-vinyl]-1,2,4-triazole]	C ₁₁ H ₁₀ N ₃ ClS O	Off-white	279.737	196-212	81
4	 Poly[3-(2-azido ethanethioate) 4-phenyl-5-vinyl]-1,2,4-Triazole]	C ₁₂ H ₁₁ N ₆ OS	Off-white	286.302	250-265	78
5	 Poly[3-(2-(5-vinyl-tetrazolo-2-yl)ethanethioate-4-phenyl-5-vinyl)-1,2,3-triazole]	C ₁₅ H ₁₃ N ₇ OS	Brown	339.362	211-226	64
6	 Poly[3-(2-(5-poly vinyl tetrazolo-2-yl)ethanethioate)-4-phenyl-5-vinyl]-1,2,3-triazole]	C ₁₅ H ₁₃ N ₇ OS	Light yellow	339.362	188-200	72

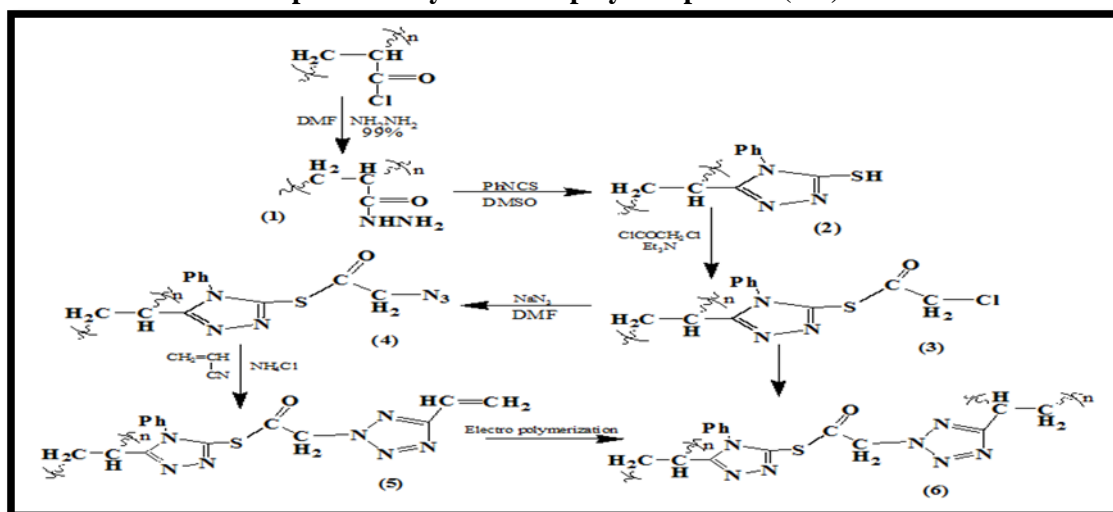
4. Results and discussion

4.1. Synthesis

Scheme 1 illustrates all the steps of compound synthesis. The experimental section above provided characterization data for all compounds (polymers 1–6). All newly synthesized compounds received a

satisfactory analysis of the proposed structures, which was confirmed using FTIR, ¹HNMR and ¹³CNMR.

Schem1: The chemical steps for the synthesis of poly compounds (1-6)



2. FT-IR spectra

The FTIR spectra of compound (1) showed significant characteristic stretching vibration bands corresponding to the (C = O) amide band at 1674cm⁻¹, (-NH) at 3265cm⁻¹, (NH₂) at 3242,3286 cm⁻¹ and (CH aliphatic) at 2929 cm⁻¹. The FTIR spectra of compounds 2- 6 [31] are demonstrated in Table-2.

Table 2-FT-IR spectra of the synthesized compounds (2-6) in cm⁻¹

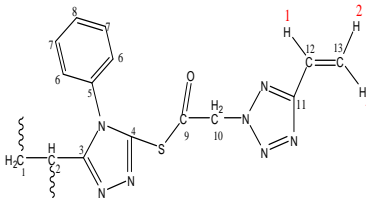
Comp. No.	ν C-H aromatic	ν C-H aliphatic	ν C=N	ν C=O	ν C=C aromatic	Others
2	3053	2981,2882	1635	-	1596.1494	SH(2722) NH(3444) tautomerism with SH
3	3080	2941,2894	1637	1732	1600, 1492	C-Cl(811)
4	3037	2921,2880	1632	1737	1595,1495	N ₃ (2138)
5	3078	2952, 2872	1649	1730	1596,1492	C=C(1630) (C-H)Olefin (3118)
6	3082	2973, 2832	1638	1733	1587	-

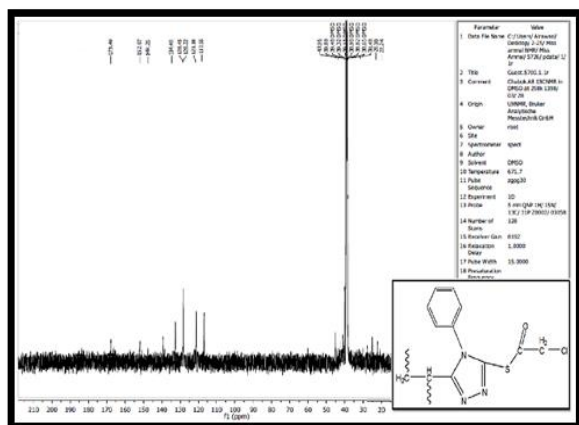
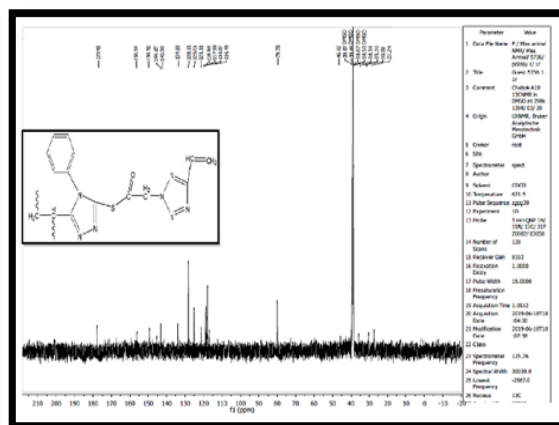
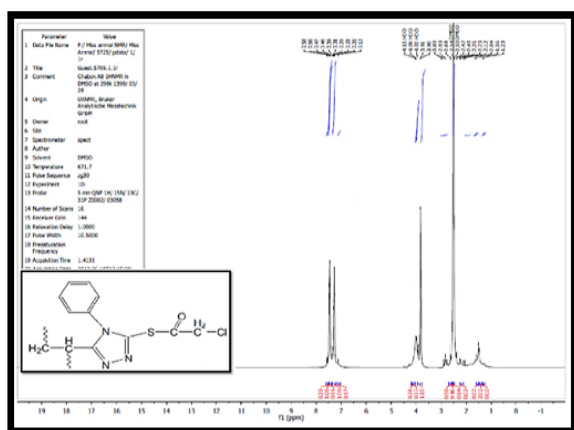
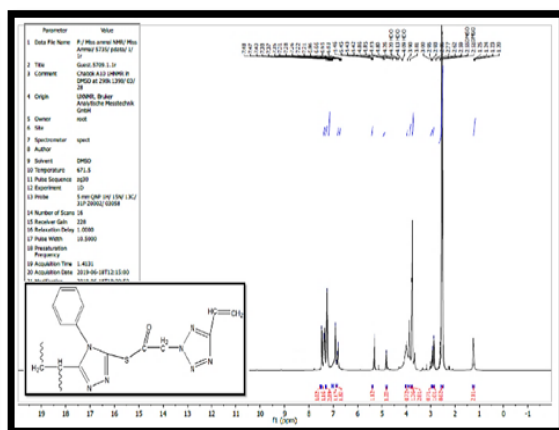
4.3. NMR Spectra

The spectra of compounds ¹HNMR and ¹³CNMR (3 and 5) are shown in Table-3[32].

Table 3-¹HNMR and ¹³CNMR data (3 and 5) for compounds in ppm

Compd No.	Compound structure	¹ HNMR data in ppm	Fig. No.	¹³ C-NMR data in ppm	Fig. No.
3		δ 1.23(t,-2H(CH ₂ -CH-), δ 2.40-3.00(m,-1H(CH ₂ -CH-), δ 7.12-7.58(m, 5H, ArH), δ 3.90 (s, 2H, CH ₂)	1	C1=22.24;C2=26.30; C3=149.25;C4=152.07; C5,C6,C7,C8=117.55 -134.48;C9=173.49; C10=43.95	3

5		δ 1.20(t,-2H(<u>CH₂-CH-</u>)), δ 2.59-3.00(m,-1H(<u>CH₂-CH-</u>)), δ 7.21-7.47(m, 5H, ArH), δ 3.81(s, 2H, CH ₂), δ 6.63(dd, 1H, H-1), δ 5.42(dd, 1H, H-2), δ 4.80(dd, 1H, H-3)	C1=27.24;C2=30.59; C3=144.50; C4=150.59; C5=134.59;C6,C7,C8 ,C12,C13=116.49- 128.15; C9=177.48; C10=79.70;C10=158. 54	4
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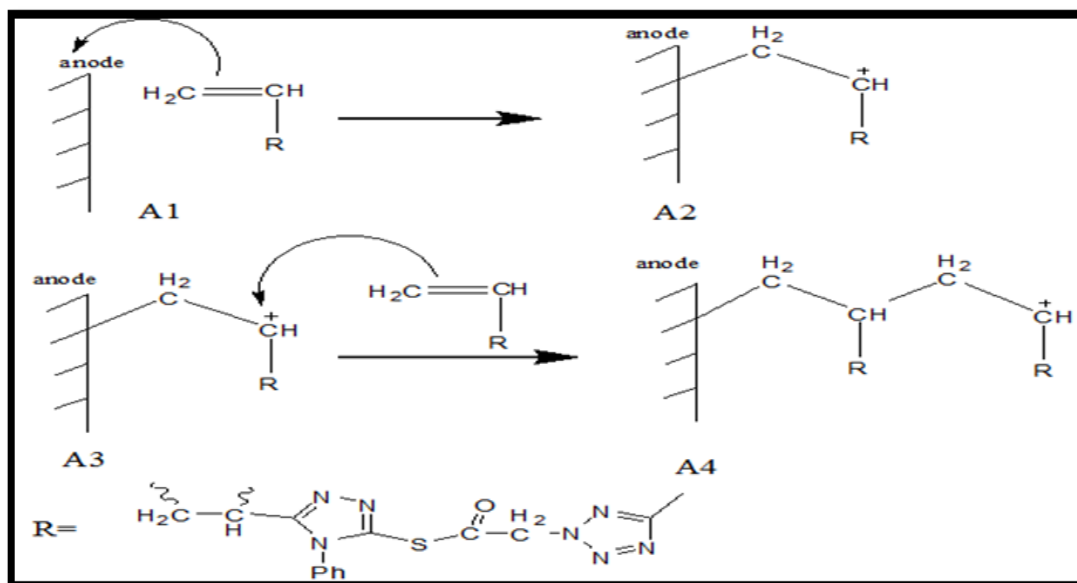
Figure 1-¹HNMR of comp. 3Figure 2-¹HNMR of comp. 5Figure 3-¹³CNMR of comp. 3Figure 4-¹³CNMR of comp. 5

4.4. Mechanism of polymerization

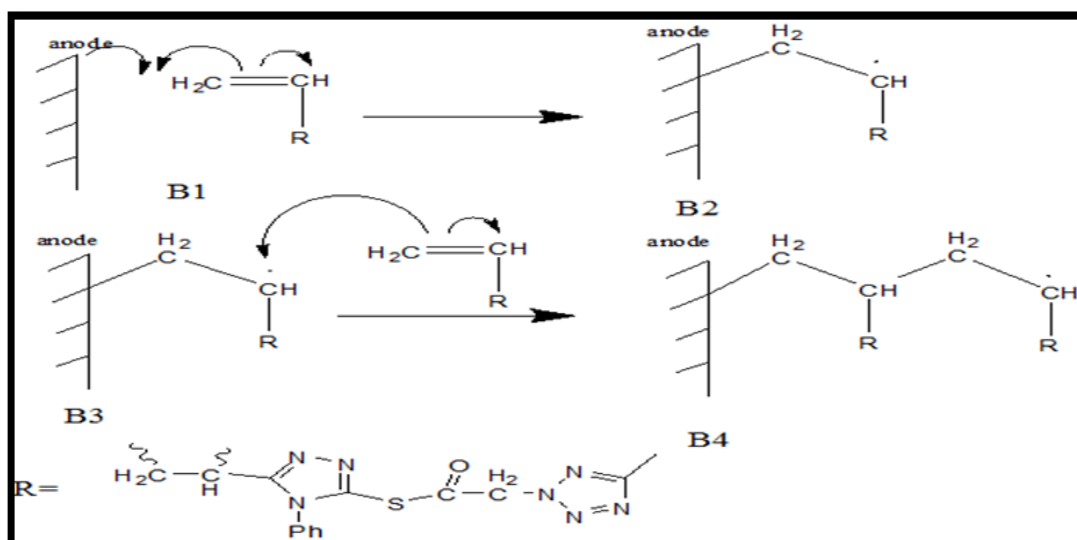
Electro-polymerization reactions, in particular the growth of polymer 6 film on the metal surface, occurred on the basis of the cationic and the radical mechanisms [33-36].

Cationic mechanism (Scheme 2-A)

The first step involved the motion of electrons (working electrode) from the monomer to the surface. This transformation led to radical cation formation, which was adsorbed on the metal surface shown in the structure (A2). Such radical cations could be disorbed and reacted in a solution to give rise to a low molecular weight (A3). Then compound 6 was added to the disorbed oxidized compound 6 (A4) through a cationic mechanism at the charged end.



Scheme (2-A): Cationic Growth Mechanism (polymer 6 Film).



Scheme (2-B): Radical Mechanism Growth (polymer 6 Film).

Radical mechanism (Scheme 2-B)

The corresponding radical to (A) is (B). The chemisorbed radical referred to in (B2) cannot be an electrochemical cycle product. If we assume that, the step of grafting is disconnected from the electrochemical process. We were confronted with the fact that the existing electrochemical conditions do not support the radical mechanism in particular. Furthermore, the radical process proceeds through the homolytic fusion of the dual bond (Fig1-B), but the breakup of the (C = C) is very unlikely given the bond's initial polarization, which is further promoted by the dual-layer electric field [37]. This electric field catalyzed the reorientation of the molecule. These observations together make it unlikely that the radical mechanism represents the growth of compound 6 film under the anode's electrochemical condition.

4.5. Atomic force microscopy (AFM)

Using the AFM method, the surface topography of stainless steel coated with the polymer, in the absence and presence of Nano materials (ZnO, 0.002 and 0.04 g), was examined. Figure- 5 shows the AFM 3D images of all coated films. In the AFM analysis, the most commonly used parameters for characterizing surface roughness are the average diameter, the average roughness (Ra), and the Root Mean Square (RMS). The results of such parameters are shown in Table-4. The findings suggest a

decrease in surface roughness with an average decrease in diameter for the three coated films. Also, the lower roughness surfaces acted as a strong barrier to protect the coatings against corrosion [38].

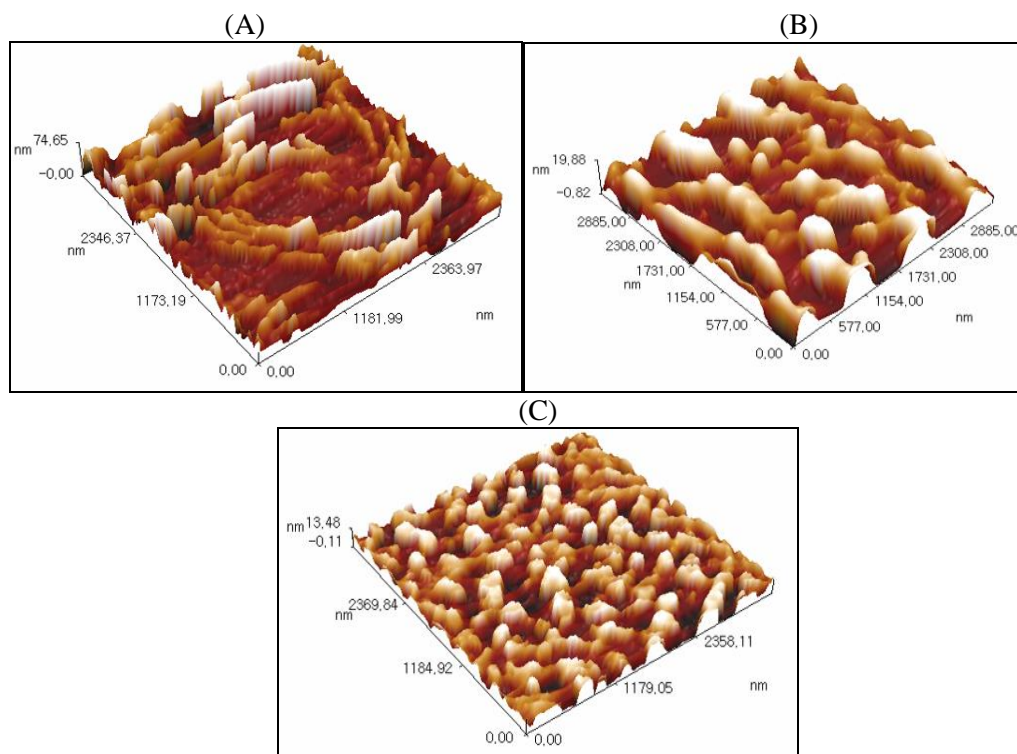


Figure 5-AFM 3D images of (A) stainless steel coated with polymer 6 without nano material, (B) stainless steel coated with polymer 6 with ZnO (0.02), (C) stainless steel coated with polymer 6 with ZnO (0.04).

Table 4-Average values for diameter, mean roughness (Ra) and root mean square (RMS) for steel coated with different preparations.

Coating	Diameter	Ra (nm)	RMS (nm)
Polymer 6	93.82	13.7	17
Polymer 6 & ZnO(0.02g)	77.98.	4.44	5.2
Polymer 6 & ZnO(0.04g)	66.99	3.13	3.65

4.6. Scanning electron microscopy (SEM)

SEM results of morphologies of 316 stainless steel-coated polymers with or without nano materials (ZnO) are shown in Figure- 6. The first SEM image (A) for the polymer without nanomaterial showed spaced apart spherical grains of various sizes. The second SEM image (B) with 0.04 g ZnO showed particle aggregates of irregular shapes and different sizes [39].

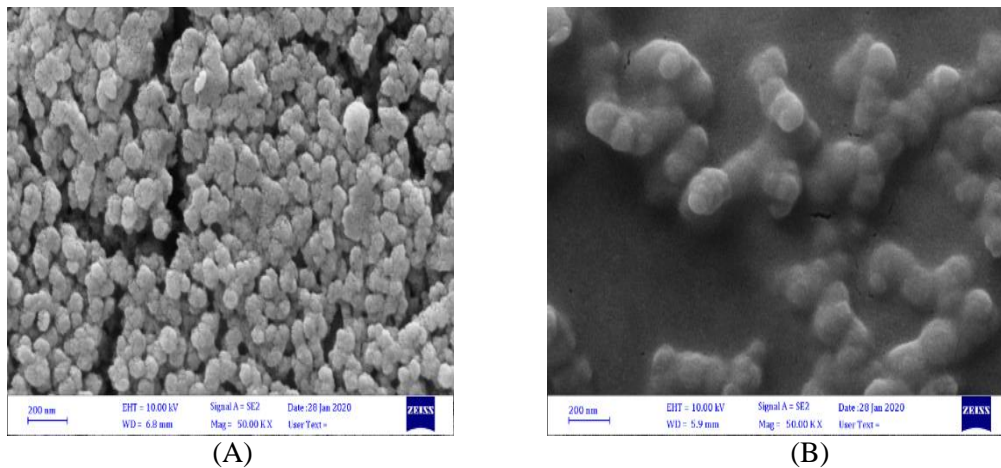


Figure 6-SEM image of (A) Stainless steel (polymer6) coated without nano material (B) Stainless steel (polymer6) coated with ZnO (0.04)

4.7. Potentiostatic polarization measurement

The effects of polymeric coating films on the anodic and cathodic polarization curves of 316L S-steel were studied in 0.1 M HCl at a temperature of 293 K. For polymer 6, the effects of adding various concentrations of the nanomaterial are shown in Figure-7. Corrosion current density (i_{corr}) was determined using the anodic and cathodic Tafel plot table extrapolation (6). The effects of polymer coating on the corrosion parameters of 316Ls-steel electrode appeared in the presence and absence of nanomaterials,. These parameters include i_{corr} , E_{corr} , anodized Tafel slope (b_a), cathodic Tafel slope (b_c), weight loss, penetration loss, and safety efficiency (PE percent) [40]. The following equation [41] indicates the calculated protection efficiency (PE %).

$$PE\% = (i_{corr})_{uncoated} - (i_{corr})_{coated} / (i_{corr})_{uncoated} \dots \dots \dots (1)$$

where i_{corr} uncoated and i_{corr} coated refer to the corrosion current densities of the uncoated and coated S.S, respectively. The polarization curves for the coated and uncoated S.S at 293 K are shown in Figure-6.

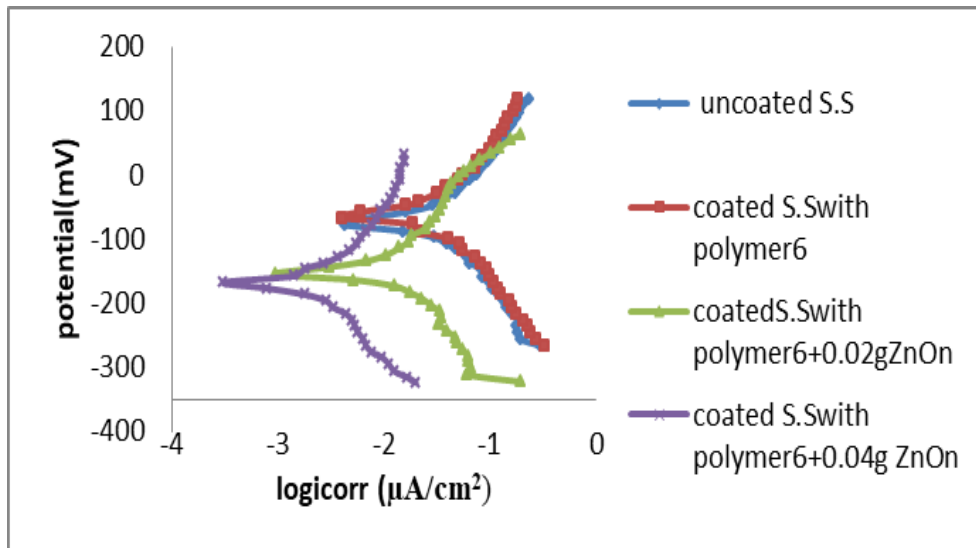


Figure 7-Polarization plots of 316 S-steel coated with polymer and nanomaterial in 0.2 M HCl at 293K.

Table 5-Corrosion data of 316 stainless steel in 0.2M HCl with and without coating

	T/K	-E _{corr} (mV)	I _{corr} (μ A/cm ²)	-bc (mV/sec)	Ba (mV/sec)	WL (g/m ² .d)	PL (mm/y)	PE%
Uncoated S.S	293	63.8	34.33	210	234.5	2.76	0.373	
coated S.S with polymer(6)	293	112.6	2.6	232.9	232.4	0.209	0.0283	92.43
Coated S.S with polymer (6) modified with 0.02g ZnO	293	153.6	2.27	43.4	62.9	0.182	0.0247	93.39
Coated S.S with polymer (6) modified with 0.04gZnO	293	168.6	1.16	82.4	91.2	0.0935	0.0126	96.31

Table-5 shows a change in corrosion potential of polymer 6- coated film to more favorable values and a decrease in corrosion current density, as nano materials add the inhibiting effect of these materials to the monomer solution. After coating, the E_{corr} changed to the less negative (more noble) values at the same temperature [42]. This indicates the coating's corrosion-resistance.

5. Conclusions

We synthesized a new chain of polymers containing tetrazole and triazole. These systems were found to be of active anti-corrosion potential. Electro-polymerized 316LS-steel coating (compound 6) was found to provide effective safety in 0.2 M HCl solution. Polymer protection performance was increased considerably with the introduction of different concentrations of ZnO nano materials to the monomer solution. The corrosion potential principles of the coated film on stainless steel moved to the noble path. The i_{corr} and E_{corr} values were decreased as the concentration of (ZnO nano) was increased. The AFM analysis for polymer 6 with and without ZnO showed that the roughness of the surface decreases as the average diameter decreases and that the smooth and uniform surfaces serve as a strong barrier to the safety of the corrosion coatings, forming a ground composition of inoxidable steel coating.

6. References

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