

Synthesis, Characterization and Corrosion Inhibitive Properties of New Thiazole Based Polyamides Containing Diarylidenecyclohexanone Moiety

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Abstract The present work aimed to synthesize a new interesting series of thiazole based polyamides containing diarylidenecyclohexanone moiety **5_a–5_f** using low temperature solution polycondensation technique. The new polymers were synthesized by the reaction of thiazole based monomer namely, bis(2-aminothiazol-4-ylbenzylidene)cyclohexanone **3** with different aliphatic and aromatic diacid chlorides using NMP, and in the presence of anhydrous LiCl as catalyst. Adipoyl, sebacoyl, oxaloyl, terephthaloyl, isophthaloyl dichlorides and biphenyl dicarbonyl dichloride were used as diacid chlorides. The structure of the model compound **4** as well as the new polymers was confirmed by correct elemental and spectral analyses. The thermal properties of those polymers were evaluated by TGA and DTG measurements and correlated to their structural units, beside X-ray diffraction analysis, solubility and viscometry measurements. The inherent viscosities for the synthesized polymers were in the range 0.6–1.03 dL/g. On the other hand the corrosion inhibitive properties of monomer **3** as well as polyamides **5_d** and **5_f** as selected examples were carried out on carbon-steel in 0.5 mol/L H₂SO₄ at 40 °C. The calculated inhibition efficiency (IE%) for polymer **5_d** was in the range (82 ± 6)% in all selected concentrations. The best value of IE% was obtained at 1 mg/L to reach 98.24% for polymer **5_d** and at 0.5 mg/L to reach 87.75% for polymer **5_f**.

Keywords: Diarylidenecyclohexanone; Polyamides; Synthesis; Characterization; Thiazole; Corrosion inhibitive properties.

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INTRODUCTION

Polyamides are a class of engineering thermoplastics which are used in wide range of applications in variable fields and play an important role in modern industrial & commercial applications. This kind of polymers have special features such as high thermal stability, photo-curing ability, fluorescence, electronic conductivity, high tensile strength, good chemical resistance, good abrasion, low friction coefficient and fire retarding property^[1, 2]. However, these polymers also have some disadvantages such as high moisture absorption, poor dimensional stability, low heat distortion temperature and poor low-temperature impact strength^[3, 4]. Furthermore, aromatic polyamides are thermally stable polymers with an attractive combination of excellent chemical, physical and mechanical properties^[5]. However, the applications of aromatic polyamides are often hampered by problems in their fabrication. For instance, the poor solubility and high softening or melting temperatures caused by high crystallinity and high stiffness of polymer backbone lead to difficulties in processing of polyamides.

A lot of efforts have been made to synthesize structurally modified polyamides having improved solubility and processability with retention of their high thermal stability. The insertion of thiazole-arylidene-thiazole tri

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blocks into the polymer main chains will help the targeted polymer to gain new properties. It is well known that, thiazole, like most sulfur containing heterocyclic moieties, is considered as one of the most important conducting or semiconducting species that can be used in photovoltaic devices and applications due to the interesting electrochemical and optical properties and great synthetic flexibility in the generation of a large number of different derivatives^[6–8]. Beside that thiazole oligomers can often exhibit photoactive liquid-crystalline properties^[8, 9]. Where as, arylidene moieties have been inserted in variable types of arylidene polymers which have interesting properties, attractive morphology, liquid crystalline behavior, corrosion protection, higher thermal stability, antimicrobial activity, conducting properties and many other properties, which have been published in our previous work^[10–12].

Corrosion inhibitions of metals have high technological importance and progress made in this field has been phenomenal in the last few decades. Industrial applications like acid pickling, acid cleaning of boilers, decaling and oil well acidizing utilize several of acidic solutions^[13, 14]. The important prerequisites for a compound to be an efficient inhibitor are: (i) it should form a defect free, compact barrier film, (ii) easily chemisorbed on to the metal surface, (iii) it should be polymeric or polymerized *in situ* on the metal and (iv) the barrier thus formed should increase the inner layer thickness. Compounds containing nitrogen, sulfur and oxygen have been established as good inhibitors for iron in acidic media^[15]. Organic compounds having π bonds are found to inhibit corrosion of steel by getting adsorbed over the electrode surface through electron sharing^[16]. The importance of inhibitive protection in acidic solutions is increased by the fact that iron materials, which are more susceptible to be attacked in aggressive media, are the commonly exposed metals in industrial environments. Numerous works have been devoted to the corrosion inhibiting effect of aqueous soluble polymers on metallic materials. Poly(vinylpyridine) (PVP) and their derivatives, polyethylenimine, polyurethane and polyvinylimidazoles have been widely examined^[17–20].

The expected attractive properties of the synthesized new polymers are mainly arrived from the presence of thiazole and arylidene moieties in the polymer main chain. Hence, the present investigation in this paper deals with the synthesis and characterization of a new series of thiazole based polyamides of diarylidenecyclohexanones. A major purpose of this work has been to investigate the corrosion inhibitive properties of selected examples of the desired polymers and the corresponding thiazole based monomer as well. This property was carried out on carbon-steel in 0.5 mol/L H₂SO₄ at 40 °C. Furthermore, the effect of cyclohexanone moiety on the polymer properties was also studied. Moreover, the crystallinity, thermal stability, morphology and viscometry of the synthesized polyamides have been examined and the data were discussed.

EXPERIMENTAL

Reagents and Solvents

Cyclohexanone, *N*-methylpyrrolidone (NMP) and anhydrous lithium chloride (Merck) were used without purification. Benzoyl chloride from El-Nasr chemical Company (Egypt) was freshly distilled (b.p.183–184 °C). Terphthaloyl chloride (Aldrich) and Isophthaloyl chloride (Aldrich) were recrystallized from *n*-hexane (m.p. 83–84 °C and 40 °C respectively). Adipoyl and sebacoyl dichlorides were freshly distilled at 125 °C/11 Torr, and at 182 °C/16 Torr, respectively^[21]. All other reagents were of high purity and were further purified as reported in literature^[22].

Instrumentation

Elemental analyses were carried out using an Elemental Analyses System GmbH, VARIOEL, V_{2.3} July 1998 CHNS Mode. IR spectra were recorded on an IR-470, Infrared spectrophotometer, Shimadzu by using the KBr pellet technique. The ¹H-NMR spectra were recorded on a GNM-LA 400-MHz NMR spectrophotometer at room temperature in DMSO or CDCl₃ using TMS as the internal reference. Mass spectra were recorded on a Jeol JMS600 mass spectrometer.

Polymer Identification

The solubility of polymers was examined using 0.02 g of polymer in 3–5 mL of solvent at room temperature.

Inherent viscosities of polymer solutions (0.5% *W/V*) in DMSO were determined at 30 °C using an Ubbelohde suspended level viscometer. The X-ray diffractographs of the polymers were obtained with a Philips X-ray PW1710 diffractometer, and Ni-filtered CuK α radiations. Thermogravimetric analysis (TGA) and differential thermal gravimetry (DTG) were carried out with a TA 2000 thermal analyzer at heating rate 10 K/min in air. In addition, potentiodynamic polarization studies were carried out using an EG&G PARC potentiostat/galvanostat (model 273).

Corrosion Inhibition Properties

Material preparation

AR grade H₂SO₄ (Merck) was used for preparing solutions. Double distilled water was used to prepare solutions of 0.5 mol/L H₂SO₄. The synthesized inhibitor was characterized through their elemental and spectral data (as described in the experimental part). The investigated monomer or polymer was added to 1 mL concentrated H₂SO₄ to swelling and diluted by volume to take the desired “mol/L”.

Electrochemical measurements

The electrochemical experiments were made using a conventional three electrode cell assembly at 40 °C. All the solutions were prepared using AR grade chemicals using double distilled water. The working electrode was of commercial grade provided by various suppliers and was received in annealed condition. Specimens were machined in cylindrical form 2 cm in length and 0.2 cm in diameter. It was inserted in Teflon so that only the flat surface was in contact with solution. The composition on examined sample was (C: 0.1, Mn: 0.6, P: 0.035, S: 0.035). The working electrode was polished with different grades of emery papers, degreased with ethanol and washed with water. The experiments were carried out at a temperature of (40 $\pm$ 1) °C as Fisher Scientific Isotemp Model 9000. Potentiodynamic polarization studies were carried out using an EG&G PARC potentiostat/galvanostat (model 273).

The data in the Tafel region (–0.15 V to + 0.1 V versus corrosion potential) have been processed for evaluation corrosion kinetic parameters by plotting *E* versus lg*I* curves. The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential for obtaining the corrosion current values. The inhibition efficiency was evaluated from the measured *i*_{corr} values using the relationship:

$$IE\% = \{ i_{\text{corr}} - i'_{\text{corr}} / i_{\text{corr}} \} \times 100$$

where *i*_{corr} and *i'*_{corr} are the corrosion current values without and with the addition of various concentrations of inhibitors respectively.

Monomer Synthesis

All diarylidenecyclohexanone starting materials were synthesized as described in our previous work; this include: 2,6- diarylidenecyclohexanone **1**, bis(4-chloroacetylbenzylidene)cyclohexanone **2** and monomer bis(2-aminothiazol-4-ylbenzylidene)cyclohexanone **3**^[23–25].

Preparation of Acid Chlorides

Acid chlorides were prepared as reported in our previous studies^[26, 27].

Synthesis of Model Compound

A mixture of bis(2-aminothiazol-4-ylbenzylidene)cyclohexanone monomers **3** (1.88 g, 0.004 mol), in LiCl/NMP (1 g in 20 mL), was stirred at room temperature. Benzoyl chloride (1.21 g, 0.008 mol) diluted with NMP (8 mL) was added to the stirred solution under N₂ at 0 °C. The mixture was subsequently stirred at room temperature in a steam of N₂ for 2 h, after that the stirring was continued for further 4 h. The solid product was filtered off, washed with dilute aq. NaHCO₃, then with water, dried and recrystallized from benzene as brownish crystals, yield 82%, m.p 190 °C. Elemental analysis for C₄₀H₃₀N₄O₃S₂ (%): Calcd.: C, 70.79; H, 4.42; N, 8.26; S, 9.44; Found: C, 70.77; H, 4.44; N, 8.31; S, 9.37.

Polymer Syntheses

A low temperature solution polycondensation technique was used in the synthesis of the desired thiazole based polyamides as the following: In a 250 mL three-necked round-bottomed flask equipped with a mechanical stirrer (2000 r/min), dry nitrogen inlet and outlet and dropper, a mixture of bis(2-aminothiazol-4-ylbenzylidene)cyclohexanone monomers **3** (0.004 mol), in LiCl/NMP (1 g in 20 mL), and a solution of the diacid chlorides (0.004 mol) in NMP (15 mL) was added in a drop wise manner while maintaining the stirred solution at 0 °C under N₂. The mixture was subsequently stirred at ambient temperature in a stream of N₂ for 6 h, then it was poured into ice-water to give a yellowish to brown colored solid. It was filtered off, washed with dilute aqueous NaHCO₃, then with water, ethanol and acetone and finally dried under reduced pressure (0.133 kPa) at 70 °C for two days.

By using the above general procedure the following polyamides were obtained.

Polyamide 5_a

Obtained by the polymerization of 2,6-bis(2'-aminothiazol-4'-ylbenzylidene)cyclohexanone **3** (0.004 mol, 1.88 g) and adipoyl chloride (0.004 mol, 0.583 mL) for 6 h, as yellowish powder; yield 85%. Elemental analysis for (C₃₂H₂₈N₄O₃S₂)_n (%): Calcd.: C, 66.20; H, 4.82; N, 9.65; S, 11.03; Found: C, 66.15; H, 4.76; N, 9.61; S, 10.96.

Polyamide 5_b

Obtained by the polymerization of 2,6-bis(2'-aminothiazol-4'-ylbenzylidene)cyclohexanone **3** (0.004 mol, 1.88 g) and sebacoyl chloride (0.004 mol, 0.854 mL) for 6 h, as brownish powder; yield 75%. Elemental analysis for (C₃₆H₃₆N₄O₃S₂)_n (%): Calcd.: C, 67.92; H, 5.66; N, 8.80; S, 10.06; Found: C, 67.87; H, 5.77; N, 8.73; S, 10.00.

Polyamide 5_c

Obtained by the polymerization of 2,6-bis(2'-aminothiazol-4'-ylbenzylidene)cyclohexanone **3** (0.004 mol, 1.88 g) and oxaloyl chloride (0.004 mol, 0.508 g) for 6 h, as yellowish powder; yield 69%. Elemental analysis for (C₂₈H₂₀N₄O₃S₂)_n (%): Calcd.: C, 64.12; H, 3.81; N, 10.68; S, 12.21; Found: C, 64.16; H, 3.83; N, 10.75; S, 12.24.

Polyamide 5_d

Obtained by the polymerization of 2,6-bis(2'-aminothiazol-4'-ylbenzylidene)cyclohexanone **3** (0.004 mol, 1.88 g) and terephthaloyl chloride (0.004 mol, 0.812 g) for 6 hrs, as brown powder; yield 77%. Elemental analysis for (C₃₄H₂₄N₄O₃S₂)_n (%): Calcd.: C, 68.00; H, 4.00; N, 9.33; S, 10.66; Found: C, 67.33; H, 4.08; N, 9.39; S, 10.72.

Polyamide 5_e

Obtained by the polymerization of 2,6-bis(2'-aminothiazol-4'-ylbenzylidene)cyclohexanone **3** (0.004 mole, 1.88 g) and isophthaloyl chloride (0.004 mol, 0.812 g) for 6 h, as black powder; yield 70%. Elemental analysis for (C₃₄H₂₄N₄O₃S₂)_n (%): Calcd.: C, 68.00; H, 4.00; N, 9.33; S, 10.66; Found: C, 67.90; H, 3.92; N, 9.36; S, 10.71.

Polyamide 5_f

Obtained by the polymerization of 2,6-bis(2'-aminothiazol-4'-ylbenzylidene)cyclohexanone **3** (0.004 mol, 1.88 g) and biphenyldicarbonyl chloride (0.004 mol, 1.11 g) for 6 h, as brown powder; yield 79%. Elemental analysis for (C₄₀H₂₈N₄O₃S₂)_n (%): Calcd.: C, 71.00; H, 4.14; N, 8.28; S, 9.46; Found: C, 69.80; H, 4.17; N, 8.34; S, 9.53.

RESULTS AND DISCUSSION

In general, the synthesis of polyamide polymers is usually based on the condensation of diamines or their derivatives with dicarboxylic acid chlorides in polar solvents such as DMF, NMP or *N,N*-DMAc^[28]. The present

work deals with the synthesis and characterization of a new category of thiazole based polyamides of diarylidenecyclohexanone moiety in the polymers backbone. A major purpose of this work is to investigate the effect of cyclohexanone moiety on the polymers properties especially in the corrosion inhibitive properties. Moreover, the crystallinity, thermal stability and viscometry of the synthesized polyamides have been examined and the data were discussed.

However, these new polymers necessitate the synthesis of monomers as precursors.

Monomer Preparation

Monomeric and pre-monomeric compounds were purified by recrystallization by using appropriate solvents twice or thrice before use in the polymerization process. The structure of these monomers is checked by elemental and spectral analyses (including: IR, $^1\text{H-NMR}$ and Mass spectra) as reported in our previous studies^[23–25]. In order to prepare bis(4-chloroacetylbenzylidene)cyclohexanone **2**, first, 2,6-diarylidenecyclohexanone **1** is prepared in considerable yield as reported in the literature by the condensation of one mole of cyclohexanone with two moles of benzaldehyde in ethanol and in presence of few drops of potassium hydroxide as a basic catalyst; the formed monomer recrystallized individually from ethanol as yellow crystals. Secondly, the precursor monomer **2** is synthesized *via* Friedel-Crafts reaction by the interaction of the diarylidenecyclohexanone monomer **1** with chloroacetyl chloride using anhydrous aluminum chloride as a catalyst and in carbon disulphide as a solvent as given in Fig. 1. At the end our targeted thiazole based monomer namely: bis(2-aminothiazol-4-ylbenzylidene)cyclohexanone monomer **3** is prepared by the interaction of bis(4-chloroacetylbenzylidene)cyclohexanone pre-monomer **2** with thiourea in absolute ethanol as shown in Fig. 1. The elemental and spectral analyses (including: IR and $^1\text{H-NMR}$) for this monomer are in accordance with the proposed structure (See supporting information Figs. S1& S2).

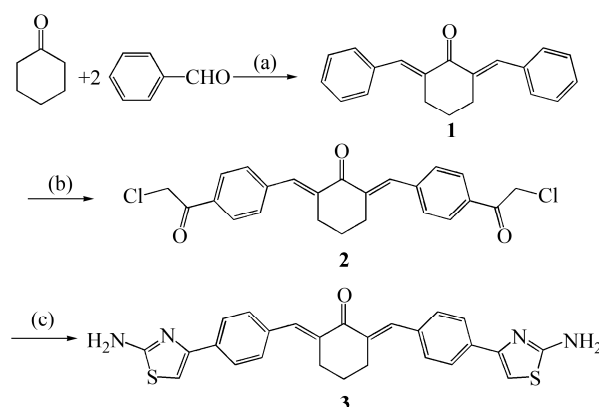


Fig. 1 Synthesis of thiophene based monomer **3**, (a) sodium hydroxide/ethanol, (b) chloroacetylation using F.C. condition ($\text{AlCl}_3/\text{CS}_2$), (c) cyclization with thiourea in ethanol/sod. acetate

Synthesis of Model Compound

Before accomplishing the polymerization, model compound **4** is synthesized by the interaction of one mole of thiazole based monomer **3** with two moles of benzoyl chloride using LiCl anhydrous as condensating agent in NMP at room temperature as shown in Fig. 2.

The structure correctness of the model compound is based on the good agreement between calculated and found analytical data, IR and $^1\text{H-NMR}$. The spectral IR data of the model compound **4** showed new characteristic absorption bands at 3340 cm^{-1} (for NH, amide), at 1690 cm^{-1} (for C=O , amide), at 1640 cm^{-1} (for C=O , cycloalkanone), and at 1600 cm^{-1} (for C=C). Beside, other characteristic absorption bands, due to common groups present in the model compound were also evident in the IR spectrum. $^1\text{H-NMR}$ spectrum of model compound **4** (in DMSO-d_6 , δ) showed the following δ values: 10.1 (s, 2H, NH amide), 8.2–7 (m, 10H, aromatic protons and 2CH=C), 3.1 (t, 4H, 2CH_2 of cyclopentanone), and at 2 (m, 2H of middle CH_2 cyclohexanone) (See supporting information Figs. S3, S4).

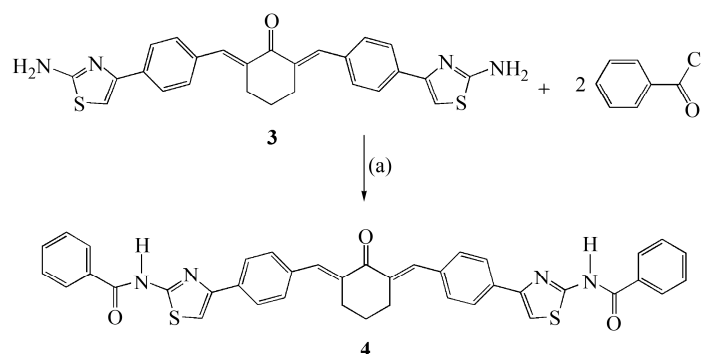


Fig. 2 Synthesis of model compound **4**, (a) benzoyl chloride NMP/LiCl anhydrous

Polymers Synthesis

New series of thiazole based polyamides **5_a–5_f** are synthesized by solution polycondensation technique at low temperature in with NMP as a solvent and in the presence of LiCl as catalyst^[29, 30]. The solvent performs two functions: whereby, the diamines dissolved and also absorbed liberated HCl gas from the polymerization process. LiCl-NMP solution is powerful enough to keep the growing polymer chain in solution as its molecular weight builds up^[31]. Our thiazole based polyamides **5_a–5_f** that containing diarylidene cyclohexanone moiety are synthesized by polycondensation reaction of monomer **3** with different aliphatic and aromatic diacid chlorides (including: adipoyl, sebacoyl, oxaloyl, terephthaloyl, isophthaloyl dichlorides and biphenyldicarbonyl dichlorides) in NMP as a solvent, using LiCl anhydrous as condensing agent at room temperature as shown in Fig. 3.

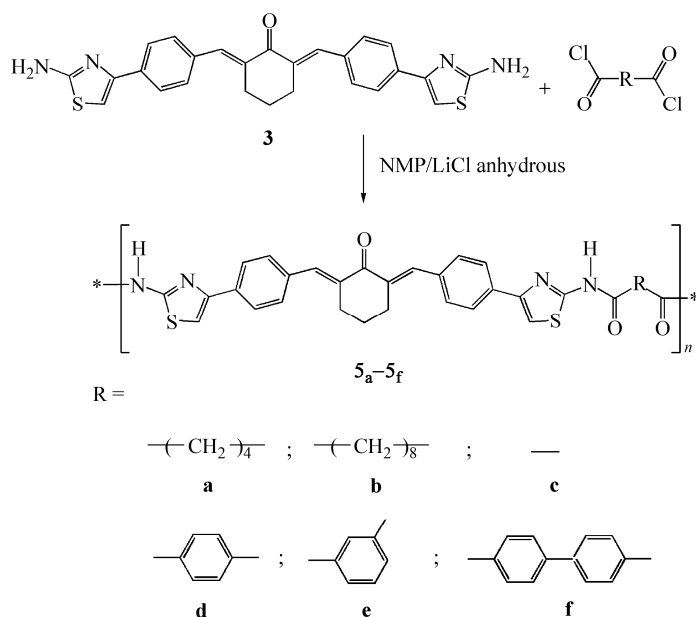


Fig. 3 Synthesis of thiazole base polyamides **5_a–5_e** by low temperature solution polycondensation in NMP/LiCl anhydrous

The reaction times of that condensation varied from 5–6 h. The expected polyamides were immediately isolated (see experimental part) when the reaction solution was poured into an ice/water mixture, with yield in the range of 69%–85%. The current polymerization reaction proceeded rapidly to produce high molecular weight polyamides with inherent viscosities in the range 0.6–1.03 dL/g. The resulting polyamides are characterized by elemental analysis, IR, solubility, viscometry, thermal analysis and morphological properties. However, it is not

uncommon for polymers to trap solvents within the matrix, especially for polyamides of high molecular mass and those containing polar groups, which are capable of hydrogen bonding with solvent molecules^[27].

The IR data obtained with KBr pellets for all the polyamides showed the absorption band for N—H stretching at 3350–3200 cm^{-1} characteristic for secondary amino groups. The appearance of carbonyl absorptions at 1695–1680 cm^{-1} , known as the amide I band, is due to carbonyl stretching vibration. A strong amide II band, due to the coupling of N—H bending and C—N stretching of the C—N—H group was noted at 1535–1515 cm^{-1} as reported in our previous study^[23]. In addition, there are 1630–1645 cm^{-1} band for C=O, cycloalkanone, and band at 1600 cm^{-1} –1590 cm^{-1} for C=C. Other characteristic absorption bands, due to common groups present in the various polymers were also evident in the IR spectra (See supporting information Fig. S5). The lowering of the usual carbonyl frequency from 1715 to 1690–1680 cm^{-1} is due to the resonance effect. Because the polyamides were examined in the solid state, hydrogen bonding could be the major contributing factor in their low carbonyl absorption frequency^[32, 33].

Polymer Characterization

The various characteristics of the resulting thiazole based polyamides **5a–5f** including: solubility, viscometry, thermal analysis, X-ray diffraction analysis, and morphological properties were determined and the data were discussed below.

The solubility characteristics of polyamides **5a–5f** are tested as described in the experimental part using DMF, DMSO, DMA, THF, chloroform/acetone mixture (1:1), CH_2Cl_2 , HOOH and H_2SO_4 as solvents and the solubility data are listed in Table 1. The majority of polymers have good solubilities in polar aprotic solvents such as DMSO and DMF except polyamides **5a–5c** which are partially soluble in DMF and **5a** and **5b** which are partially soluble in DMSO. In DMA and THF, it is observed that, all the polyamides are partially soluble except polymers **5d–5f** which are completely soluble at room temperature. Neither solubility nor swelling was observed in common organic solvents like methanol, acetone or benzene. Moreover, 50% of the polymers are completely insoluble in chloroform/acetone mixture and methylene chloride and the other 50% are partially soluble in the same solvents. On the other hand, in concentrated H_2SO_4 and formic acid all the polyamides were readily soluble giving an orange to intense deep red color except polyamides **5c** and **5d** gave brownish color. These results are clearly indicated that polyamides based on aromatic moieties **5d–5f** exhibited slightly more fair solubilities than polyamides based on aliphatic methylene linkage **5a–5c**, which is in agreement with that observed in our previous work for similar chains^[24, 25]. More particularly, the presence of cyclohexanone moiety in the polymer backbones gave the polymer slightly more solubility than other similar polymers that mainly based on the presence of cyclopentanone moiety^[24]. This difference in solubility appeared clearly in DMA, chloroform/acetone mixture and methylene chloride solvents. This observation is may be attributed to the higher flexibility of the cyclohexanone moiety^[34].

Table 1. Solubility characteristics of polyamides **5a–5f**

Polymer number	DMF	DMSO	DMA	THF	Chloroform + Acetone (1: 1)	CH_2Cl_2	HCOOH	Conc H_2SO_4	η_{inh}^* (dL/g)
5a	+	+	+	+	–	–	++	++	–
5b	+	+	+	+	–	–	++	++	–
5c	+	++	+	+	–	–	++	++	0.60
5d	++	++	++	+	+	+	++	++	1.03
5e	++	++	++	+	+	+	++	++	0.81
5f	++	++	++	+	+	+	++	++	0.62

++: Soluble at room temperature (RT)

+: Partially soluble at (RT)

–: Insoluble

*: Inherent viscosity was measured in DMSO at 30 °C.

The inherent viscosities (η_{inh}) of polyamides **5_a**–**5_f** are determined in dimethylsulfoxide at 30 °C with an Ubbelohde suspended level viscometer and the viscometry results are given in Table 1. It can be seen from the data shown in Table 1 and also according to the well known relation between the viscosity and the molecular weight of polymers that, polyamide **5_d** had high viscosity (1.03 dL/g) and this may be attributed to high molecular weight of the polymer. On the other hand, polyamide **5_e** had lower viscosity (0.6 dL/g) this may be attributed to low molecular weight of this polymer.

The X-ray diffractograms of selected examples of polyamides **5_a** and **5_b** are measured in the region $2\theta = 5^\circ$ – 60° as shown in Fig. 4. The polymers **5_a** and **5_b** are semi-crystalline and showed a few diffraction peaks that are intermediate between crystalline and amorphous interference. This indicates that there is a large class of structures that are intermediate in the ordered states between crystals in the arrangement of their atoms and molecules. The crystallinity behavior may be due to the increase in the polymer chain flexibility and that might be responsible for the approach and mutual attractions of adjacent chains^[35]. On comparison between these crystallinity of these selected polyamides and the similar polymers^[24], it should be noted that polyamides based on cyclopentanone have low degree of crystallinity than those based on cyclohexanone, this may be attributed to the rigidity of cyclopentanone moiety as reported in the literature^[36].

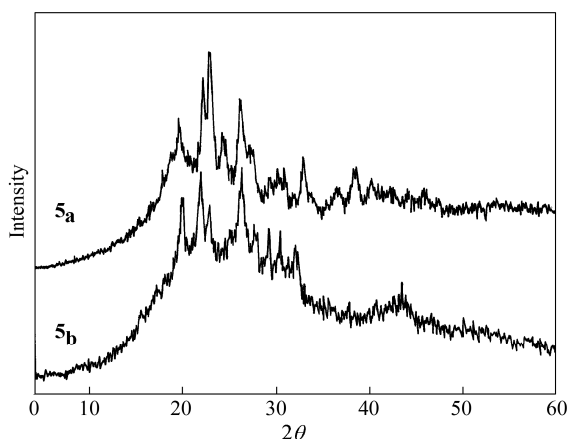


Fig. 4 X-ray diffraction patterns of polyamides **5_a** and **5_b**

The thermal properties of polyamides **5_a**–**5_f** are evaluated by thermogravimetric analysis (TGA) and differential thermal gravimetry (DTG) in air at a heating rate of 10 K/min. TGA curves show a small weight loss in the range 4%–6% starting at 50 °C until 125 °C which may be attributed to loss of moisture and entrapped solvents. The thermographs of polymers **5_d** and **5_e** as selected samples from these polymers are given in (Fig. 5 and Fig. S6, see supporting information), while (Table 2) gives the temperatures for various percentages of weight loss. All the polyamides showed similar decomposition patterns, (two main degradation steps). For polyamides **5_a** the first region showed mass loss in the range of about 165 to 350 °C, and polyamide **5_b**, the first region showed mass loss in the range of about 155 to 335 °C. While, the second region showed rapid mass loss in the range of about 396–482 °C (–99.01% and –96.38% respectively). Furthermore, for polyamides **5_d** and **5_e** the mass loss is seen to be between about 178–256 °C (–23.00% and –22.02% respectively) in the first region; and rapid mass loss between about 373–559 °C (about –100% for both polymers) in the second region. The initial decomposition of these polymers (10% loss) is considered to be the polymer decomposition temperature (PDT), it occurred in the range 211 °C to 239 °C for polyamides **5_a**, **5_b**, **5_d** and **5_e**^[37, 38]. Therefore, the previous data indicate that, all the polymers have nearly similar decomposition temperatures at 10% weight loss although the thermal stabilities of the prepared thiophene based polyamides (at 10%) are in the order: **5_a** > **5_b** > **5_d** > **5_e**. The maximum polymer degradation temperature (PDT_{max}) corresponds to the temperature at which the maximum rate of weight loss occurred and appeared in a wide range of temperatures from 450 °C for polymer **5_b**

up to 535 °C for polymer **5_e**. Polyamide **5_e** is the most thermally stable polymer which is clearly observed at 40% and 50% weight losses. The thermal stability temperatures reach 472 °C and 503 °C at 40% and 50% weight losses respectively. Whereas, polyamide **5_a** is the lowest stable polymer in the same range. The final decomposition temperature (FDT) corresponds to the temperature at which the degradation that may occur is nearly completed. The TG curves show that the FDT for all polymers is nearly completed at around 470–520 °C for aliphatic substituent polymers **5_a** and **5_b** and at around 570–580 °C for aromatic substituent polymers **5_d** and **5_e**. These results indicate that polyamides derived from aliphatic diacid chlorides are less thermally stable than those derived from aromatic diacid chlorides, which appeared clearly in 40% and 50% decomposition.

Table 2. Thermal Properties of polyamides **5_a**, **5_b**, **5_d** and **5_e**

Polymer Code	FDT * (°C)	Temperature for various percentage decompositions (°C)*				
		10%	20%	30%	40%	50%
5_a	~ 520	165	248	342	423	412
5_b	~ 470	155	257	390	422	435
5_d	~ 570	224	250	411	462	495
5_e	~ 580	225	249	393	472	503

* The values were determined by TGA at a heating rate of 10 K/min.

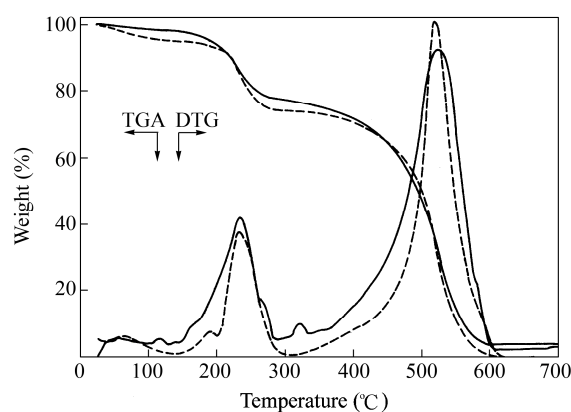


Fig. 5 The TGA and DTG traces of polyamides **5_d** (—) and **5_e** (-----)

Corrosion Inhibition Properties

One of our main target in this work is concentrated on the study of corrosion inhibitive properties of thiazole based monomer **3**, and selected examples of its corresponding polyamides on C- steel in 0.5 mol/L H₂SO₄ at 40 °C.

The corrosion inhibitive properties of our thiazole based monomer **3** are represented in Table 3, and Fig. 6 & Fig. S7 show the Tafel polarization curves for carbon steel in 0.5 mol/L H₂SO₄ with the addition of various concentrations. It is evident from Table 3 that the corrosion current values ($I_{corr.}$) for monomer **3** is decreased from 1.001 mA/cm (blank) to the less value 0.1977 mA/cm at 0.2 mg/L. The calculated inhibition efficiency (IE%) is in the range 6.98% – 80.24% within the added concentration range 0.1–1000 mg/L. The best value of IE% is obtained at some what high concentration (0.2 mg/L) to reach 80.24%. Furthermore, the corrosion rate and accordingly the inhibition efficiency within 0.2–50 mg/L tends to be concentration independent. The increase of monomer concentration decreases the IE% while, at higher values tends to be less effective. So that, it is found that the lower concentrations are more effective than the higher ones for this monomer. The decrease of IE% by increasing the concentrations indicated that the adsorbed molecules will be loosed due to the electrostatic attraction between the mobile molecule and the adsorbed one. The corrosion potential ($E_{corr.}$) within the examined monomer concentrations are approximately constant (0.479 ± 3) mV and this indicates that it is affected in both cathodic and anodic processes. The high values IE% that is presented for such monomer due to

big difference in I_{corr} in presence of monomer **3** than the blank sample which may be attributed to the increase of electron density leading to electron transfer mechanism from functional group to metal surface, producing greater coordinate bonding with greater adsorption and inhibitor efficiency. The higher values of inhibition efficiency from 100–1000 mg/L were due to blocking the examined surface area by high molecular weight of the added material^[39].

Table 3. Corrosion parameters for mild steel in 0.5 mol/L H_2SO_4 in the absence and presence of inhibitor monomer **3** from Tafel technique at 40 °C

Inhibitor conc. (mg/L)	$E_{\text{corr.}}$ (V)	0.5 mol/L	H_2SO_4	CR (mpy)
		$I_{\text{corr.}}$ (mA/cm ²)	IE%	
Blank	−0.484	1.001	–	0.4622×10^3
3				
0.1	−0.476	0.3034	69.69	0.1401×10^3
0.2	−0.479	0.1977	80.24	0.0913×10^3
0.5	−0.477	0.7175	28.32	0.3314×10^3
1	−0.477	0.2293	77.09	0.1059×10^3
2	−0.478	0.7212	27.95	0.3331×10^3
5	−0.480	0.2741	72.61	0.1266×10^3
10	−0.481	0.5966	40.39	0.2756×10^3
50	−0.480	0.5407	45.98	0.2498×10^3
100	−0.477	0.4457	50.47	0.2290×10^3
500	−0.476	0.9311	6.98	0.4457×10^3
1000	−0.476	0.6555	34.51	0.1155×10^3

Figure 6 describes the cathodic and anodic polarization of C-steel in presence of monomer **3** at lower concentrations. This monomer acts as anodic inhibitor, it is evident from the shift of cathodic branch to higher current value at any constant potential value as the concentrations increased, but in case of anodic branch the increase of concentrations is not largely effective because most of lines are applicable or have a small shift to lower values. The low values for I_{corr} corresponding to it can be related to anodic/cathodic ratio on the examined sample. Furthermore, the corrosion inhibition behavior of monomer **3** at higher concentrations is given in Fig. S7 (see supporting information). Monomer **3** acts as mixed inhibitors, but tends to show predominantly anodic which is confirmed by the clear shift on the anodic branch to lower current values as the concentration increases and has the same slope. Furthermore, the lines of approximate steady state value of $E_{\text{corr.}}$ in cathodic branch are co inside and this means that it is not affective in both hydrogen evolution and adsorption process.

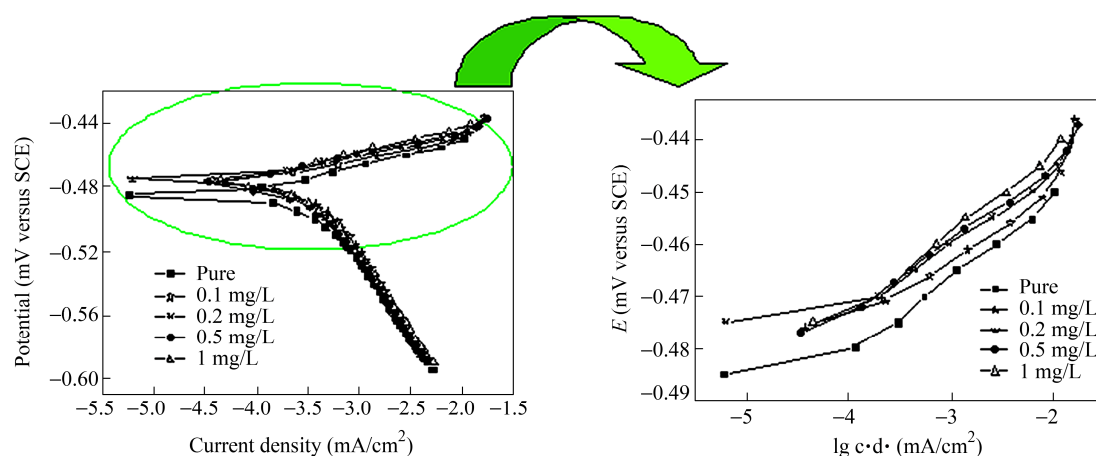


Fig. 6 Potentiodynamic polarization curves of mild steel of monomer **3** in 0.5 mol/L H_2SO_4 at 40 °C (low conc.)

On the other hand, the corrosion inhibition properties of selected examples of our targeted polymers **5_d** and **5_f** are presented in Table 4 and Figs. 7, 8 & S8, S9 show the Tafel polarization curves for carbon steel in 0.5 mol/L H₂SO₄ with the addition of various concentrations. It is evident from Table 4 that the corrosion current values I_{corr} for polyamide **5_d** are decreased from 1.001 mA/cm² (blank) to reach the less value 0.1029 mA/cm² at 10 mg/L. It is a well known fact that compounds with high molecular weight and bulky structure may cover more area on the active electrode surface^[39–41]. The calculated inhibition efficiency IE% is in the range 82 ± 6% within the added concentration range 0.1–50 mg/L for all selected concentrations of this polymer. The best value of IE% is obtained at 1 mg/L to reach 89.24%. From the data for the corrosion rate I_{corr} and inhibition efficiency IE% for such polymer, it is clear to observe that, the polymer have the same I_{corr} and IE% values by increasing the concentration 500 time, this indicates the stability of polymer on the electrode surface at the lower used concentrations. Furthermore, the calculated inhibition efficiency IE% for polyamide **5_f** ranging within (75 ± 13)% within the added concentration range 0.1 – 1 mg/L and IE% tends to decrease at higher concentrations. The best value of IE% is obtained at 0.5 mg/L to reach 87.75%. It is clear from the data listed in Table 4 that, polyamides **5_d** are preferable to use as corrosion inhibitor at all the concentrations selected. By comparing between the selected polyamides it was found that, polymer **5_d** has better inhibition efficiency at the lowest examined polymer concentration (89.24% at 1 mg/L) than polymer **5_f**.

Table 4. Corrosion parameters for mild steel in 0.5 mol/L H₂SO₄ in the absence and presence of various inhibitors (polyamides **5_d** and **5_f**) from Tafel technique at 40 °C

Inhibitor conc. (mg/L)	$E_{\text{corr.}}$ (V)	0.5 mol/L	H ₂ SO ₄	CR (mpy)
		I_{corr} (mA/cm ²)	IE%	
Blank	– 0.484	1.001	–	0.4622×10^3
5_d				
0.1	– 0.484	0.1772	82.24	0.0820×10^3
0.2	– 0.481	0.1312	86.89	0.0995×10^3
0.5	– 0.483	0.1537	84.64	0.0709×10^3
1	– 0.487	0.1077	89.24	0.0497×10^3
2	– 0.485	0.1287	78.14	0.1787×10^3
5	– 0.482	0.2254	77.48	0.2566×10^3
10	– 0.480	0.1029	89.22	0.0475×10^3
50	– 0.476	0.1201	88.00	0.0896×10^3
5_f				
0.1	– 0.487	0.2509	74.93	0.1159×10^3
0.2	– 0.488	0.3178	68.25	0.1468×10^3
0.5	– 0.486	0.1245	87.75	0.0574×10^3
1	– 0.486	0.3766	62.37	0.1740×10^3
2	– 0.484	0.7839	21.68	0.3621×10^3
5	– 0.483	0.7275	27.32	0.3361×10^3
10	– 0.483	0.9407	6.02	0.4345×10^3
50	– 0.481	0.4509	54.95	0.2083×10^3

Figures 7, 8 & S8, S9 (see supporting information) describe the corrosion inhibition properties for our thiophene based polyamides **5_d** and **5_f** in all the selected concentrations. It is clear from these figures to show that polyamides **5_d** and **5_f** have similar behavior to the previous described polyamides with a small difference at lower concentrations^[24]. Where, the type of inhibition at lower concentrations is a mixed type but it is predominantly anodic. This is due to the relative large shift compared to the shift occurs in the cathodic branch. This means that the value as accelerating action increases as the concentration of these polymers increases.

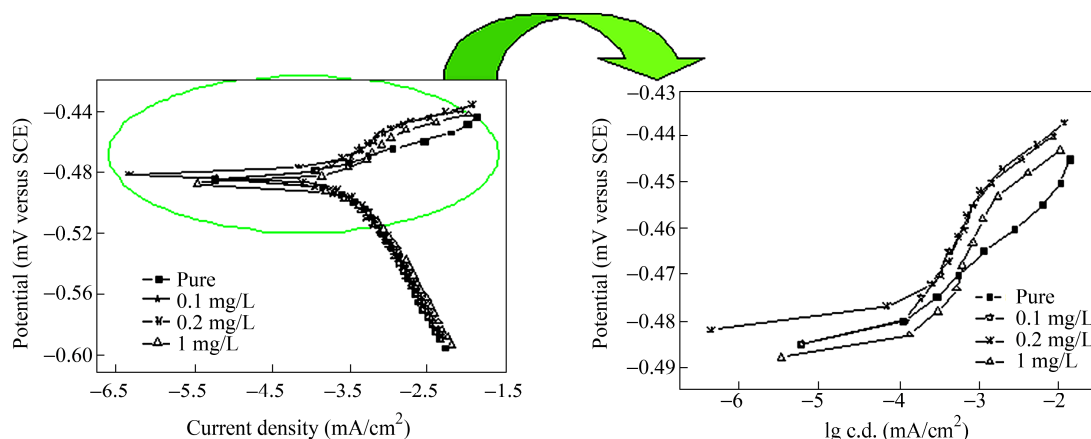


Fig. 7 Potentiodynamic polarization curves of mild steel of polyamide **5_d** in 0.5 mg/L H₂SO₄ at 40 °C (low conc.)

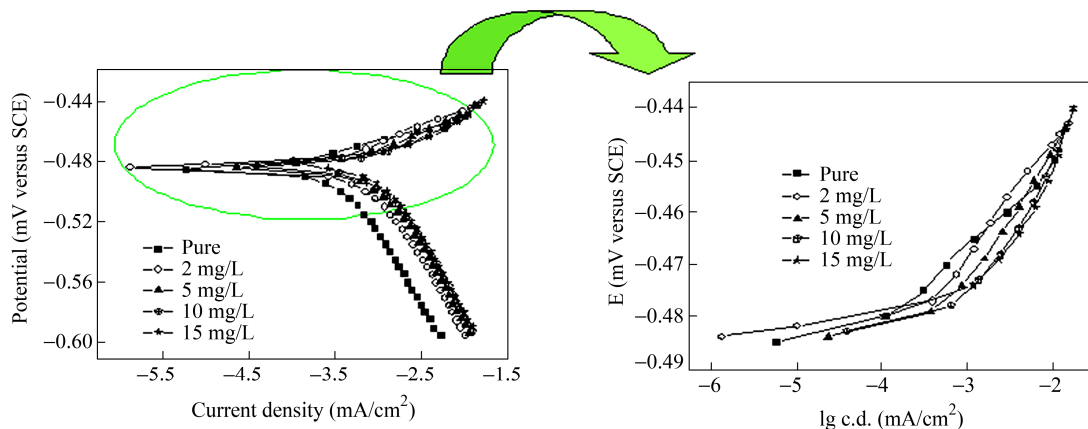


Fig. 8 Potentiodynamic polarization curves of mild steel with polyamide **5_f** in 0.5 mg/L H₂SO₄ at 40 °C (high conc.)

CONCLUSIONS

Some new interesting thiazole based polyamides that containing diarylidencyclohexanone moiety in the polymer main chains were synthesized using low temperature solution polycondensation technique in NMP as a solvent and in the presence of LiCl catalyst. The structure of the model compound **4** as well as the new polymers was confirmed by correct elemental and spectral analyses. Polyamides based on aromatic moieties **5_d** and **5_f** exhibited slightly more fair solubilities than polyamides based on aliphatic methylene linkages **5_a**–**5_c**. Polymer **5_a** surface shows rod-like shape with the help of SEM images. Polyamides **5_a** and **5_b** that contain four and eight methylene groups show semi-crystalline character detected by X ray diffraction in the region $2\theta = 5^\circ$ – 60° . All the polymers have nearly similar decomposition temperatures at 10% weight loss. Furthermore, thiazole monomer **3** acts as anodic inhibitor at lower concentrations and as mixed inhibitors, but tends to show predominantly anodic at higher concentrations. I_{corr} and accordingly the inhibition efficiency IE% tends to be concentration independent. Also, polyamides **5_d** and **5_f** act as mixed inhibitors, but tends to show predominantly anodic at lower concentrations. Polyamides **5_d** are preferable to use as corrosion inhibitor at all the concentrations.

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