

New Polymer Syntheses, Part 43: Novel Polyamides-Based Diarylidencyclopentanone: Synthesis, Characterization, and Corrosion Inhibition Behavior

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ABSTRACT: A new interesting class of polyamides containing diarylidencyclopentanone moiety **III_{a-f}** was synthesized by polycondensation reaction of the new diamino arylidene monomer **I** with different aliphatic and aromatic diacid chlorides (including adipoyl, sebacoyl, oxaloyl, terephthaloyl, isophthaloyl, biphenyldicarbonyl) and LiCl anhydrous as a catalyst at room temperature in NMP. The model compound **II** was synthesized by the interaction of one mole of diarylidencyclopentanone monomer **I** with two moles of benzoyl chloride in NMP/LiCl at room temperature. The structure of the model compound was confirmed by correct elemental and spectral analyses. The resulting polymers were characterized by elemental and spectral analyses, beside solubility and viscometry mea-

surements. The thermal properties of those polymers were evaluated by TGA, DTG, and DTA measurements and correlated to their structural units. X-ray analysis showed that polymers having high degree of crystallinity in the region $2\theta = 5 - 60^\circ$. In addition, the UV-visible spectra of some selected polymers were measured in DMSO solution and showed absorption bands in the range 260 – 475 nm, due to $n - \pi^*$ and $\pi - \pi^*$ transition. On the other hand, the corrosion inhibition behavior of selected examples of polyamides was carried out on carbon-steel in 0.5M H₂SO₄ at 40°C. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 513–523, 2009

Key words: polyamides; synthesis; characterization; diarylidencyclopentanone; thiazole; corrosion

INTRODUCTION

Polyamides are common multipurpose synthetic polymers used in a wide range of industrial settings and consumer products. They can be classified into two main families: aliphatic and aromatic polyamides. These materials have excellent mechanical properties,^{1,2} thermal properties,^{3,4} and chemical resistance.^{5,6}

In these respects, aromatic polyamides are superior to aliphatic polyamides. For this reason, there have recently been several detailed studies of aromatic polyamides.^{7–9} The synthesis of these polymers is usually based on the condensation of aromatic diamines or their derivatives with dicarboxylic acid chlorides in polar solvents such as DMF, NMP or N,N'-DMAC. Moreover, a number of studies have been made on the synthesis and characterization of aromatic polyamides.^{10,11} However, they are difficult to process owing to their limited solubility in organic solvents and high melting or softening temperatures. Many attempts have been made to increase the solubility of polyamides by

introducing bulky groups into the polymer backbone.^{12,13}

Inhibition of corrosion of metals is of high technological importance and progress made in this field has been phenomenal in last few decades. Industrial applications like acid pickling, acid cleaning of boilers, decaling, and oil well acidizing utilize several of acidic solutions.^{14,15} The important prerequisites for a compound to be an efficient inhibitor are as follows: (i) it should form a defect free, compact barrier film, (ii) it should chemisorbed on to the metal surface, (iii) it should be polymeric or polymerize *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.¹⁶ Organic compounds having π bonds are found to inhibit corrosion of steel by getting adsorbed over the electrode surface through electron sharing.¹⁷

The present investigation in this article deals with the synthesis and characterization of new category of polyamides based on diarylidencyclopentanone which containing aliphatic or aromatic moieties in the polymer backbone. A major purpose of this work has been to investigate the effect of cyclopentanone moiety in the polymer backbone, on polymer

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properties. Moreover, the crystallinity, thermal stability, morphology, absorption of water, spectroscopy, and viscometry of the synthesized polyamides have been examined, and the data are discussed. On the other hand, the corrosion inhibition behavior of selected examples of polyamides was carried out on carbon-steel in 0.5M H₂SO₄ at 40°C.

EXPERIMENTAL

Measurements

Elemental analyses were carried out using an Elemental Analyses system GmbH, VARIOEL, V_{2.3} July 1998 CHNS Mode. IR spectra were recorded on 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. Inherent viscosities of polymer solutions (0.5% w/v) in DMSO were determined at 30°C using an Ubbelohde suspended level viscometer. The solubility of polymers was examined using 0.02 g of polymer in 3–5 mL of solvent at room temperature. 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 gravimetric (DTG) were carried out in air with TA 2000 thermal analyzer at heating rate of 10°C/min in air. In addition, potentiodynamic polarization studies were carried out using EG&G PARC potentiostat/galvanostat (model 273).

Reagents and solvents

Cyclopentanone, *N*-methylpyrrolidone 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 Iso-phthaloyl chloride (Aldrich) were recrystallized from *n*-hexane (m.p. 83–84°C and 40°C, respectively). Adipoyl and sebacoyl dichlorides¹⁸ were freshly distilled at 125°C/11 Torr, and at 182°C/16 Torr, respectively. All other reagents were of high purity and were further purified as reported in literature.¹⁹

Monomer syntheses

The premonomer bis (4-chloroacetylbenzylidene) cyclopentanone and bis (2-aminothiazol-4-ylbenzylidene)cyclopentanone monomer **I** were synthesized as described in our previous works.^{20,21}

Synthesis of model compound: 2,5-bis (2-aminothiazol-4-ylbenzylidene)-cyclopentanone dibenzamide **II**

A mixture of bis (2-aminothiazol-4-ylbenzylidene) cyclopentanone monomer **I** 1.82 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 brown crystals, yield 79%, m.p 282°C. Anal. Calc. for C₃₉H₂₈N₄O₃S: C, 70.48; H, 4.21; N, 8.43; S, 9.63.

Found %: C, 70.56; H, 4.34; N, 8.39; S, 9.56.

Polymer syntheses

A solution polycondensation technique was used in the synthesis of these polyamides which described as following:

General Procedure: In a 250-mL three-necked round-bottomed flask equipped with a mechanical stirrer (2000 rpm/min), dry nitrogen inlet and outlet and dropper, a mixture of bis (2-aminothiazol-4-ylbenzylidene)cyclopentanone monomer **I** (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 dropwise manner. The solution was stirred at 0°C under N₂, after that the mixture was subsequently stirred at ambient temperature in a steam of N₂ for 6 h, then it was poured into ice-water to give a yellowish to brown colored solid. This was filtered off, washed with dilute aqueous NaHCO₃, then with water, ethanol, acetone and finally dried under reduced pressure (1 mmHg) at 70°C for two days.

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

Polyamide III_a

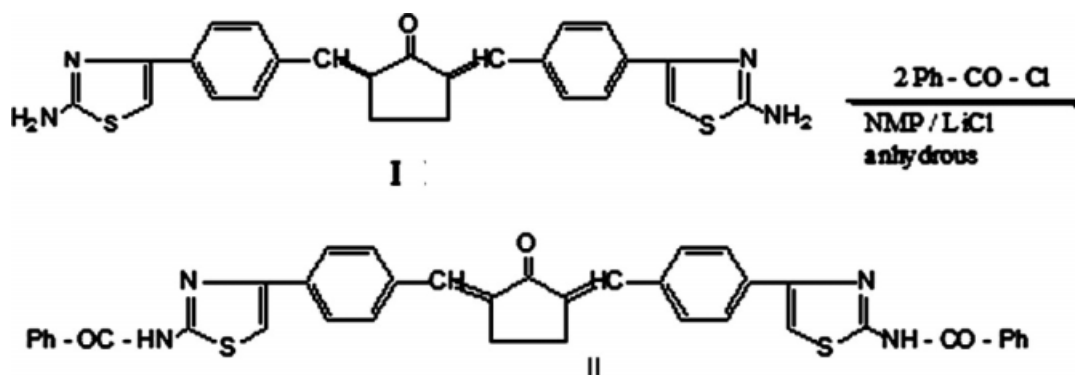
Obtained by the polymerization of 2,5-bis (2-aminothiazol-4-ylbenzylidene)-cyclopentanone **I** 1.82 g (0.004 mol) and adipoyl chloride 0.583 mL (0.004 mol) for 6 h, as yellowish powder; yield: 83%.

Anal. Calc. for (C₃₁H₂₆N₄O₃S₂)_n: C, 65.72; H, 4.59; N, 9.89; S, 11.30.

Found %: C, 65.80; H, 4.53; N, 9.98; S, 11.34.

Polyamide III_b

Obtained by the polymerization of 2,5-bis (2-aminothiazol-4-ylbenzylidene)cyclopentanone **I** 1.82 g



Scheme 1 Synthesis of model compound II.

(0.004 mol) and sebacoyl chloride 0.854 mL (0.004 mol) for 6 h, as brownish powder; yield: 85%.

Anal. Calc. for $(C_{35}H_{34}N_4O_3S_2)_n$: C, 67.52; H, 5.46; N, 9.00; S, 10.28.

Found %: C, 67.59; H, 5.52; N, 8.86; S, 10.23.

Polyamide III_c

Obtained by the polymerization of 2,5-bis(2-aminothiazol-4-ylbenzylidene)cyclopentanone **I** 1.82 g (0.004 mol) and oxaloyl chloride 0.508 g (0.004 mol) for 6 h, as yellowish powder; yield: 74%.

Anal. Calc. for $(C_{27}H_{18}N_4O_3S_2)_n$: C, 63.52; H, 3.52; N, 10.98; S, 12.54.

Found %: C, 63.49; H, 3.45; N, 11.06; S, 12.56.

Polyamide III_d

Obtained by the polymerization of 2,5-bis(2-aminothiazol-4-ylbenzylidene)cyclopentanone **I** 1.82 g (0.004 mol) and terephthaloyl chloride 0.812 g (0.004 mol) for 6 h, as brownish powder; yield: 87%.

Anal. Calc. for $(C_{33}H_{22}N_4O_3S_2)_n$: C, 67.57; H, 3.75; N, 9.55; S, 10.92.

Found %: C, 67.62; H, 3.82; N, 9.61; S, 10.95.

Polyamide III_e

Obtained by the polymerization of 2,5-bis(2-aminothiazol-4-ylbenzylidene)cyclopentanone **I** 1.82 g (0.004 mol) and isophthaloyl chloride 0.812 g (0.004 mol) for 6 h, as black powder; yield: 72%.

Anal. Calc. for $(C_{33}H_{22}N_4O_3S_2)_n$: C, 67.57; H, 3.75; N, 9.55; S, 10.

Found %: C, 67.55; H, 3.80; N, 9.49; S, 10.87.

Polyamide III_f

Obtained by the polymerization of 2,5-bis(2-aminothiazol-4-ylbenzylidene)cyclopentanone **I** 1.82 g (0.004 mol) and biphenyldicarbonyl chloride 1.11 g (0.004 mol) for 6 h, as brown powder; yield: 77%.

Anal. Calc. for $(C_{39}H_{26}N_4O_3S_2)_n$: C, 70.69; H, 3.92; N, 8.45; S, 9.66.

Found %: C, 70.79; H, 4.02; N, 8.49; S, 9.59.

RESULTS AND DISCUSSION

The work described in this article outlines the synthesis, characterization, and corrosion inhibition behavior of new series of polyamides containing diarylidene-cyclopentanone with different aliphatic or aromatic moieties in the polymer backbone. The various characteristics of the resulting polymers have been examined and the data are discussed. The main target was directed to study the corrosion inhibition behavior on carbon-steel in 0.5M H_2SO_4 at 40°C for the synthesized polyamides. Moreover, comparative study was carried out between the inhibition behaviors of selected example of polyamide and diarylidene-cyclopentanone monomer.

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

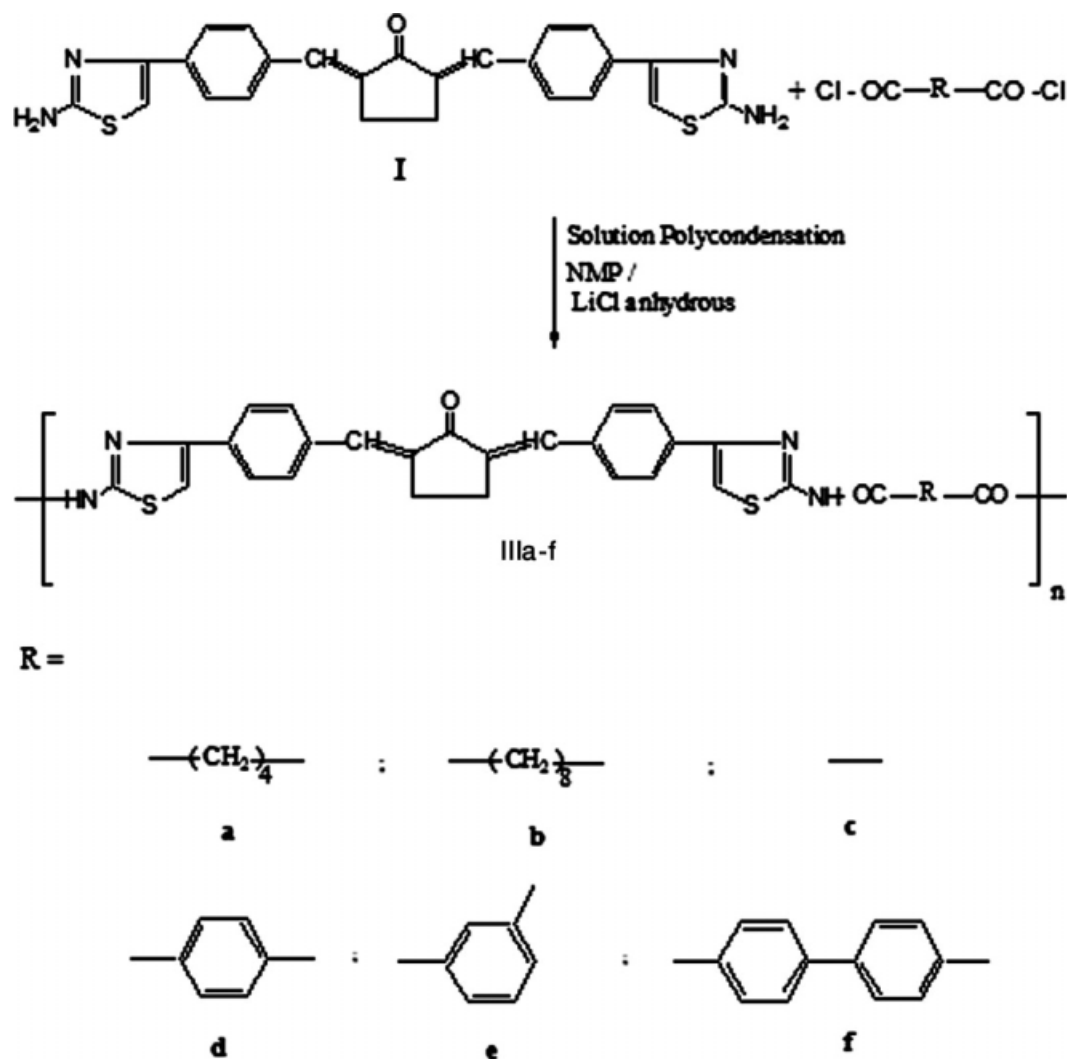
Monomer synthesis

The monomeric compound was purified by recrystallization by using appropriate solvents twice or thrice before using in the polymerization process. The structure of the desired monomer is elucidated by elemental and spectral analyses (including: IR, 1H -NMR, and Mass spectra).

Synthesis of model compound

Before attempting polymerization, model compound **II** was synthesized by the interaction of one mole of diarylidene-cyclopentanone monomer **I** with two moles of benzoyl chloride using LiCl anhydrous as catalyst in NMP at room temperature as shown in Scheme 1.

The structure of model compound was checked on the bases of good agreement between calculated

Scheme 2 Synthesis of polyamides III_{a-f}.

and found analytical data, IR and ¹H-NMR. The spectral data showed a new characteristic absorption bands at 3340 cm⁻¹ for (NH) sec. amino group, at 1690 cm⁻¹ for (C=O, amide), at 1640 cm⁻¹ for (C=O, cyclopentanone), and at 1600 cm⁻¹ for (C=C). In addition, other characteristic absorption bands, due to specific groups present in the various model compound was also evident in the IR spectrum. ¹H-NMR spectrum (in CHCl₃, ppm) showed the following δ values: 9.8 (s, 2H, NH sec. amino group), 7.8–7.2 (m, 10H, aromatic protons and 2CH=C), and 3.0 (t, 4H, 2CH₂ of cyclopentanone). Moreover, when the ¹H-NMR spectrum was carried out in (CF₃COOD) we obtained the same δ values except value for sec. amino group, which disappeared.

Synthesis of polyamides

A new interesting series of polyamides containing diarylidencyclopentanone moieties III_{a-f} was syn-

thesized by a low temperature solution polycondensation technique²² in a solvent like NMP which dissolves the diamines and acts as a good acid acceptor for the HCl liberated during the polymerization reaction and also in the presence of LiCl, as catalyst. LiCl-NMP solution is powerful enough to keep the growing polymer chain in solution as its molecular weight builds up.²³

The desired polyamides III_{a-f} were synthesized by polycondensation reaction of diaminocyclopentanone monomer I with different aliphatic and aromatic diacid chlorides (including: adipoyl, sebacoyl, oxaloyl, terephthaloyl, isophthaloyl, biphenyldicarbonyl) in NMP as a solvent, using LiCl anhydrous as catalyst at room temperature as shown in Scheme 2.

Reaction times varied from 5 to 6 h. Polyamides were immediately isolated (see experimental part) when the reaction solution was poured into an ice/water mixture, with yields in the range of 72–85%.

The polymerization proceeded rapidly to yield high molecular weight polyamides with inherent

TABLE I
Solubility Characteristics of Polyamides III_{a-f}

Polymer number	DMF	DMSO	DMA	THF	Chloroform + acetone (1 : 1)	CH ₂ Cl ₂	HCOOH	Conc H ₂ SO ₄	η_{inh}^a (dL/g)
III _a	+	+	-	-	-	-	++	++	-
b	+	+	+	-	-	-	++	++	-
c	+	+	+	-	-	-	++	++	-
d	+	++	+	+	+	-	++	++	0.86
e	+	++	+	+	-	-	++	++	0.76
f	++	++	+	+	+	+	++	++	1.08

^a Inherent viscosity was measured in DMSO at 30°C. ++: Soluble at room temperature (RT). +: Partially soluble at (RT). -: Insoluble.

viscosities in the range 1.08–0.76 dL/g. The resulting polyamides were characterized by elemental analysis, IR, solubility, absorption of water, viscometry, thermal analysis, and morphological properties. The elemental analyses of all the different polymers coincided with the characteristic repeating units of each polymer (see experimental part). It should be noted that the elemental analyses for the polymers deviated up to 1.12% from the theoretical values. 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.²⁴

Spectral data supported the structural assignments for the polymers and are in good agreement with spectral data obtained for the model compounds. The IR data obtained in KBr discs for all the polyamides showed the absorption band for N–H stretching at 3350–3200 cm⁻¹ characteristic for secondary amino group. 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. In addition, 1630–1645 cm⁻¹ for (C=O, cyclopentanone), and at 1590–1600 cm⁻¹ for (C=C). 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 lower carbonyl absorption frequency.²⁵ Other characteristic absorption bands, due to specific groups present in the various polymers were also evident in the IR spectra.

POLYMER CHARACTERIZATION

The various characteristics of the resulting polyamides, including solubility, viscometry, UV-visible spectra, thermal analysis, absorption of water, and

X-ray diffraction analysis, were also determined and the data are discussed later.

The solubility characteristics of polyamides III_{a-f} were tested using various solvents including DMF, DMSO, DMA, THF, chloroform–acetone (1 : 1), methylene chloride, formic acid, and conc. H₂SO₄. A 5% (w/v) solution was taken as a criterion for solubility. It can be clarified from Table I that, the majority of polyamides had good solubility in polar aprotic solvents such as DMSO and DMF except polyamides III_{a-c} were partially soluble in DMSO, III_{a-e} were partially soluble in DMF. In THF, all the polyamides were partially soluble except III_{a-c} was completely insoluble at room temperature. Neither solubility nor swelling was observed in common organic solvents like methanol, acetone, or benzene. Moreover; in (chloroform acetone mixture and methylene chloride) polyamides containing aromatic moieties were partially soluble except polymer III_e was completely insoluble. In concentrated H₂SO₄ and formic acid all the polyamides were readily soluble giving an orange to intense deep red color except polyamide III_d gave brownish color. These results clearly indicated that polyamides based on aromatic moieties (polymers III_{d-f}) exhibited slightly more fair solubility than polyamides based on aliphatic methylene linkage (polymers III_{a,b}), as unexpected results. More particularly, the presence of cyclopentanone moiety in the polymers backbone lowers the solubility of the resulting polymers due to the higher rigidity, which appeared clearly in (DMA, chloroform/acetone mixture, and methylene chloride) as described in our previous work.²⁰

The inherent viscosities (η_{inh}) of polyamides III_{d-f} were determined in dimethylsulfoxide (DMSO) at 30°C with an Ubbelohde suspended level viscometer. The inherent viscosity value is defined as:

$$\eta_{inh} = [2.3 \log \eta / \eta_0] / C$$

The solution concentration C is 0.5 g/100 mL, η / η_0 = relative viscosity (or viscosity ratio). It can be shown from Table I that polyamide III_f had high

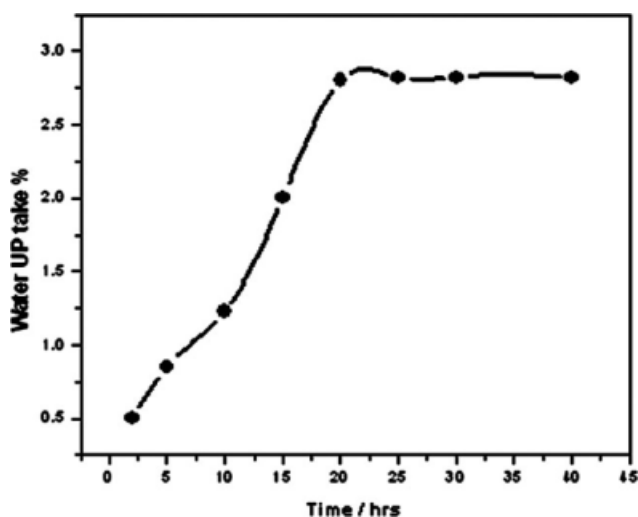


Figure 1 Water absorption (%) versus time for polyamide III_d.

viscosity (1.08 dL/g) and this may be attributed to high molecular weight of the polymer. But, the inherent viscosity of the polyamides III_{d,e} nearly the same (0.86, 0.76 dL/g respectively) this may be attributed to lower molecular weight of these polymers than in the former polymer.

An important characteristic of polyamides is the ability to absorb water. Generally, moisture absorption is proportional to the frequency of amide groups.²⁶ The hydrophilicity of polyamides was estimated by measuring the isothermal water absorption (Fig. 1). Saturation in water absorption was observed for the selected polyamide III_d after a time exposure of about 40 h, which is dependent on the sample particle size. The water absorbed for polyamide III_d (as a selected example) was 2.82%, after 40 h.

The ultra-violet and visible spectra of selected examples of polyamides III_{c,d,e} were measured in dimethylsulfoxide (DMSO) at a concentration of 10^{-6} M. The UV spectra of these polyamides III_{c,d,e} showed absorption band with λ_{\max} near 259–275 nm, which was due to the π - π^* transition within the benzenoid system for the polyamides. These two polymers showed absorption band at λ_{\max} near 319–365 nm which was due to the π - π^* and n - π^* excitation of C=C and C=O groups (cf. Fig. 2).

The X-ray diffractograms of selected examples of polyamides III_{b,d} in (Fig. 3) were measured in the region $2\theta = 5$ – 60° . Polyamide III_d showed amorphous halo pattern in the selected region and this indicates that this polymer was amorphous. While, polyamide III_b was semicrystalline, which showed a few reflection 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. More

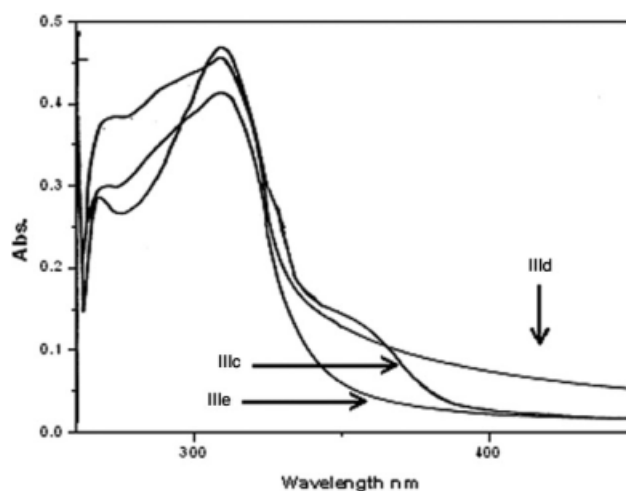


Figure 2 UV visible spectra of polyamides III_{c,d,e}.

particularly, Figure 3, showed that polyamide III_b, which contain eight methylene groups-(CH₂)₈-in the backbone became semicrystalline, which 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.²⁷

On comparison between the crystallinity of the selected examples of polyamides, it should be noted that polyamides which based on cyclopentanone has low degree of crystallinity, than those represented in our previous publications²⁸ which based on cyclohexanone moiety, this may be attributed to the rigidity of cyclopentanone moiety (appeared clearly in polyamide III_a) as reported in the literature.²⁹ The X-ray diffractograms of polyamides based on aromatic were amorphous, which showed an amorphous halo pattern in the region $2\theta = 5$ – 60° and this

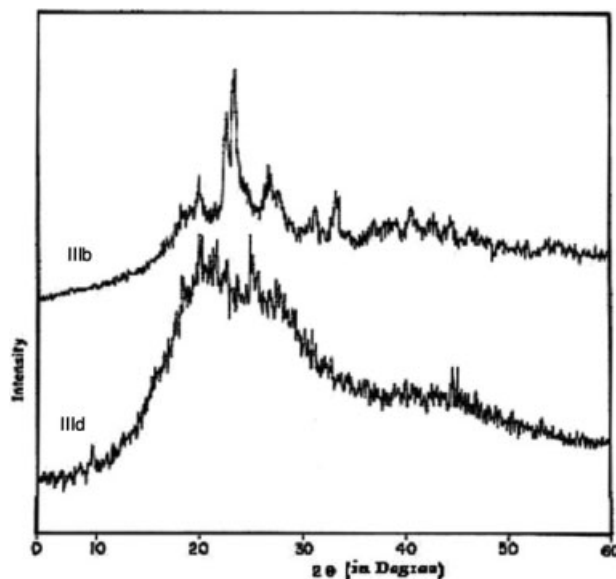


Figure 3 X-ray diffraction patterns of polyamides III_{b,d}.

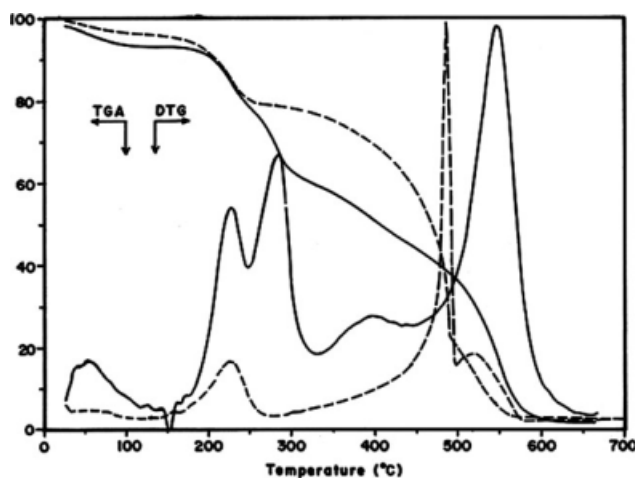


Figure 4 The TGA and DrTGA trace of polyamides III_a (---) and III_d (—) in air at a heating rate of $10^\circ\text{C}/\text{min}$.

indicates a low degree of crystallinity (appeared clearly in polyamide III_d).

The thermal properties of polyamides III_{a-f} were evaluated by thermogravimetric analysis (TGA) and differential thermal gravimetric (DTG) in air at a heating rate of $10^\circ\text{C}/\text{min}^{-1}$. The thermal behavior of polyamides containing diarylidencyclopentanone $\text{III}_{a,b,d}$ was evaluated by TGA and DTG in air at a heating rate of $10^\circ\text{C}/\text{min}^{-1}$. TGA curves show a small weight loss in the range 4–5% starting at 50°C until 125°C which may be attributed to loss of moisture and entrapped solvents. The thermographs of selected samples from these polymers are given in (Fig. 4), while (Table II) gives the temperatures for various % weight loss. All the polyamides showed similar decomposition patterns, (two main degradation steps) except polyamides III_{a-d} showed different decomposition patterns (three or multi decomposition steps). The initial decomposition of these polymers (10% loss) is considered to be the polymer decomposition temperature (PDT),^{30,31} it occurred in the range 215 to 256°C for polyamides $\text{III}_{a,b,d}$. In Figure 4, for polyamide III_a (multi degradation steps) the mass loss is between ~ 200 and 245°C (-19.44%) in the first region; the mass loss is between ~ 252 and 325°C (-37.96%) in the second region; rapid mass loss between ~ 335 and 445°C (-54.06%) in the third region and finally mass loss is between 450 and 570°C (-98.36%) in the fourth region. In addition, for polyamide III_d (three degradation steps) the mass loss is between ~ 165 and 260°C (-21.07%) in the first region; rapid mass loss is between ~ 280 and 475°C (-77.67%) in the second region; and mass loss between ~ 490 and 555°C (-96.99%) in the third region. These results indicate that polyamides derived from aliphatic diacid chloride are less thermally stable than those derived from aromatic diacid

chloride, which appeared clearly in T_{40} and T_{50} decomposition values for polyamides $\text{III}_{a,b}$.

CORROSION INHIBITION PROPERTIES

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.^{32–35} The inhibitive action of polymers is related structurally to the various active centers of adsorption as cyclic rings, heteroatom as oxygen and nitrogen. The work described in this property, concentrated on the study the corrosion inhibition properties of selected example of polyamide III_d on steel in $0.5\text{M H}_2\text{SO}_4$ at 40°C and compare it with the desired diarylidencyclopentanone monomer.

Material preparation

AR grade H_2SO_4 (Merck) were used for preparing solutions. Double distilled water was used to prepare solutions of $0.5\text{M H}_2\text{SO}_4$. The synthesized inhibitor was characterized through their elemental and spectral data (as described before).

The investigated polymer was added to 1 mL concentrated H_2SO_4 to swelling and diluted by volume to take the desired ppm wanted to added to 200 mL of $0.5\text{M H}_2\text{SO}_4$.

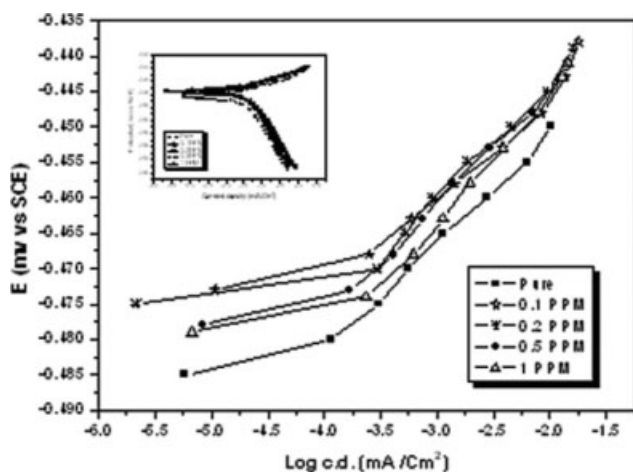
Electrochemical measurements

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

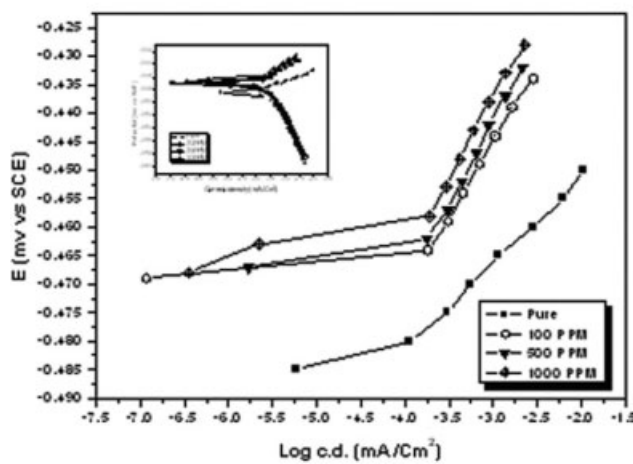
TABLE II
Thermal Properties of polyamides $\text{III}_{a,b,d}$

Polymer code	Temperature ($^\circ\text{C}$) for various percentage decompositions ^a				
	10%	20%	30%	40%	50%
III_a	222	257	290	334	410
III_b	256	321	350	387	427
III_d	220	265	400	445	472

^a The values were determined by TGA at heating rate of $10^\circ\text{C}/\text{min}^{-1}$.



(a)



(b)

Figure 5 (a). Potentiodynamic polarization curves of mild steel of monomer I in 0.5M H₂SO₄ at 40°C (Low Conc.). (b) Potentiodynamic polarization curves of mild steel of monomer I in 0.5M H₂SO₄ at 40°C (High Conc.).

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 $40 \pm 1^\circ\text{C}$ as Fisher Scientific Isotemp Model 9000. Potentiodynamic polarization studies were carried out using EG&G PARC potentiostat/galvanostat (model 273).

The data in the Tafel region (-0.15 to $+0.1$ V versus corrosion potential) have been processed for evaluation corrosion kinetic parameters by plotting E versus log 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

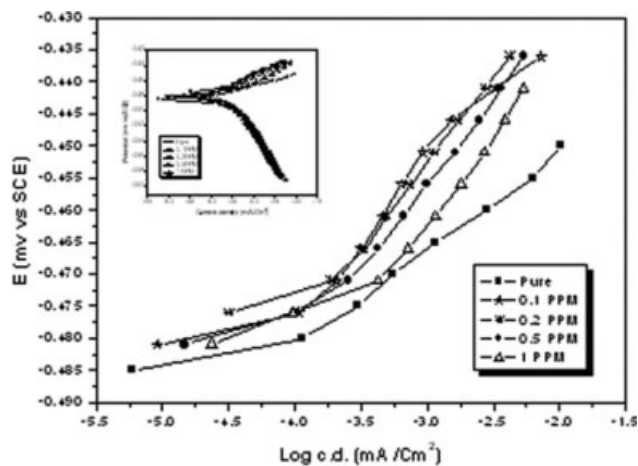
from the measured i_{corr} values using the relationship:

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

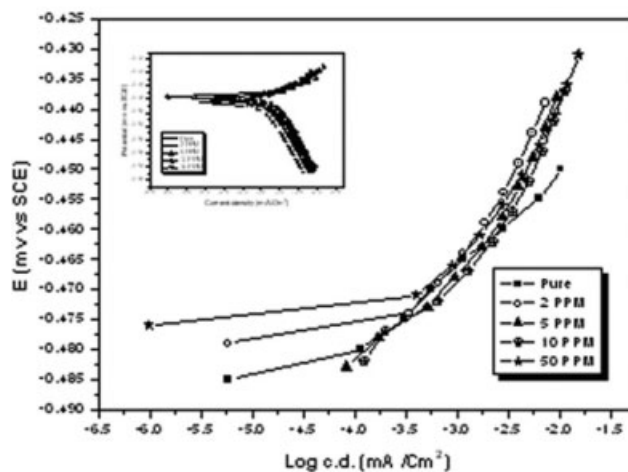
Where i_{corr} and i'_{corr} are the corrosion current values without and with the addition of various concentrations of inhibitors respectively.

Results and discussion

The potentiodynamic polarization behavior of C-steel in 0.5M H₂SO₄ with addition of various concentrations of monomer I and polyamide III_d within the Tafel region are shown in Figures 5–6 and Table III represent the corrosion kinetic parameters in the absence and presence of the selected sample. It is a



(a)



(b)

Figure 6 (a). Potentiodynamic polarization curves of mild steel of polyamide III_d in 0.5M H₂SO₄ at 40°C (Low Conc.). (b) Potentiodynamic polarization curves of mild steel of polyamide III_d in 0.5M H₂SO₄ at 40°C (High Conc.).

TABLE III
Corrosion Parameters for Mild Steel in 0.5M H₂SO₄ in the Absence and Presence of Monomer I and Polyamide III_d Inhibitors From Tafel Technique

Inhibitor Conc. (ppm)	E_{corr} (volt)	0.5M H ₂ SO ₄		CR (mpy)
		I_{corr} (mA)	IE %	
Blank	-0.484	1.001	-	0.4622×10^3
Monomer I				
0.1	-0.477	0.2811	71.91	0.1298×10^3
0.2	-0.479	0.3333	66.70	0.1540×10^3
0.5	-0.477	0.2462	75.40	0.1137×10^3
1	-0.478	0.2174	78.28	0.1004×10^3
2	-0.481	0.5412	45.93	0.2500×10^3
5	-0.478	0.6094	39.12	0.2815×10^3
10	-0.478	0.6286	37.20	0.2904×10^3
50	-0.477	0.2904	70.98	0.1341×10^3
100	-0.471	0.1635	83.66	0.2365×10^3
500	-0.470	0.1464	85.37	0.2099×10^3
1000	-0.468	0.1002	89.99	0.1792×10^3
Polyamide III _d				
0.1	-0.481	0.1503	84.98	0.0694×10^3
0.2	-0.480	0.2429	75.73	0.1122×10^3
0.5	-0.480	0.2695	73.07	0.1245×10^3
1	-0.482	0.238	76.22	0.1099×10^3
2	-0.481	0.1962	80.39	0.1541×10^3
5	-0.481	0.4705	50.99	0.2174×10^3
10	-0.479	0.1220	87.81	0.0563×10^3
50	-0.480	0.0469	95.31	0.0188×10^3

well known fact that compounds with high molecular weight and bulky structure may cover more area on the active electrode surface.³⁶

Polarization studies

The corrosion inhibition properties of diarylidene-cyclopentanone monomer I represented in Table III and Figure 5 showed the Tafel polarization curves for carbon steel in 0.5M H₂SO₄ with the addition of various concentrations. It is evident from Table III that the corrosion current values (I_{corr}) for monomer I was decreased from 1.001 mA cm⁻² (blank) to reach the less value at 1000 ppm to be 0.1002 mA. The calculated inhibition efficiency (IE%) ranging within $72 \pm 6\%$ within the added concentration range 0.1–1 ppm. and within $86 \pm 3\%$ within the added concentration range 100–1000 ppm which may be attributed to that (IE%) increase with increase the concentration of the monomer. The best value of (IE%) is obtained at 1000 ppm to reach 89.99%, which means that the higher concentrations are the best than the lower ones. The order of (IE%) are about the same within 100–1000 ppm. Corrosion potential (E_{corr}) shifted towards the negative direction in the presence of monomer I ranging from 3–14 mv. This indicates that the process was predominantly control the cathodic reaction. The higher (IE%) due to highly difference in (I_{corr}) in presence of monomer I than the pure one which may be

attributed to the increased 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 ppm were due to blocking the examined surface area by high molecular weight of the added material.³⁷

Figure 5(a) describes the cathodic and anodic polarization of steel in presence of monomer I in lower concentrations. This monomer act as anodic inhibitor, it is evidence from the shift of cathodic branch to higher current value at any constant (IE%) value as the concentrations increased, but in case of anodic branch the increase of concentrations are not largely effective because most of lines are applicable or have a small shift to lower values. The lower values of (I_{corr}) corresponding to it can be related to anodic/cathodic ratio on the examined sample.

Moreover, Figure 5(b) describes the corrosion inhibition behavior of monomer I in higher concentrations. It was found that, monomer I act as mixed inhibitor, but tends to show predominantly anodic and this clear by shift on the anodic branch to lower current values as the concentration increases and have the same slop and approximate steady state value of (E_{corr}) in cathodic branch the lines co inside and this means that it is not affective in both hydrogen evolution and adsorption process. The anodic inhibition properties are clearer in higher concentrations than that obtained in the lower one. The best concentration of inhibition as anodic can be illustrated by 1000 ppm.

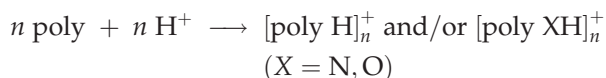
The corrosion inhibition behavior of selected example of the synthesized polyamides III_d were presented in Table III and Figure 6 showed the Tafel polarization curves for carbon steel in 0.5M H₂SO₄ with the addition of various concentrations. It is evident from Table III that the corrosion current values (I_{corr}) for polyamide III_d are decreased from 1.001 mA cm⁻² (blank) to reach the lest value at 50 ppm to be 0.0469 mA. It is a well known fact that compounds with high molecular weight and bulky structure may cover more area on the active electrode surface.^{36,37} The calculated inhibition efficiency (IE%) ranging within $80 \pm 7\%$ within the added concentration range 0.1–10 ppm. The best value of (IE%) is obtained at 50 ppm to reach 95.31%.

Figure 6(a,b) describe the cathodic and anodic polarization of steel in presence of selected example of polyamides III_d in both lower and higher concentrations. The selected polyamide are mainly anodic inhibitor, which are more pronounced at lower concentrations where, anodic branch shifted to the lower values accompanied by positive potential shift. By comparing the cathodic branch in both lower and higher concentrations, it is clear that the

increase of concentration increase the related current density which shows them as stimulators. By comparison the IE% of both monomer I and the new synthesized polymer **III_d**, it was found that the new polymer is more effective (higher values) in both lower and higher concentrations which means that polyamide **III_d** is more protective.

Inhibition mechanism

The suggested inhibition mechanism was due to the abundance of π electrons and unshared electron pairs on nitrogen and oxygen atoms which can be interact with the empty d -orbitals of iron to provide a protective barrier film. The desired polyamide in aqueous solutions exist as either neutral molecules or in the form of cations^{38,39} depending on the concentration of H^+ ions in solutions. The protonated molecules are mostly the predominant.



The positively charged polyamide cation interacts electrostatically with negatively charged metal surface.⁴⁰ In case of active center free positively charged (unprotonated) which have high electron cloud or free electron interacts with positively charged metal surface which play an important rule.⁴¹ The point of zero charge (pzc) of iron in sulfuric acid is positive with respect to corrosion potential.⁴² The inhibitive effect of the same compound at high concentration may be due to the higher coverage with blockage of the more active sites of the metal surface, but it is limited due to the healing according to higher weight of the polymer structure which causes the lowering value of inhibition efficiency. In our case, the higher inhibition efficiency mainly may be due to the effect of electron interaction containing polymer and structure of the molecule on the metal surface.

Adsorption isotherm

The values of surface coverage (θ), that is defined as $IE\%/100$ and obtained from weight loss measurements at $40^\circ C$, have been used in the study of the predominant isotherm on the process of carbon steel dissolution in $0.5M H_2SO_4$ in the presence of polyamide **III_d**. The adsorption of an organic adsorbate at a metal-solution interface can be represented as a substitution adsorption process between the organic molecule in the aqueous solution $Org(sol)$ and the water molecules on the metallic surface $H_2O(ads)$ ⁴³:

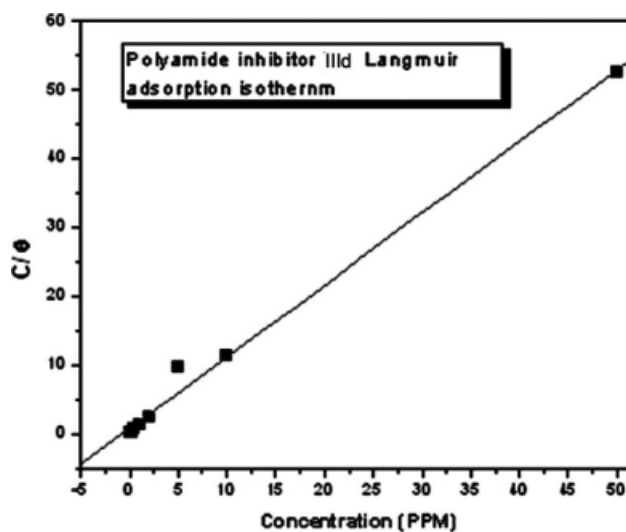
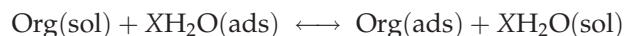


Figure 7 Langmuir adsorption isotherm for the polyamide **III_d** on C-steel at $40^\circ C$.



in which $Org(sol)$ and $H_2O(sol)$ and $Org(ads)$ and $H_2O(ads)$ are the organic and water molecules in the aqueous solution and the adsorbed organic and water molecules on the surface, respectively. X is the size ratio representing the number of water molecules replaced by a molecule of organic adsorbate. This process can be entered on the iron dissolution mechanism and affect the iron dissolution rate.⁴⁴

Figure 7 illustrates the relationship between C/θ against C . The experimental results give a straight line with unit slope suggesting that the adsorption of the inhibitor molecules on C-steel/produced water interface obeys Langmuir adsorption isotherm which is represented by the following equation:

$$C/\theta = 1/K + C$$

where C is the concentration of the inhibitor and k represents the adsorption equilibrium constant. The adsorption of the inhibitor depends on chemical structure of the compound, chemical composition of the electrolyte, temperature, nature of metal surface and electrochemical potential at the metal/solution interface.⁴⁵

CONCLUSIONS

A new interesting series of polyamides containing diarylidencyclopentanone moiety was synthesized by polycondensation technique in NMP using LiCl anhydrous as catalyst at room temperature. Neither solubility nor swelling was observed in common organic solvents. Polyamides containing aromatic moieties were partially soluble except polymer **III_e** was

completely insoluble. The water uptake for polyamide **III_d** (as a selected example) was 2.82%, after 40 h. The thermal stability of polyamides which contain aliphatic chains is less thermally stable than those containing aromatic. By comparison the IE% of both monomer **I** and the new synthesized polymer **III_d**, it was found that the new polymer is more effective (higher values) in both lower and higher concentrations which means that polyamide **III_d** is more protective.

References

1. Nakamae, K.; Nishino, T.; Shimizu, Y.; Matsumoto, T. *Polymer J* 1987, 19, 451.
2. Tashiro, K.; Yoshioka, Y.; *Polymer* 2004, 45, 4337.
3. Bulte, A. M. W.; Folkers, B.; Mulder, M. H. V.; Smolders, C. A. *J Appl Polym Sci* 1993, 50, 13.
4. Li, X. G.; Huang, M. R. *J Appl Polym Sci* 1999, 71, 565.
5. Arpin, M.; Strazielle, C. *Polymer* 1977, 18, 591.
6. Aharoni, S. M. *J Appl Polym Sci* 1992, 45, 813.
7. Hearle, J. W. S. *High Performance Fibres*; Woodhead Publishing Ltd: Cambridge, UK, 2001.
8. Nelson, G. L.; Wilkie, C. A. *Fire and Polymers*. American Chemical Society: Washington, DC, 2003.
9. Odian, G. *Principles of Polymerization*. Wiley: Hoboken, New Jersey, 2004.
10. Hill, H. W.; Kwolek, S. L.; Morgan, P. W. U.S. Pat. 3006899, October 1961.
11. Morgan, P. W.; Kwolek, S. L. *J Polym Sci (C)* 1962, 1, 33.
12. Akutsu, F.; Kataoka, T.; Naruchi, K.; Miura, M.; Nagakubo, K. *Polymer* 1987, 28, 1787.
13. Akutsu, F.; Suzuki, A.; Saitoh, F.; Naruchi, K.; Miura, M.; Nagakubo, K. *Makromol Chem* 1987, 188, 1253.
14. Ali, S. A.; Saeed, M. T.; Rahman, S. V. *Corros Sci* 2003, 45, 253.
15. Sastry, V. S. *Corrosion Inhibitors—Principles and Application*; Wiley: England, 1998.
16. Lagrnee, M.; Mernari, B.; Bouanis, M.; Traisnel, M.; Bentiss, F. *Corros Sci* 2002, 44, 573.
17. Bentiss, F.; Lagrnee, M.; Traisnel, M.; Hornez, J.C. *Corros Sci* 1999, 41, 789.
18. Vogel, A. *Text Book of Practical Organic Chemistry*; Longmans, Green: London, 1967, 1, 464.
19. Perrin, D. D.; Armarigo, W. L. F.; Perrin, D. F. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, 1980.
20. Aly, K. I.; Abbady, M. A.; Mahgoub, S. A.; Hussein, M. A. *Polym Int* 2002, 51, 125.
21. Aly, K. I.; Hussein, M. A. *Polym Int*, to appear.
22. Bair, T. I.; Morgan, P. W.; Killian, F. L. *Macromolecules* 1977, 10, 1396.
23. Suh, D. H.; Ju, S. Y.; Park, S. H.; Lee, J. W. *J Macromol Sci Chem* 2001, A38, 751.
24. Aly, K. I.; Khalaf, A. A. *J Appl Polym Sci* 2000, 77, 1218.
25. Aly, K. I.; Kandeel, M. M. *High Performance Polymers* 1996, 8, 307.
26. Campa, J. G.; Guijarro, E.; Serna, F. J.; Abajo, J. *Eur Polym J* 1985, 12, 1013.
27. Li, C. H.; Chang, T. C. *Eur Polym J* 1991, 27, 35.
28. Abd-Alla, M. A.; Aly, K. I. *High Performance Polymer* 1990, 2, 235.
29. Mandelkern, L.; *Crystallization of Polymers*; McGraw Hill: New York, 1964.
30. Aly, K. I. *Polym Int* 1998, 47, 483.
31. Aly, K. I. *J Appl Polym Sci* 2004, 94, 1440.
32. Nikles, D. E.; Warren, G. W. *Polym. News* 1998, 23, 223.
33. Jianguo, Y.; Lin, W.; Otieno-Alego, V.; Schweinsberg, D. P. *Corros Sci* 1995, 37, 975.
34. Kim, H.; Jang, J. *Polym Bull* 1997, 38, 249.
35. Yongqi Hu, D. E.; Nikles, D. E. *J Polym Sci A, Polym Chem* 2000, 38, 3278.
36. Abdel Aal, M. S.; Ahdan, M. H. *Br Corros J* 1981, 16, 205.
37. Khamis, K.; Atea, M. *Corrosion* 1994, 50, 106.
38. Mann, C. A. *TransElectrochem* 1936, 69, 105.
39. Jeyaprabha, C.; Sathiyarayanan, S.; Phani, K. L. N.; Venkatachari, G. *Appl Surface Sci* 2005, 252, 966.
40. Luo, H.; Gyn, Y. C.; Han, K. N. *Corrosion* 1998, 54, 721.
41. Gerovich, M. A.; Rybalchenko, G. F. *Zh. Fiz Khim* 1958, 32, 109.
42. Murakawa, T.; Hackerman, N. *Corrosion Sci* 1964, 4, 387.
43. Moretti, G.; Quartarone, G.; Tassan, A.; Zingales, A.; *Werkst Korros* 1994, 45, 641.
44. Ashassi-Sorkhabi, H.; Nabavi-Amri, S. A. *Electrochim Acta* 2002, 47, 2239.
45. Riggs, O.L. Jr. in: C.C. Nathan (Ed.), *Corrosion Inhibitors*, NACE, Houston, TX 1973, p 7.