New Polymer Syntheses, Part 44: Synthesis, Characterization, and Corrosion Inhibition Behavior of New Polyurea Derivatives Based on Diaryl Ether in the Polymers Backbone

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ABSTRACT: A new interesting class of polyurea derivatives 5_{a-c} was synthesized using solution polycondensation technique by the interaction of 1 mol of 4,4′-bis(2″-aminothiazol-4″-yl)diphenyl ether monomer **3** with 1 mol of diisocyanate compounds in pyridine. The model compound **4** was synthesized by the interaction of 1 mol of monomers **3** with 2 mol of phenylisocyanate in pyridine, and the structure was confirmed by correct elemental and spectral analyses. The resulting polymers were characterized by elemental and spectral analyses besides solubility and viscometry measurements. The thermal properties of those polymers were evaluated by TGA, DTG, and DTA measurements and correlated to their structural units. In addition, the morphological properties of a selected example were tested by SEM, and the electrical properties of these polymers were measured. On the other hand, the corrosion inhibition properties of selected example of polyurea derivatives were carried out on steel in $0.5M$ H_2SO_4 at 40°C giving cathodic inhibition. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 620–628, 2009

Key words: synthesis; characterization; thiazole; polyurea; diaryl ether

INTRODUCTION

Polyurea is a unique polymer with a wide range of physical and chemical properties such as abrasion resistance, water repellency, leather appearance, etc. These properties provided by polyurea coating to cotton or cotton–polyester blended fabrics are very attractive in many textile applications: transportation (e.g., car seats), apparel (e.g., waterproof breathable jackets), and furnishings (e.g., artificial leather upholstery). But, these polyurea coatings have poor flame retardancy.[1] The isocyanate group can react with water to make possible moisture-curing polyurea coatings.[2] The addition of a flame retardant to polyurea coatings is necessary to improve the fire behavior of the coating and the underlying material. Polyurethaneephosphate combinations are known to form flame retardant intumescent systems.[3–6] A number of methods have been used to prepare polyureas, but the best method includes the reaction of diamine with diisocyanates. This reaction is a step-growth addition reaction of amine across the carbon–nitrogen double bond, and there is no byproduct. Polyureas are very tough materials with high

hardness and good chemical resistance. They can be tailor-made to obtain properties that lead to versatile applications such as coating systems for waterproofing and corrosion protection.[7] Attempts to synthesize new types of thermally stable polyureas such as phosphorus-containing and heterocyclic polyureas to obtain different properties have been reported.[8–10]

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 such as acid pickling, acid cleaning of boilers, decaling, and oil well acidizing utilize several of acidic solutions.[11,12] The important prerequisites for a compound to be an efficient inhibitor are: (i) it should form a defect free, compact barrier film, (ii) it should be 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.[13] Organic compounds having π bonds are found to inhibit corrosion of steel by getting adsorbed over the electrode surface through electron sharing.[14] The presence of functional groups such as NH, —N=N—, —CHO, R—OH, R=R, etc., in the inhibitor molecule[15] and also the steric factors, aromaticity, electron density at the donor atoms are found to influence the adsorption of the inhibitor molecule

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over corroding electrode surface. Recently, some polymers[16–18] have attracted a great deal of attention because of their wide range of industrial applications and economics. Because of the presence of extensive delocalization of π-electrons, these polymers could serve as better corrosion inhibitors at very low concentrations. The investigation in this article deals with the synthesis and corrosion inhibition behavior of new polyurea derivatives based on diaryl ether, which contain aliphatic or aromatic moieties in the polymer backbone.

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 ^{1}H-NMR spectra were recorded on a varian EM-390-NMR (90 MHz) spectrometer or GNM-LA (400 MHz) spectrophotometer at room temperature in DMSO or CDCl$_3$ using TMS as the internal reference. 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. Thermogravimetric analysis (TGA), differential thermal gravimetric (DTG), and differential thermal analysis (DTA) were carried out in air with TA 2000 thermal analyzer at heating rate of 10°C/min in air. The electrical conductivities were measured using a Keithly electrometer (610C). The morphologies of polymers were examined by scanning electron microscopy (SEM) using a Jeol JSM-5400 LV instrument. The corrosion properties were carried out at a temperature of 40 ± 1°C as Fisher Scientific Isotemp Model 9000. Potentiodynamic polarization studies were carried out using EG and G PARC potentiostat/galvanostat (model 273).

Reagents and solvents

Diphenylether (Merck) and Chloroacetyl chloride (Aldrich) were used without purification. Diisicyanate monomers (Aldrich) were also used without purification. Absolute ethanol and thiourea is obtained from El-Nasr Chemical Company (Egypt). All other solvents were of high purity and were further purified by standard methods.[19]

Monomer syntheses

Bis (4-chloroacetyl)diphenylether 2

To a conical flask containing 1.6 mL (10 mmol) of diphenylether 1, and 1.59 mL (20 mmol) of chloroacetylchloride dissolved in 60 mL of carbon disulphide, anhydrous aluminum chloride 5.34 g (40 mmol) was added in small portions. The reaction mixture was stirred in an ice-bath for 6 h. The carbon disulphide was evaporated, and the residue was poured into cold hydrochloric acid, and the resulting yellow precipitate was collected and recrystallized from ethanol (m.p 103°C, yield 82%).

Anal. Calcd. for C$_{16}$H$_{12}$O$_3$Cl$_2$:Calcd.% C, 59.44; H, 3.71; Cl, 21.98.

Found%: C, 59.38; H, 3.64; Cl, 21.91.

Synthesis of 4,4′-bis(2″-aminothiazol-4″-yl) diphenyl ether 3

A mixture of 1 g (3.09 × 10^{-3} mol) of 4,4′-bis(chloroacetyl)diphenyl ether 2; and 0.47 g (6.18 × 10^{-3} mol) of thiourea in 20 mL absolute ethanol was refluxed for 4 h. The clear solution was poured onto cold sodium acetate solution and the precipitated product was collected by filtration and crystallized from ethyl acetate as yellowish crystals, m.p 240°C, yield 87%.

Anal. Calcd. for C$_{18}$H$_{14}$N$_4$OS$_2$:Calcd% C, 59.01; H, 3.82; N, 15.30; S, 17.48

Found%: C, 58.95; H, 3.86; N, 15.13; S, 17.59

Synthesis of model compound

In a 100-mL round flask, (0.002 mol), 0.732 g of monomer 3 was dissolved in dry pyridine, and (0.004 mol), 0.476 g of phenylisocyanate was introduced. The reaction mixture was heated under reflux for 12 h. After cooling at room temperature, the reaction mixture was poured on to ice-water, and white needles appeared and are separated out by filtration, air dried, and recrystallized as needles from ethanol; yield: 83%, m.p. 205°C.

Anal. Calcd. for C$_{32}$H$_{24}$ N$_6$O$_3$ S$_2$:Calcd% C, 63.57; H, 3.97; N, 13.90; S, 10.59.

Found%: C, 63.66; H, 4.05; N, 13.77; S, 10.64.

Polymerization

A solution polycondensation technique was used in the synthesis of polyurea derivatives as follows:

General procedure

In a three-necked flask equipped with a condenser, dry nitrogen inlet and outlet. A mixture of (0.002 mol) of monomer was dissolved in 30–40 mL of dry pyridine. The different aromatic and aliphatic diisocyanate (0.002 mol), dissolved in 15 mL of dry pyridine, were added in drop-wise manner during stirring. After complete addition of the diisocyanate, the reaction mixture was heated under reflux for 12–

TABLE I
Results of Elemental Analyses, and Some Physical properties of Polyurea Derivatives 5$_{a-c}$

Poly. No.	Analysis								Yield%	η_{inh}*(dI/g)	Electrical Conductivity $(\Omega \text{ cm})^{-1}$
	C%		H%		N%		S%				
	Calc.	Found	Calc.	Found	Calc.	Found	Cal.	Found			
5$_a$	58.42	58.47	4.86	4.80	15.73	15.76	11.98	12.06	87	–	8.97×10^{-13}
b	64.28	64.12	3.89	3.95	13.63	13.69	10.38	10.45	82	1.11	–
c	60.00	59.87	3.70	3.75	15.55	15.46	11.85	11.82	84.6	1.02	7.46×10^{-11}

* Inherent viscosity measured in DMSO at 30°C.

14 h. After cooling at room temperature, the reaction mixture was poured on to ice-water; a white–yellowish precipitate appeared. The solid polymers separated out, filtered off, washed with water, hot alcohol, hot acetone, and then dried under reduced pressure at 80°C for 2 days. The synthesized polymers, their yield and some of their properties are listed in Table I.
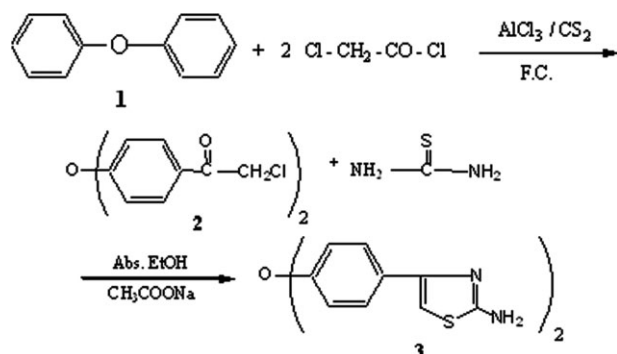
RESULTS AND DISCUSSION

A new interesting class of polyurea derivatives that containing diaryl ether in the polymer backbone was synthesized. These polymers were necessitating the synthesis of monomer and model compound.

Monomer syntheses

Synthesis of 4,4′-bis(2″-aminothiazol-4″-yl)diphenyl ether 3

Chloroacetylation of diphenyl ether **1** using normal condition of Friedel-Crafts reaction (anhydrous aluminum chloride, carbon disulphide) led to the formation of 4,4′-bis(chloroacetyl)diphenyl ether **2** as a highly crystalline pale yellow compound with a sharp melting point. The structure of this premonomer was confirmed by elemental and spectral analysis as represented in our previous work.[20]

The monomer compound **3** was synthesized by the interaction of 4,4′-bis(chloroacetyl)diphenyl ether **2** with thiourea in absolute ethanol, mostly according to the known mechanism,[21] described in our previous work,[20,22] as shown in Scheme 1.

Elucidation of the structure of monomer **3** was based on correct elemental and spectral data. The IR spectrum displayed characteristic absorption bands at 3400–3290 cm^{-1} because of primary amino group and absorption band at 1625 cm^{-1} because of C=N (cf. Fig. 1). The ^{1}H-NMR spectrum (in DMSO-d$_6$, ppm) showed the following δ values: at 7.8–6.95 (m, 8H of aromatic and 2-CH-S) and at 6.97 (s, 4H of primary amino group, interfered with the aromatic protons and exchangeable with D$_2$O) (cf. Fig. 2). The mass spectrum exhibited a molecular ion peak at m/z = 365.80 (100%) which is in agreement with its molecular formula (C$_{18}$H$_{14}$N$_4$OS$_2$). Other peaks were observed at m/z = 333.80 (M$^+$—2NH$_2$, 0.4%); at m/z = 267.77 (M$^+$—C$_3$H$_3$N$_2$S, 19.1%) and at m/z = 167.86 (M$^+$—C$_6$H$_6$N$_4$S$_2$, 0.4%).

Synthesis of model compound

Before attempting polymerization, model compound **4** was synthesized by the interaction of 1 mol of monomer **3** with 2 mol of phenylisocyanate in pyridine as described in Scheme 2.
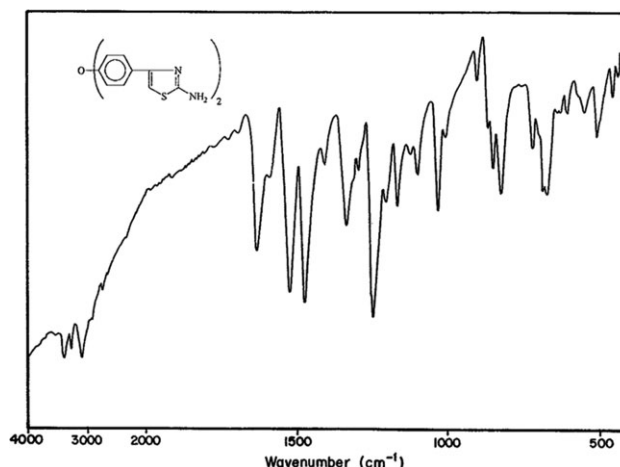

Scheme 1 Synthesis of bisamino thiazole monomer 3.

Figure 1 IR spectrum of monomer 3.

Figure 2 ^{1}H-NMR spectrum of monomer 3.

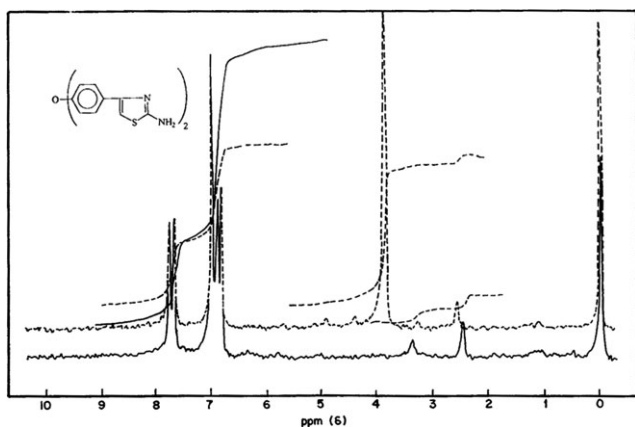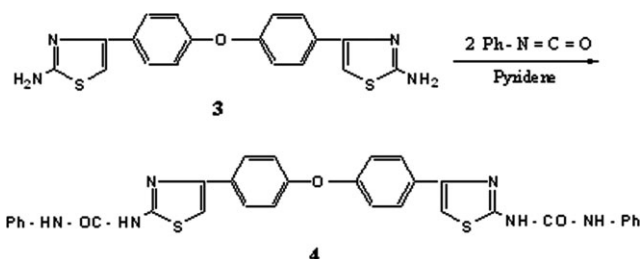**Figure 3** ^{1}H-NMR spectrum of model 4.

The structure of this model compound was confirmed by correct elemental and spectral data. The IR spectra showed a new characteristic absorption bands at 3330 cm^{-1} for (NH) of urea derivative, at 1680 cm^{-1} for (C=O) of urea derivative, at 2940 cm^{-1} for CH stretching of aliphatic, at 3030 cm^{-1} for CH stretching of aromatic, at 1595 cm^{-1} for C=N (thiazole ring), and at 1240–1270 for C—O—C (ether linkage). In addition, other characteristic bands due to specific groups present in the various model compounds were also evident in the IR spectrum. The ^{1}H-NMR spectrum of model compound **4** (in DMSO-d_6, ppm) showed the following δ values: at 8.6–8.9 (m, 4H, for 4 NH groups); and at 7.80–6.90 m, (20 H for aromatic and 2—CH—S in thiazole rings). The bands at 2.49 and 3.33 for the DMSO which used as a solvent. (cf. Fig. 3).

Polymer syntheses

Our interest was focused on the synthesis and characterization of new series of polyurea derivatives **5$_{a-c}$**, using solution polycondensation technique[23,24] by the interaction of 1 mol of monomer **3** with 1 mol of diisocyanate compounds in pyridine as described in Scheme 3.

The structure of the resulting polymers was also established from elemental analyses and spectral data. The elemental analyses of all the polymers coincided with the characteristic repeating units of each polymer; the data are included in the experi-
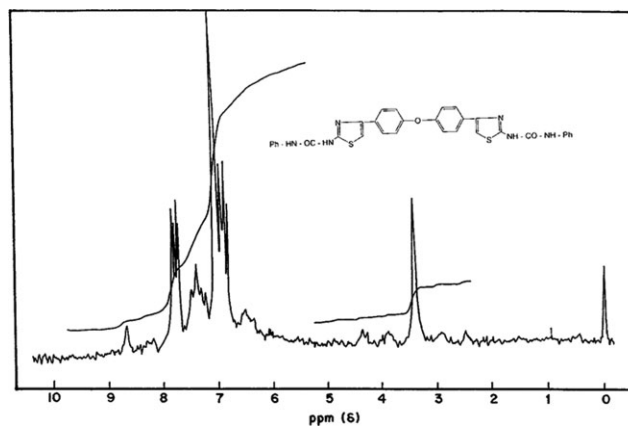
mental part. The IR spectral data of all polyurea derivatives showed a new characteristic absorption bands at 3330 cm^{-1} for (NH) of urea derivative and at 1680 cm^{-1} for (C=O) of urea derivative. Other characteristic absorption bands due to specific groups present in the various polymers were also evident in the IR spectra (cf. Fig. 4).

Polymer characterization

The various characteristics of the resulting polyurea derivatives including solubility, viscometery, thermal analysis (TGA and DTA), SEM, and electrical conductivity were also determined and the data are discussed below. On the other hand the corrosion inhibition properties of selected examples of polyurea derivatives were carried out on steel in 0.5M H$_2$SO$_4$ at 40°C.

Room temperature solubility characterizations of all the synthesized polyurea derivatives 5a–c were tested using various solvents including: DMF, DMSO, DMA, THF, chloroform–acetone (1 : 1; v/v), methylene chloride, formic acid and conc. H$_2$SO$_4$. A 5% (w/v) solution was taken as a criterion for

Scheme 2 Synthesis of model compound **4**.
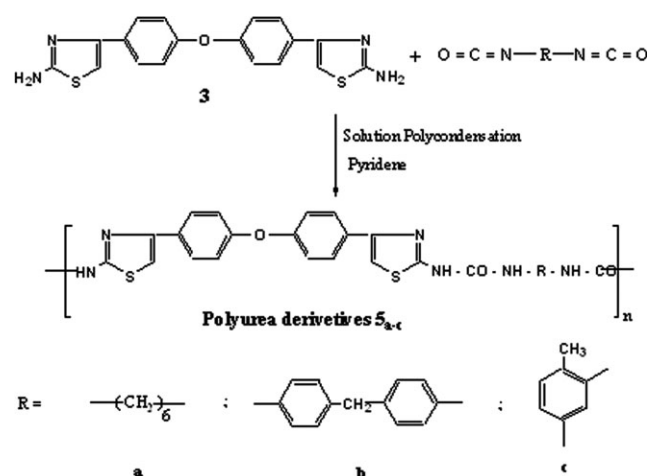
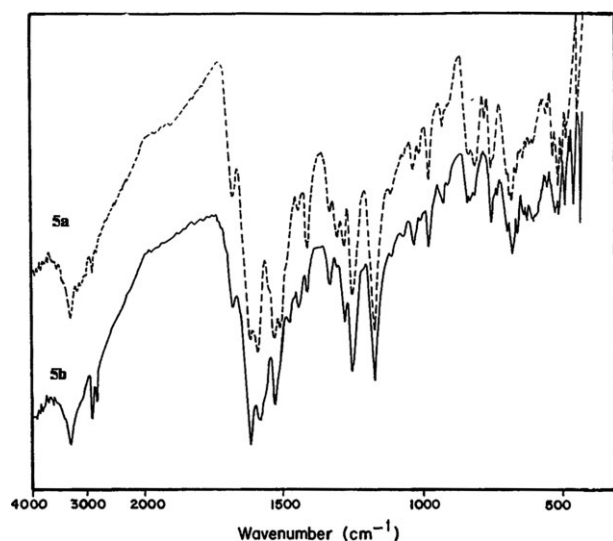**Scheme 3** Synthesis of polyurea derivatives **5$_{a-c}$**.

Figure 4   IR spectra of polyurea **5$_{a,b}$**.

solubility. It can be clarified from Table II that all the polyurea derivatives 5a–c were partially soluble in most simple organic solvents such as: alcohols, benzene, and acetone but dissolved completely in concentrated sulfuric acids giving a yellow color. In other protonic solvents such as formic acid, these polymers were partially soluble. It can be clarified from Table II that all the synthesized polymers were partially soluble in methylene chloride and chloroform acetone mixture. In polar aportic solvents such as DMSO, DMF, DMA, and even in THF it was found that the resulting polyurea derivatives based on diaryl ether 5a–c were partially soluble in these solvents except polymer 5b which was completely soluble in (DMSO) and polymer 5c which was completely soluble in (DMSO and DMA).

The inherent viscosities (η_{inh}) of polyurea derivatives **5$_{a–c}$** were determined in DMSO at 30°C with an Ubbelohde suspended level viscometer The inherent viscosity value is defined as:

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

The solution concentration C is 0.5g/100 mL, η/η_o = relative viscosity (or viscosity ratio). It can be shown from Table I that polyurea **5$_{b,c}$** had high vis-

cosities (1.11, 1.02 dL/g receptivity) and this may be attributed to high molecular weight of these polymers. The study of selected examples of polyurea derivatives using SEM measurements showed that the surface of polyurea **5$_c$** [Fig. 5(a), magnification X = 200] consisted of fibrous structure, with higher magnification X = 1500, X = 2000 (Fig. 5(b,c), respectively) showed aggregates of layers structure.

The thermal properties of polyurea derivatives **5$_{a,c}$** were evaluated by thermogravimetric analysis (TGA), differential thermal gravimetry (DTG), and by differential thermal analysis (DTA) in air at a heating rate of 10°C min^{-1}. The thermographs of selected samples from these polymers are given in (Fig. 6), while the temperatures for various % weight loss for the synthesized polymers were as the following: for polyurea **5$_a$** 275°C (10%), 354°C (20%), 420°C (30%), 474°C (40%), and 508°C (50%); for polyurea **5$_c$** 256°C (10%), 327°C (20%), 450°C (30%), 530°C (40%), and 560°C (50%). The initial decomposition of all the selected polymers (10% loss) is considered to be the polymer decomposition temperature (PDT)[25,26]; it occurred in the range 256 to 294°C. Therefore, the previous data indicate that the thermal stabilities of the selected polyurea (at 10%) are in the order **5$_a$** > **5$_c$**. It should be noted that the T_{10}% and T_{20}% were unexpected for both the two polymers **5$_a$** and **5$_c$**, where T_{10} and T_{20} for polymer **5$_c$** is somewhat less than polymer **5$_a$**, starting from T_{30} and T_{40} and so on..., the **5$_c$** begin to more thermal stable and this is also indicated from the DTA curves which showed that the **5$_c$** was decomposed at more thermally stable The thermal stability for both the polymer **5$_c$**, which contain aromatic linkage and the polymer **5$_a$**, which contain (CH$_2$)$_6$ aliphatic linkage unit was appeared clearly at T_{30}, T_{40}, and T_{50}% i.e., the only exception in the values of T_{10} and T_{20}. It should be noted that the initial decreased thermal stability of the polymer **5c** and increased thermal stability of polymer **5a** are probably due to the substitution in the benzene ring of **5c** and even number of aliphatic carbon atoms in **5a** which aids close proximity in the hydrogen bonding in the polyurea derivatives.
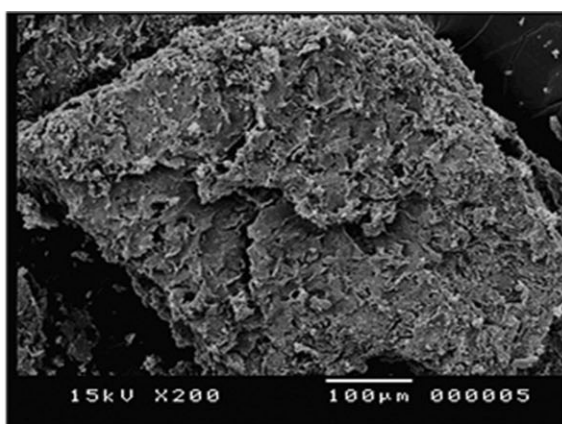
For the selected examples of polyurea derivatives, the thermographs (Fig. 6) showed that the polymers

TABLE II
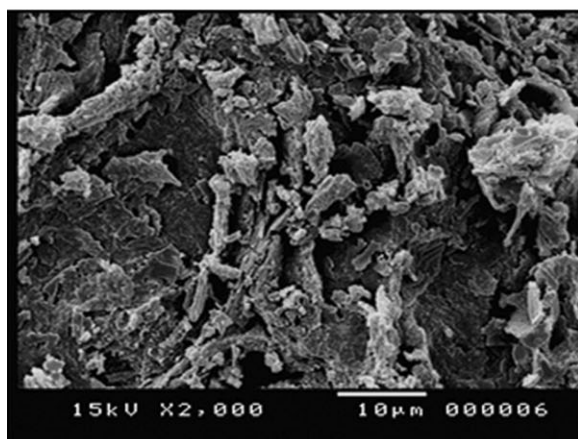**Solubility Characteristics of Polyurea Derivatives 5$_{a–c}$**

Polymer number	DMF	DMSO	DMA	THF	Chloroform + Acetone (1 : 1)	CH$_2$Cl$_2$	HCOOH	Conc H$_2$SO$_4$
5$_a$	+	+	+	+	+	+	+	++
b	+	++	+	+	+	+	+	++
c	+	++	++	+	+	+	+	++

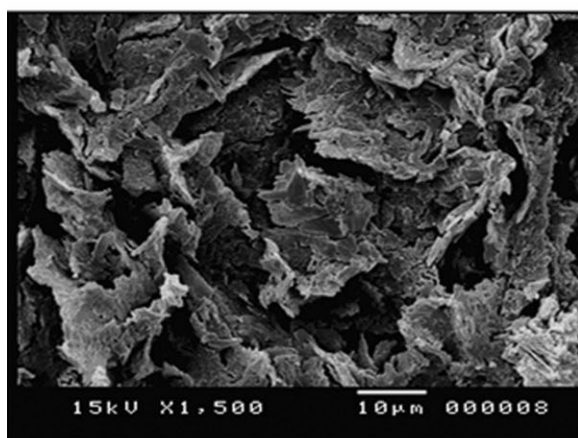++ Soluble at room temperature (RT).
+ Partially soluble at (RT).

(a)

(b)

(c)

Figure 5 The SEM images of the polymer surface of polyurea 5_c. (a) $X = 200$, (b) $X = 1500$ and (c) $X = 2000$.

decomposed in four steps. The first three steps are overlapped and ranged between 200 and 440°C, whereas the fourth step is some what separate and ranged between 460 and 611°C. The degradation is maximum at around 537–577°C generally in the fourth step. The rate of degradation in the fourth

step is some what faster than in the three overlapped steps. The determination of glass transition temperature T_g by using DTA measurements is a well known technique. Most long chain synthetic polymers show characteristic sequence of changes as they are heated. From the DTA curves of polyurea, 5_c as a selected example showed very broad T_g at 136.83°C, and T_m at 227.93°C.

The electrical conductivity was measured as follows: The sample was inserted in a laboratory made holder between two copper disks (insulated with Teflon) after which the sample resistivity was measured directly at 25°C with polymer disks, which had been prepared by compressing the finely powdered polymers at 2.92 N/m^2 under vacuum. The resistivity values were calculated from the following equation:

$$Resistivity = RA/D \, ohm \, cm$$

where R represents resistance (ohm), a is area of the polymer disk (cm^2) and D is the disk thickness (cm).

The conductivity σ of selected polyurea derivatives was calculated using Arrhenius equation as (σ = 1/resistivity) $ohm^{-1} \, cm^{-1}$. The values were in the range 10^{-11}–10^{-13} $ohm^{-1} \, cm^{-1}$ being obtained, this indicates that the polymers are in the range of insulator materials, which means that these polymers acting as non conducting polymers. (cf. Table I).

Corrosion inhibition properties

The work described in this property concentrated on the study of the corrosion inhibition properties of selected example of polyurea derivative 5_a on C-steel in 0.5M H_2SO_4 at 40°C.

Material preparation

AR grade H_2SO_4 (Merck) were used for preparing solutions. Double distilled water was used to prepare solutions of 0.5M H_2SO_4. The synthesized inhibitor was characterized through their elemental and spectral data (as described before).

The inhibitor solution was prepared by dissolving the appropriate weight in 1 mL concentrated H_2SO_4. The resultant solution was transferred into 10 mL measuring flask and completed with bidistilled water. The required concentration was added to the cell via a digital micro-pipetter.

Electrochemical measurements

The electrochemical experiments were performed using a conventional three electrode cell assembly at
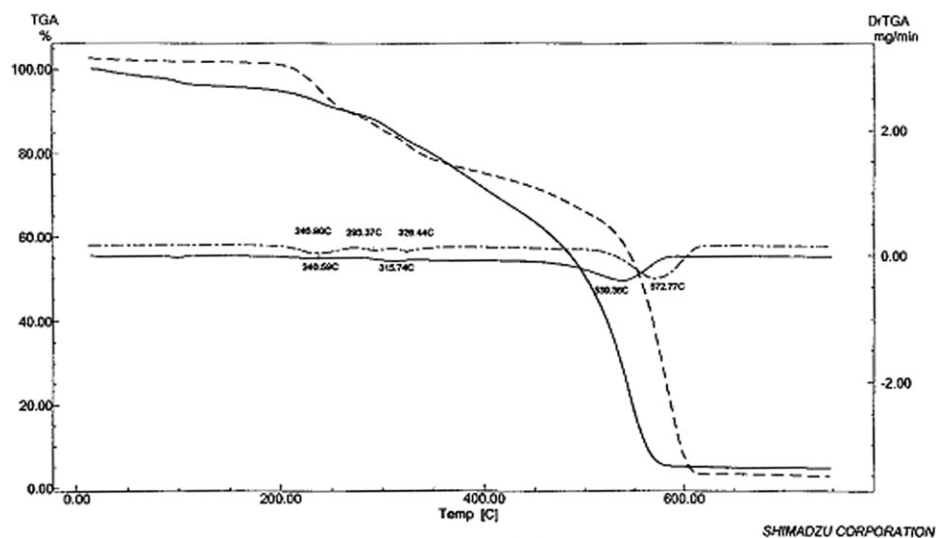
Figure 6 The TGA and DTG traces of polyureas $5_{a,c}$ in air at a heating rate of 10°C/min.

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; M_n, 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 ± 1°C as Fisher Scientific Isotemp Model 9000. Potentiodynamic polarization studies were carried out using EG and 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:

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

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

Results and discussion

The potentiodynamic polarization behavior of C-steel in 0.5M H_2SO_4 with addition of various concentrations of polyurea 5_a within the Tafel region are shown in Figures 7, 8 and Table III represent the corrosion kinetic parameters in the absence and presence of the selected sample. It is a well known fact that compounds with high molecular weight and bulky structure may cover more area on the active electrode surface.[27] For the polyurea 5_a, it is evident from Table III that The calculated inhibition efficiency (IE%) ranging within 64 ± 15% within the added concentration range 0.1–2 ppm. The increase of polymer concentration (10, 50 ppm) decrease sharply the (IE%) which means that, at higher values tends to be accelerator. The best value of (IE%) is obtained at 2 ppm to reach 78.52%, so that it is not preferable to use the higher concentrations of polyurea as corrosion inhibitor due to the lower value of (IE%) obtained.
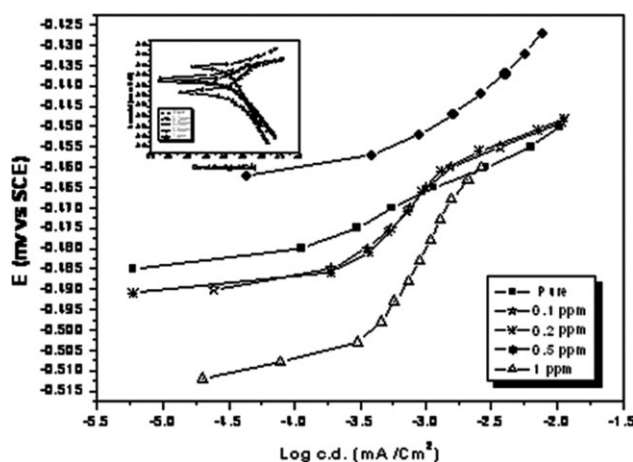

Figure 7 Potentiodynamic polarization curves of mild steel of polyurea 5_a in 0.5M H_2SO_4 at 40°C (low conc.).

TABLE III
Corrosion Parameters for Mild Steel in 0.5M H$_2$SO$_4$ in the Absence and Presence of Various Inhibitor (Polyurea) from Tafel Technique at 40°C

| Inhibitor Conc. (ppm) | Ecorr. (volt) | 0.5M H$_2$SO$_4$ | | |
		Icorr. mA	IE %	CR (mpy)
Blank	−0.484	1.001	–	0.4622×10^3
5$_a$				
0.1	−0.491	0.3775	62.28	0.1744×10^3
0.2	−0.492	0.3413	65.90	0.1577×10^3
0.5	−0.490	0.5072	49.33	0.2343×10^3
1	−0.513	0.2304	76.98	0.1064×10^3
2	−0.513	0.2151	78.52	0.3558×10^3
5	−0.517	0.9346	6.63	0.4317×10^3
10	−0.524	0.7713	22.94	0.3563×10^3

Polarization studies. Both anodic and cathodic polarization curves for C-steel in H$_2$SO$_4$ at various concentrations of polyuea **5a** are shown in Figures 7 and 8. It is clear that the presence of inhibitor causes a markedly decrease in the corrosion rate, i.e., shifts the cathodic curves to more negative potentials.

Moreover, it is clear from the desired table to show that the steady state (E_{corr}.) potential is found to be shifted by 7–40 mv in the cathodic direction in the presence of added polyurea **5$_a$** and it is clear from the slop of Tafel line changed according to the value of inhibitor concentration. This means that polyurea **5$_a$** acts as cathodic inhibitor, which may be because of the large increase in (E_{corr}.) in the negative direction (c.f. Figs. 7, 8).

The inhibitor has a significant effect on the rate of hydrogen evolution reaction. On the other hand, the nonionic surfactant has slight effect on the anodic curves. It may be concluded that polyurea **5a** acts as a cathodic-type inhibitor. The cathodic Tafel slopes changed upon addition of increasing inhibitor concentration, whereas the anodic Tafel slopes did not changed obviously upon addition of polyurea **5a**. Therefore, it can be arranged mainly as cathodic-type inhibitor than anodic in H$_2$SO$_4$.

The decrease of (IE%) at the most highly concentrations (10,50 ppm) can be attributed to the higher adsorbed molecular weight of **5$_a$** which case healing from the electrode surface to leave it uncovered surface (clear) to show active surface.

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 parier film. The desired polyurea in aqueous solutions exist as either neutral molecules or in the form of cations[28,29] depending on the concentration of H$^+$ ions in solutions. The protonated molecules are mostly the predominant.
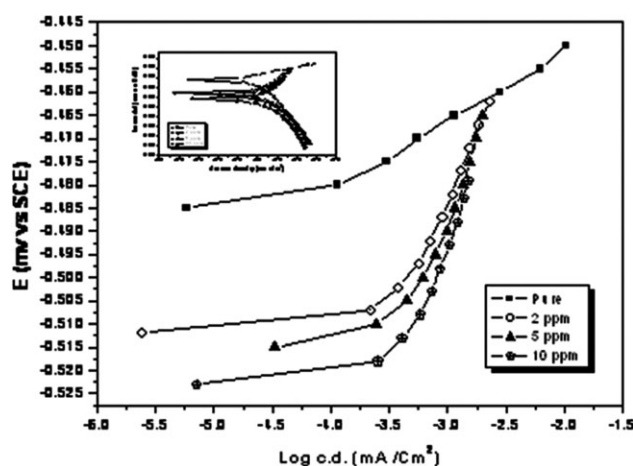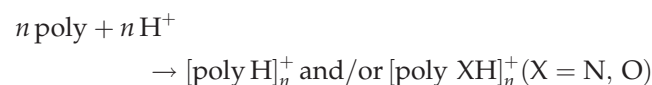
$$n\,\mathrm{poly} + n\,\mathrm{H}^+$$
$$\rightarrow [\mathrm{poly\,H}]_n^+ \text{ and/or } [\mathrm{poly\,XH}]_n^+ (\mathrm{X = N, O})$$

The positively charged polyurea cation interacts electrostatically with negatively charged metal surface.[30] 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.[31] The point of zero charge (pzc) of iron in sulfuric acid is positive with respect to corrosion potential.[32] The inhibitive effect of the same compound at high concentration may be because of 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 because of the effect of electron interaction containing polymer and structure of the molecule on the metal surface.
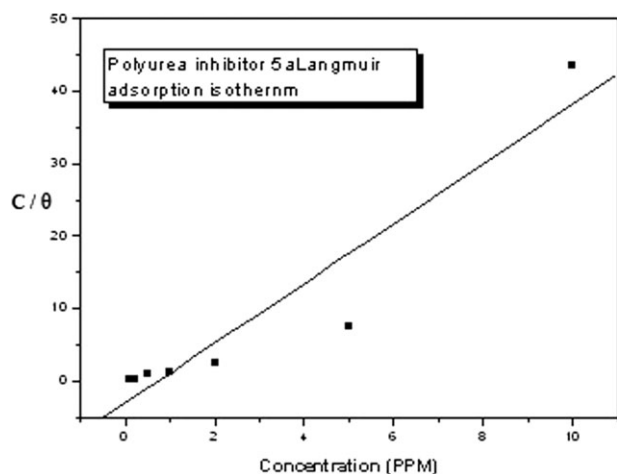

Figure 8 Potentiodynamic polarization curves of mild steel of polyurea **5$_a$** in 0.5M H$_2$SO$_4$ at 40°C (high conc.).

Figure 9 Langmuir adsorption isotherm for the polyuea 5a on carbon steel at 40°C.

Adsorption isotherm. Assuming the adsorption of polyurea **5a** on the metal surface obeys Langmuir adsorption isothermal equation[33]:

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

where C is the concentration of inhibitor, K is the adsorptive equilibrium constant and θ is the surface coverage, θ was calculated by the Sekine and Hirakawa's method.[34] Figure 9 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 carbon steel/produced water interface obeys Langmuir adsorption isotherm. 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.[35]

CONCLUSION

A new interesting series of polyurea derivatives containing diaryl ether moiety in the polymers main chain were synthesized by polycondensation technique in pyridine. Neither solubility nor swelling was observed in common organic solvents. The resulting polymers were partially soluble in polar aportic solvents except polymer $5_{b,c}$, which was completely soluble in (DMSO). The order of higher solubility was $5_c > 5_b > 5_a$. The conductivity σ of selected polyurea derivatives was in the range of insulator materials (10^{-11}–10^{-13} ohm cm^{-1}). Polyurea 5_a acts as cathodic-type inhibitor.

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