

A novel cyclopolymer containing residues of essential amino acid methionine: synthesis and application

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Abstract Ethyl ester hydrochloride of essential amino acid methionine upon treatment with allyl bromide affords *N,N*-diallyl methionine ethyl ester (**I**) which after treatment with HCl leads to a novel monomer *N,N*-diallyl methionine ethyl ester hydrochloride (**II**). Monomer **II** is cyclocopolymerized with sulfur dioxide in acetone or ethanol to obtain the corresponding water-insoluble alternate cocyclopolymer **III** (i.e., **II**-*alt*-SO₂), while quite surprisingly, the polymerization carried out in dimethyl sulfoxide (DMSO) affords a water-soluble terpolymer **IV**: (**II**{in sulfide form}-*alt*-SO₂)-*ran*-(**II**{in sulfoxide form}-*alt*-SO₂) in which half of the sulfide groups has been oxidized to sulfoxide groups via oxygen exchange with solvent DMSO. Polymer **IV** containing the residues of methionine demonstrates superior inhibition of mild steel corrosion in 1 M HCl at 60 °C; inhibition efficiency (IE) of 99 % is achieved at a concentration of 25 ppm. At a meager concentration of 1.25 ppm, the polymer leads to an astonishing IE of 93 %, while its corresponding monomer **II** achieves an IE of 31 % at the same concentration. The adsorption of polymer **IV** on the metal surface was found to obey the Langmuir adsorption isotherm. The high negative $\Delta G_{\text{ads}}^{\circ}$ value of $-57.7 \text{ kJ mol}^{-1}$ ensured the favorability of the adsorption process and indicated the prevalence of both electrostatic adsorption and chemisorption. The polymer having multiple adsorption sites gave superior protection of mild steel surface than methionine or its ester derivative **I** or the monomeric counterpart **II**.

Keywords Methionine · Cyclopolymerization · Sulfur dioxide · Diallylamine salt · Corrosion inhibition

Introduction

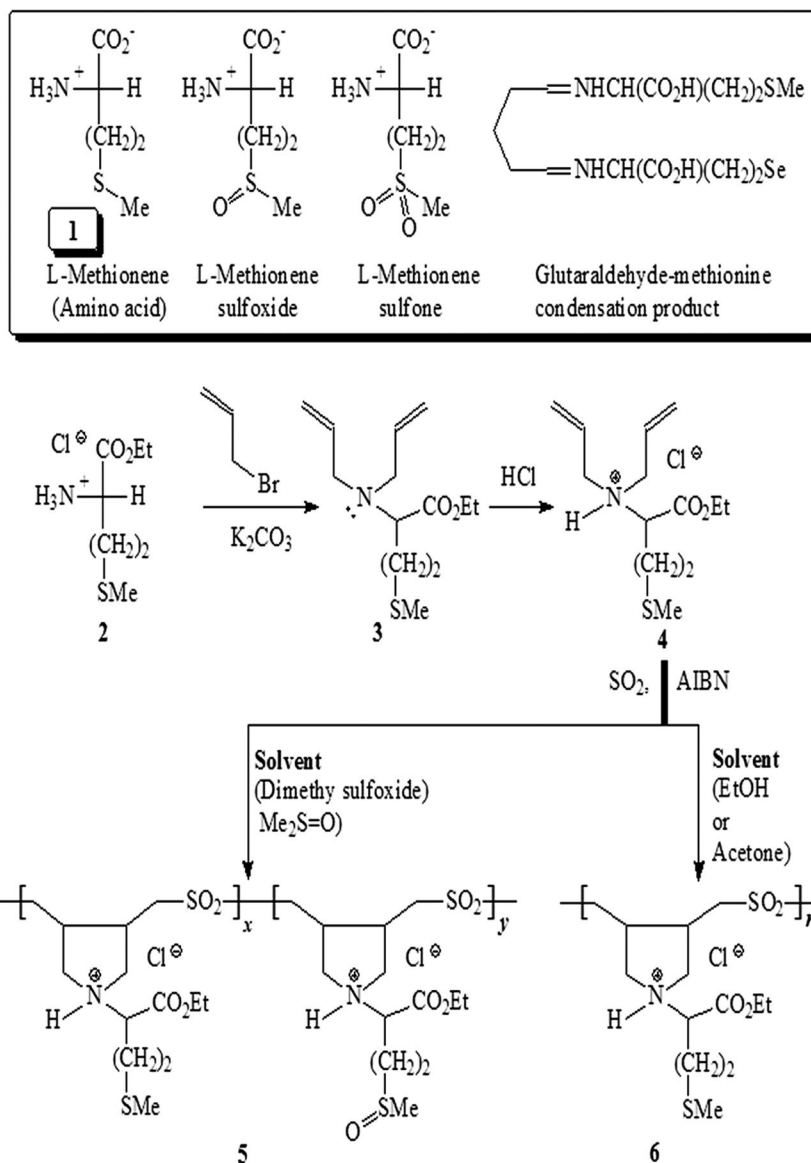
Butler's cyclopolymerization protocol [1–3] involving diallyl ammonium salts has led to a plethora of industrially significant pyrrolidine ring-embedded cyclopolymer whose architecture is considered to be the eighth most important structural type [4, 5]. Over one thousand publications and patents have been published on poly(diallyl dimethyl ammonium chloride), a Butler's cyclopolymer, and over 35 million pounds of this product alone are sold per year for water purification and personal care formulations [1]. Numerous diallyl ammonium monomers have also been copolymerized with SO₂ to give value-added products [6–8]. The work presented in this article describes for the first time the use of Butler's cyclopolymerization protocol [1–3] for the formation of cyclopolymer **5** and **6** having residue of essential amino acid methionine in each repeating unit (Scheme 1).

One of our objectives is to investigate the efficacy of functional motifs of trivalent amine and sulfide in a polymer backbone for inhibiting metal corrosion. Inhibition of metal corrosion by organic inhibitors is influenced by the presence of heteroatoms whose efficacies are known to increase in the order O < N < S < P [9]. The inhibitor molecules interfere with anodic or cathodic reactions occurring on the metal surfaces, and thus prevent or minimize corrosion process [10–12]. The greater polarizability of the lone pair of electrons in the third period elements makes them better inhibitors as a result of formation of coordinate-type bonds to cover and safeguard the metal surface. In addition to being available at low cost, the non-toxic amino acid

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Scheme 1 Cyclopolymers containing residues of amino acid methionine



methionine is attractive as a green inhibitor of mild steel corrosion since it contains three important heteroatoms: N, O and S (Scheme 1). The methionine at a concentration of 25 ppm has been shown to impart 47 % the corrosion inhibition of mild steel in 0.1 M HCl at 25 °C [13]. At respective concentrations of 149, 165 and 181 ppm of methionine, methionine sulfoxide and methionine sulfone, the inhibition efficiency (IE) against copper corrosion in 1 M HNO_3 is determined to be 79, 85 and 88 %, respectively [14]. In corrosive environments of 1 M HCl at 30 °C and 2 M HCl at 25 °C containing 149 ppm of methionine and 1000 ppm of glutaraldehyde–methionine condensation product, respectively, the corresponding IEs of mild steel corrosion are reported to be 89 [15] and 84 % [16].

The use of methionine as a green corrosion inhibitor has thus achieved modest IEs. The industry demands much

greater efficacies to the tune of 99 % or more. Corrosion is a great concern with cost, safety, health and environmental aspects, which are on the priority list of both industry and society [12, 17]; even an improvement of 1 % efficacy translates into a considerable saving. The polymers undergo stronger adsorption onto metal surfaces because of multiple anchoring sites, and thus exhibit better IE than their monomeric analogs [18–20]. We realized that a polymer, containing residue of methionine keeping intact the integrity of its sulfide motifs and unquenched nitrogen valency (i.e., a trivalent N with its lone pair of electrons), might be beneficial to prevent the corrosion of metals. To achieve this objective, the potentially green novel monomer **4** as well as its cyclopolymers **5** and **6** has been synthesized to investigate their efficacies in inhibiting mild steel corrosion in 1 M HCl.

Experimental

Materials

L-Methionine ethyl ester hydrochloride and allyl bromide were purchased from Fluka AG and used as received. Potassium carbonate was purchased from Sigma-Aldrich and used as received. Azobisisobutyronitrile (AIBN) (Fluka AG) was crystallized (CHCl_3 –EtOH). Dimethyl sulfoxide (DMSO) was dried and distilled ($\text{bp}_4 \text{ mmHg}$ 64–65 °C). Acetonitrile, diethyl ether, acetone and ethanol from Fluka AG were used as received. Concentrated HCl (Fisher Scientific) was used to prepare 1 M HCl.

Physical methods

Elemental analyses and IR spectra were carried out on a Perkin Elmer Elemental Analyzer (Series II, Model 2400) and a Perkin Elmer FTIR (16F PC FTIR) spectrometer, respectively. The ^1H and ^{13}C NMR spectra have been measured on a Jeol LA 500 MHz spectrometer in CDCl_3 , D_2O or CD_3OD . An Ubbelohde viscometer (having viscometer constant of 0.005718 cSt/s) was used for the measurements of viscosities using CO_2 -free water under N_2 to avoid CO_2 absorption that may affect the viscosity data.

Synthesis of *N,N*-diallyl-L-methionine ethyl ester (3)

A mixture of **2** (16.0 g, 75 mmol), K_2CO_3 (31.0 g, 225 mmol), allyl bromide (19.1 g, 157.5 mmol) in acetonitrile (150 mL) under N_2 was stirred at 50 °C for 24 h. The cooled mixture in ether (200 mL), after washing with water ($3 \times 75 \text{ mL}$), was dried and distilled using a vigreux distilling column to obtain **3** (15 g, 78 %), bp (2 mbar Hg) 110 °C. Anal. calcd for $\text{C}_{13}\text{H}_{23}\text{NO}_2\text{S}$: C, 60.66; H, 9.01; N, 5.44; S, 12.46; found: C, 60.5; H, 8.9; N, 5.3; S, 12.2; ν_{max} (neat) 3078, 2979, 2917, 2838, 1729, 1641, 1450, 1368, 1160, 1115, 1027, 994, and 920 cm^{-1} ; δ_{H} (CDCl_3) 1.29 (3 H, t, J 7.0 Hz), 1.87 (1H, m), 1.97 (1H, m), 2.09 (3H, s), 2.56 (2H, m), 3.08 (2H, dd, J 7.6, 14.7 Hz), 3.34 (2H, m), 3.59 (1H, dd, J 6.1, 8.9 Hz), 4.17 (2H, m), 5.14 (4 H, m), 5.76 (2H, m); δ_{C} (CDCl_3): 14.38 (1C, SCH_3), 15.32 (1C, OCH_2CH_3), 29.05 (1C, $\text{CH}_2\text{CH}_2\text{S}$), 30.87 (1 C, $\text{CH}_2\text{CH}_2\text{S}$), 53.44 (2C, NCH_2), 60.05 (1C, NCH), 60.50 (1C, OCH_2), 116.91 (2 C, $\text{CH}=\text{CH}_2$), 136.48 (2C, $\text{CH}=\text{CH}_2$), 172.83 (1C, CO_2), (77.00, middle C of CDCl_3).

Synthesis of *N,N*-diallyl-L-methionine ethyl ester hydrochloride (4)

Dry HCl was passed onto a solution of amine **3** (13 g, 50.5 mmol) in ether (75 mL) until the supernatant liquid

did no longer become turbid due to the passage of HCl. The hydrochloride salt **4**, separated as an oily liquid, was washed with ether ($2 \times 50 \text{ mL}$) to obtain *N,N*-diallyl-L-methionine ethyl ester hydrochloride **4** (14.3 g, 96 %). Anal. calcd for $\text{C}_{13}\text{H}_{24}\text{ClNO}_2\text{S}$: C, 53.14; H, 8.23; N, 4.77; S, 10.91; found: C, 52.9; H, 8.0; N, 4.7; S, 10.7; ν_{max} (neat) 3418, 3085, 2981, 2919, 1741, 1644, 1427, 1374, 1288, 1204, 1163, 1004, 950, 855 and 777 cm^{-1} ; δ_{H} (D_2O) 1.15 (3 H, t, J 7.0 Hz), 1.97 (3H, s), 2.10 (1H, m), 2.18 (1H, m), 2.48 (1H, m), 2.62 (1H, m), 3.70 (2H, dd, J 7.3, 13.5 Hz), 3.81 (2H, dd, J 7.0, 13.7 Hz), 4.19 (3H, m), 5.48 (4 H, m), 5.76 (2H, m), residual H in D_2O at 4.65 ppm); δ_{C} (D_2O): 14.02 (1C, SCH_3), 15.15 (1C, OCH_2CH_3), 25.88 (1C, $\text{CH}_2\text{CH}_2\text{S}$), 30.44 (1 C, $\text{CH}_2\text{CH}_2\text{S}$), 55.42 (2C, NCH_2), 62.50 (1C, NCH), 64.97 (1C, OCH_2), 126.41 (2 C, $\text{CH}=\text{CH}_2$), 128.06 (2C, $\text{CH}=\text{CH}_2$), 169.31 (1C, CO_2), (67.4, dioxane). The ^1H and ^{13}C NMR spectra are displayed in Figs. 1a and 2a, respectively. The DEPT-135 NMR analysis was also performed to confirm the ^{13}C spectral assignments.

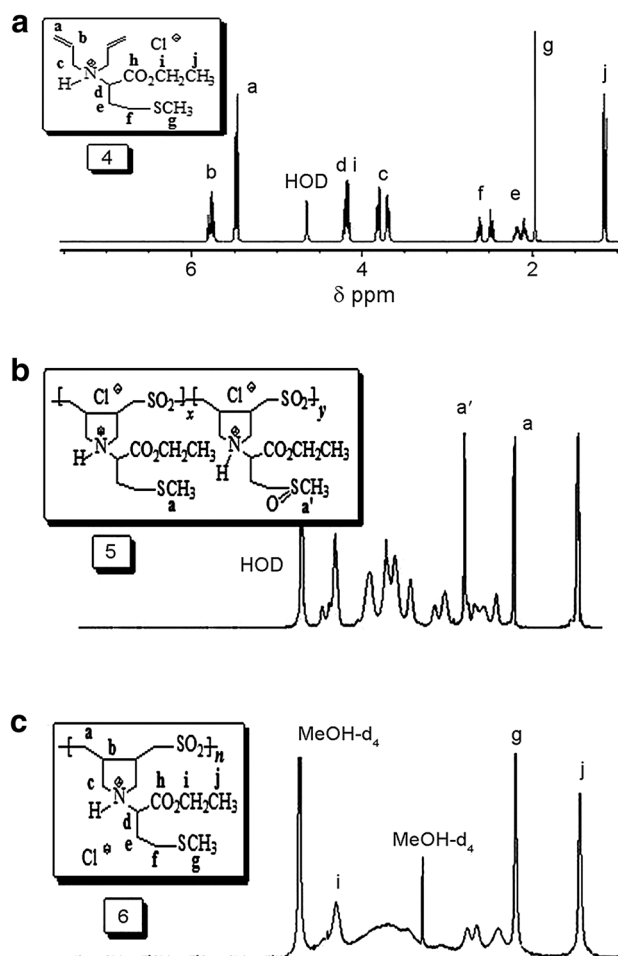


Fig. 1 ^1H NMR spectra of **a** **4** and **b** **5** in D_2O ; and **c** **6** in CD_3OD , respectively

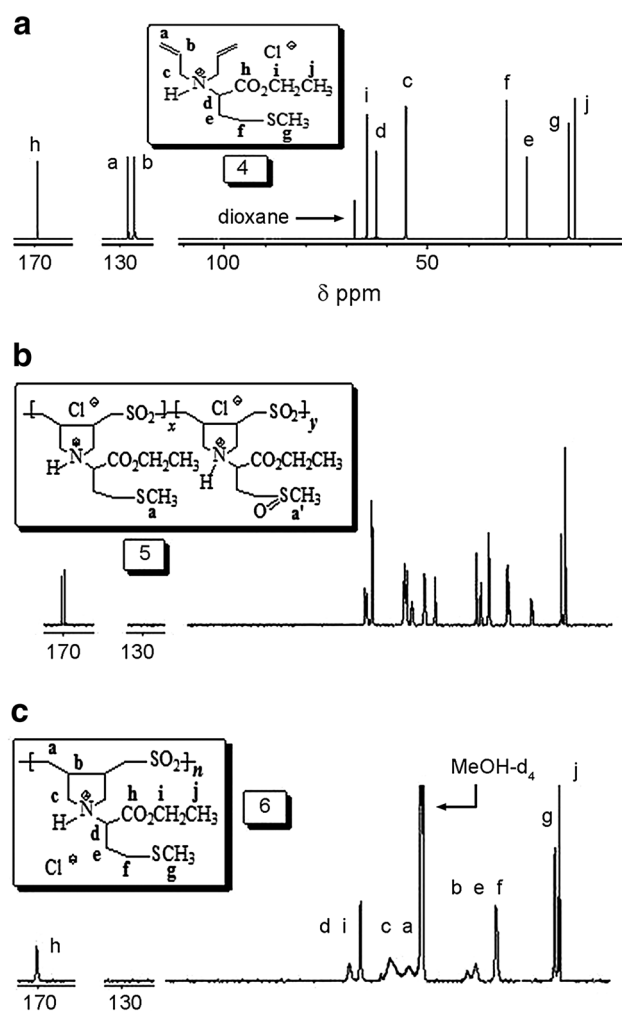


Fig. 2 ^{13}C NMR spectra of **a** **4** and **b** **5** in D_2O ; and **c** **6** in CD_3OD , respectively

Cyclocopolymerization of the monomer **4** with SO_2

As described in Table 1, the detailed procedure adapted in entry 1 is as follow: after adsorption of SO_2 (7 mmol) in a solution of **4** (7 mmol) in DMSO (2 g), AIBN (100 mg) was added. The mixture in a closed flask was stirred at 60°C for 24 h. After precipitating in acetone, polymer **5** was dried in vacuo at 55°C (6 h) (yield 75 %). When the polymerization was repeated in ethanol (2 g) or acetone (2 g), polymer **6** was obtained in 72 and 77 % yields, respectively. Anal. calcd for **6**: $\text{C}_{13}\text{H}_{24}\text{ClNO}_4\text{S}_2$: C, 43.63; H, 6.76; N, 3.91; S, 17.92 %; found: C, 43.4; H, 6.6; N, 3.8; S, 17.7; ν_{max} (KBr) 3425, 2922, 2611 (br), 1740, 1633, 1450, 1377, 1308, 1219, 1128, 1014, 853 and 594 cm^{-1} . The IR spectrum of **5** is almost identical to that of **6** except that an absorption at 1050 cm^{-1} attributed to the S=O stretching absorption of **5**; its elemental analysis supported the presence of sulfide and sulfoxide in a ratio of $\approx 1:1$. The

Table 1 **4**/ SO_2 cyclocopolymerization^a to **5**ⁱ and **6**ⁱⁱ

Entry no	Solvent (g)	AIBN(mg)	Yield (%)	Intrinsic viscosity ^b (dL g^{-1})
1 ⁱ	DMSO (2)	100	75	0.235 ^c
2 ⁱⁱ	Ethanol (2)	100	72	0.176 ^d
3 ⁱⁱ	Acetone (2)	100	77	0.205 ^d

^a Carried out using 7 mmol each of **4** and SO_2 in a solvent at 60°C for 24 h

^b Viscosity of 1–0.125 wt% solution at 30°C was measured with a Ubbelohde viscometer ($K = 0.005718\text{cSt/s}$)

^c In 0.1 M NaCl

^d In methanol

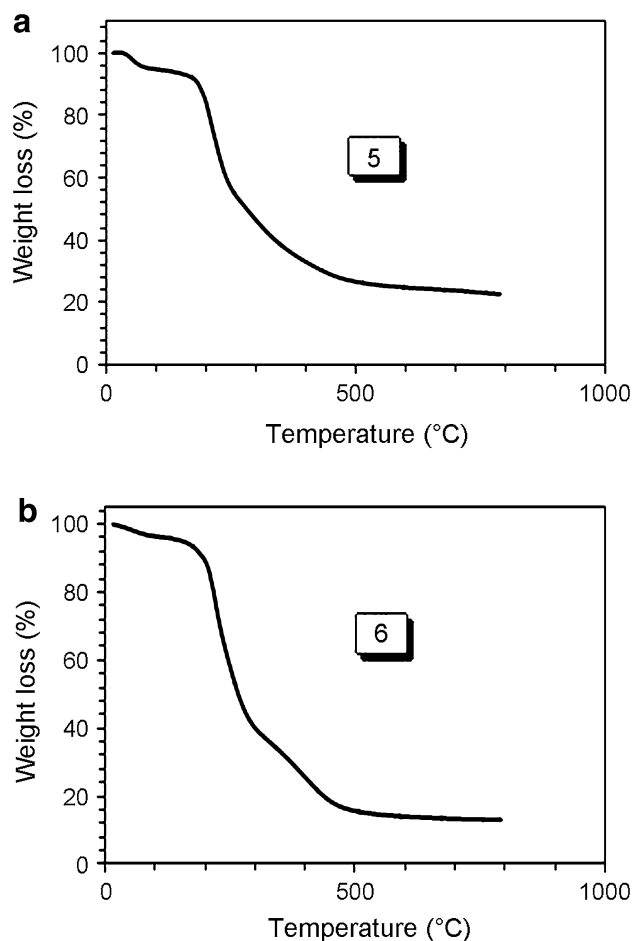


Fig. 3 TGA curves of **a** **5** and **b** **6**

^1H and ^{13}C NMR spectra of **5** are shown in Figs. 1b and 2b, respectively, while those of **6** are displayed in Figs. 1c and 2c. The thermal decomposition of **5** or **6**: $240\text{--}250^\circ\text{C}$ (decomposed, turned black). The thermogravimetric analysis (TGA) curves of **5** and **6** are given in Figs. 3a and b, respectively.

Corrosion inhibition tests

For gravimetric measurements, the coupons of mild steel have the composition (wt%): 0.082 % (C), 0.032 % (Si), 0.207 % (Mn), 0.016 % (Cr), 0.062 % (Ni), 0.012 % (Mo), 0.045 % (Al), 0.029 % (Cu), 0.042 % (W), 0.014 % (Pb), 0.048 % (Sn), 0.017 % (Zn), 0.027 % (As), <0.019 % (N), <99.3 % (Fe).

The inhibition efficiencies (IEs) were determined as described elsewhere [19–21] after immersing steel coupons having dimension of $2.5 \times 2.0 \times 0.1 \text{ cm}^3$ into 1 M HCl (Fisher Scientific Company) (250 cm^3) containing 0 (blank) or various amounts of (>0–100 ppm) the inhibitors at 60 °C for 6 h. The IE was obtained using Eq. (1):

$$\%IE = \frac{\text{Weight loss (blank)} - \text{Weight loss (inhibitor)}}{\text{Weight loss (blank)}} \times 100. \quad (1)$$

The average percent losses were used (triplicate determinations, standard deviation: 0.4–1.5 %). The relative weight loss method [21–23] was used to determine the % IEs in cases where the initial masses of the coupons differed.

A set of over 20 weight loss experiments including three blanks was carried out simultaneously in a constant temperature bath ($60 \pm 0.5 \text{ }^\circ\text{C}$). For the blanks, the initial masses of steel coupons were 3.9356, 3.8980, and 4.0645 g with respective surface area of 10.90, 10.90 and 11.16 cm^2 . They lost a mass of 0.8923, 0.8560 and 0.8910 g, respectively, after 6 h immersion in 1 M HCl at 60 °C. The corrosion rates (CR) in mmpy were calculated using the following Eq. (2):

$$\text{mmpy} = \frac{87.6 W}{DAT} \quad (2)$$

where W is the weight loss in mg, D the density in g cm^{-3} ($= 7.87 \text{ g cm}^{-3}$ for iron), A is the area in cm^2 and T is time in hours. The corrosion rates (CR) in mmpy were found to be 148.6 ± 3.1 mmpy. The blanks repeated in several other occasions gave a CR within 1–2.5 %.

Results and discussion

Synthesis of monomer, polymers and their solution properties

Methionine ester hydrochloride **2** upon reacting with allyl bromide gave its diallyl derivative **3**, which was converted into its hydrochloride salt **4** in excellent yield (Scheme 1). At the outset, we were apprehensive about the polymerizability of cationic monomer **4** under free radical conditions: In addition to the presence of degradative chain transfer allylic motifs [24, 25], the monomer also contained the

sulfide functionality, which is a known chain transfer agent. However, to our delight, the monomer readily underwent cyclocopolymerization with SO_2 using free radical initiator AIBN. One of the interesting findings of this work is the formation of cyclopolymer **5** (i.e., {4-sulfide-alt- SO_2 }-ran-{4-sulfoxide-alt- SO_2 }) in solvent DMSO while the expected polymer **6** (i.e., 4-sulfide-alt- SO_2) was obtained in solvent ethanol or acetone. The details of the polymerizations including their intrinsic viscosities are given in Table 1. The formation of polymer **5** having sulfide and sulfoxide moieties in a 1:1 ratio is quite puzzling. While terpolymer **5** was found to be water-soluble, copolymer **6** was water-insoluble, but soluble in methanol. The water-solubility of the unexpected product **5** was a blessing in disguise because the corrosion inhibition study demands its solubility in aqueous environment. The water-solubility of **5** could be attributed to the greater polarity of the sulfoxide motifs. This type of exchange of oxygen between sulfide and sulfoxide has been reported in the oxidation of methionine to methionine sulfoxide in the presence of DMSO/HCl [22]. The intrinsic viscosity $[\eta]$ was obtained from viscosities of 1–0.125 wt% solutions at 30 °C using an Ubbelohde viscometer. The $[\eta]$ values of the synthesized polymers were determined using Huggins viscosity relationship and found to be 0.235 (in 0.1 M NaCl), 0.176 and 0.205 d L g^{-1} (in methanol), respectively (Table 1). Polymers **5** and **6** were stable up to 210 °C as evident from the TGA curves (Fig. 4a, b). Major losses could be attributed to the decomposition involving the release of SO_2 .

FTIR and NMR spectra

The absorptions due to SO_2 unit in polymers **5** and **6** were assigned to the strong bands at ≈ 1315 and $\approx 1100 \text{ cm}^{-1}$, respectively, while a minor absorption at 1050 cm^{-1} is attributed to the $\text{S}=\text{O}$ stretching absorption in **5**. The presence of the ester functionality (CO_2Et) was confirmed by absorption peaks around 1740 cm^{-1} . The absence of any olefinic proton or carbon signals in the polymer spectra ascertains that the termination happens via chain transfer and/or coupling process (Figs. 1, 2) [25, 26]. A look at the proton spectrum of **5** showed the presence of two types of CH_3 signals in **a** and **a'** in Fig. 1b attributed to the presence of sulfide ($\text{S}-\text{CH}_3$) and stronger electron-withdrawing sulfoxide motifs [$\text{S}(=\text{O})\text{CH}_3$]. The two ^{13}C signals around 170 ppm are attributed to two different carbonyl groups in the repeat units of **5** (Fig. 2b). ^{13}C NMR assignments are based on our earlier works on Butler's cyclopolymer [6–8].

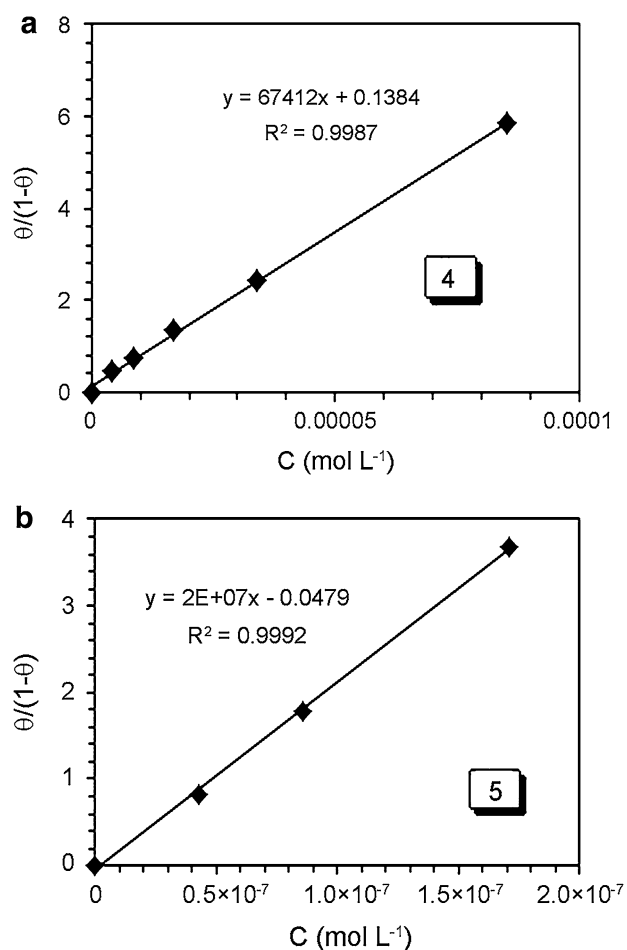
Effectiveness of polymer 5 as a corrosion inhibitor

The results of the % IE (Table 2) of mild steel corrosion at 60 °C in 1 M HCl revealed that polymer **5** gave much

Table 2 Inhibition efficiency (% IE) in the presence of various ppm of inhibitor molecules to prevent corrosion^a of mild steel in 1 M HCl (6 h, 60 °C)

Compound	IE (%) at ppm of compounds								
	0.16	0.31	0.63	1.25	2.5	5	10	25	100
1	—	—	—	—	—	—	—	—	72
2	—	—	—	—	—	57	—	—	87
4	—	—	—	31	43	58	71	85	94
5	45	64	79	93	95	96	97	99	99

^a Corrosion rate (CR) for a set of three blank experiments was found to be 148.6 ± 3.1 mmpy

**Fig. 4** Langmuir adsorption isotherms of **a** **4** and **b** **5** in 1 M HCl at 60 °C

higher protection than its monomer **4** or methionine **1** or **2**. It is an amazing performance by the novel polymer **5** containing methionine residue. The IE of 99 % was achieved at a concentration of 25 ppm, while at a meager concentration of 1.25 ppm, an astonishing % IE of 93 was achieved. The polymer having multiple adsorption sites gave superior

protection than its monomeric counterpart **4** (% IE 31 at 1.25 ppm). Desorption of a polymer chain by unlocking multiple adsorption sites from the metal surface becomes much slower than that of its smaller precursor molecules **1**, **2** and **4**. This slow desorption [18–20] is expected to impart efficient and greater protection as observed experimentally in the current work.

Adsorption isotherms

Fractional inhibition efficiency (i.e., % IE/100), obtained from the weight loss measurements, is equated to surface coverage (θ) of the metal surface by an inhibitor molecule at its lower concentration range (Table 2). The θ values obtained from weight loss measurement in 1 M HCl and C (the concentration in mol/L) were used to find the best fit among the following adsorption isotherms (Eqs. (3), (4), (5) [27] and (6) [28]):

$$\text{Temkin } (K_{\text{ads}}C = e^{f\theta}) \quad (3)$$

$$\text{Langmuir } (\theta/(1-\theta) = K_{\text{ads}}C) \quad (4)$$

$$\text{Frumkin } (K_{\text{ads}}C = \theta/(1-\theta)e^{-2\theta}) \quad (5)$$

$$\text{Freundlich } (\theta = K_{\text{ads}}C^n) \quad (6)$$

For both **4** and **5**, the Langmuir isotherms became the best fit as revealed by the correlation coefficients (Fig. 4a, b). The equilibrium constant K_{ads} and the free energy of adsorption ($\Delta G_{\text{ads}}^{\circ}$) are related by Eq. (7) [21–23]:

$$K_{\text{ads}} = \frac{1}{55.5} e^{\frac{-\Delta G_{\text{ads}}^{\circ}}{RT}}. \quad (7)$$

The K_{ads} for the adsorption of **4** and **5** were determined to be 67,412 and 2.00×10^7 L mol^{−1}, respectively, leading to the corresponding $\Delta G_{\text{ads}}^{\circ}$ values of −41.9 and −57.7 kJ mol^{−1} (Table 3). Generally, $\Delta G_{\text{ads}}^{\circ}$ up to −20 kJ mol^{−1} and in the range −80 to −400 kJ mol^{−1} are attributed to physisorption and chemisorption, respectively. The chemisorption occurs because of formation of coordinate type of bond by sharing electrons of the inhibitor molecules and the vacant orbital on the metal surface. The calculated $-\Delta G_{\text{ads}}^{\circ}$ values −41.9 kJ mol^{−1} for **4** and −57.7 kJ mol^{−1} for **5** indicate the prevalence of both electrostatic adsorption and chemisorptions [29, 30].

Table 3 The values of the adsorption equilibrium constant and free energy from Langmuir adsorption isotherms

Compound	K_{ads} (L mol ^{−1})	$\Delta G_{\text{ads}}^{\circ}$ (kJ mol ^{−1})
4	67,412	−41.9
5	2.00×10^7	−57.7

The presence of π -electrons, sulfide and sulfoxide in **5** is expected to interact with the d-orbitals of iron or accumulated Fe^{2+} on the anodic sites to form coordinate type of bond.

Conclusion

Amino acid methionine-based novel cyclopolymers **5** and **6** have been synthesized via Butler's cyclopolymerization protocol. The anticipated environment-friendly polymer **5** containing a polarizable sulfide, a sulfoxide, and amine motifs demonstrated superb corrosion inhibition behavior in 1 M HCl. Work is currently undergoing in our laboratory to hydrolyze the ester functionalities in **5** and **6** to convert them into potential anionic antiscalants [31, 32]. Gravimetric weight loss method is the simplest yet most reliable, used in this work for the determination of corrosion efficiencies; however, using various electrochemical techniques, an in-depth study of corrosion inhibition by this amazing polymer is currently underway in our laboratory.

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