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ORIGINAL PAPER

Cyclopolymers from *N*,*N*-diallyl-*N*-propargyl-(12-*N*′-formylamino)-1-dodecylammonium chloride and their use as inhibitors for mild steel corrosion

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Abstract A dodecanediamine (DDA)-based new monomer, *N*,*N*-diallyl-*N*-propargyl-(12-*N*′-formylamino)-1-dodecylammonium chloride, on homo- and co-cyclopolymerization (with SO_2) afforded cationic polyelectrolytes, which on acidic hydrolysis of the formyl group gave water-soluble polyelctrolytes. One of the allyl groups undergoes cyclopolymerization with either the propargyl or the other allyl group in competing pathways; the incorporation of the allyl group is found to be faster than the propargyl unit by a ratio of 4:1. Both the monomer and its precursor as well as the polymers were used to study the corrosion inhibition of mild steel by gravimetric and electrochemical methods in acidic and saline media at 60 °C. The inhibitor molecules (at a concentration of 200 ppm) exhibited inhibition efficiencies (%IE) in the ranges 81–99 % in 1 M HCl, 97–98 % in 4 M HCl, 87–93 % in 7.7 M HCl, 68–91 % in 0.5 M H_2SO_4, and 84–92 % in 3.5 % NaCl. There is a considerable increase in the IEs by the monomers and polymers in comparison to the parent 1,12-DDA.

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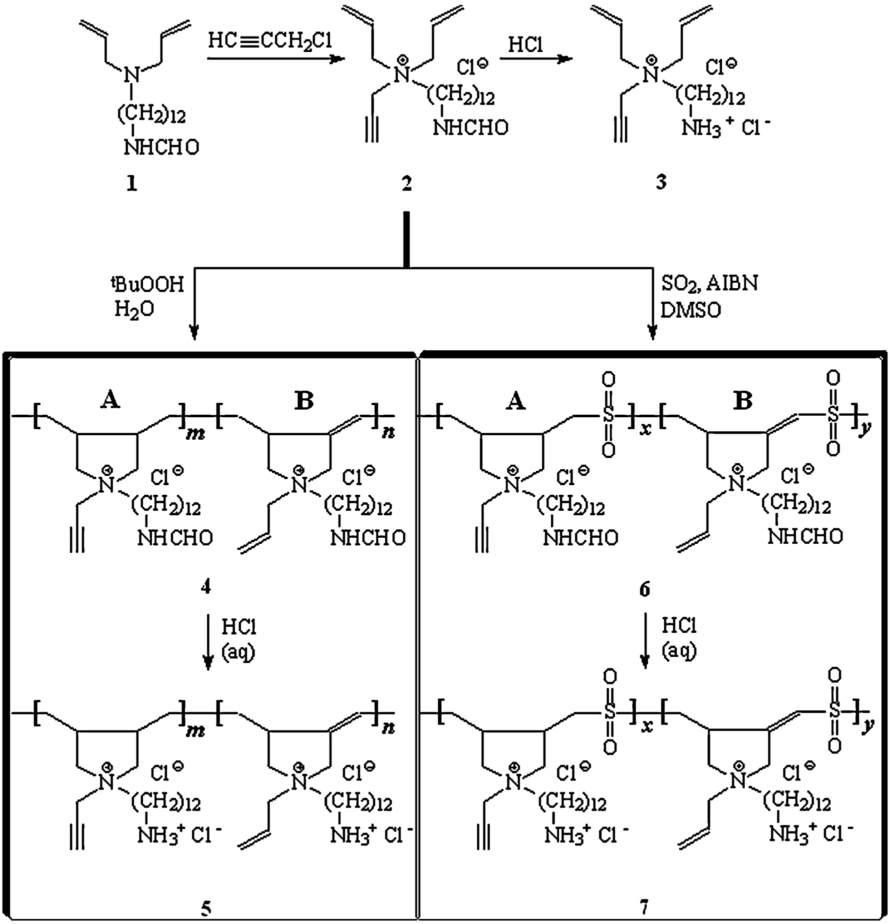
Introduction

Corrosion is a costly process that damages metal due to chemical reaction with the environment [1, 2]. Application of corrosion inhibitors (CIs) is one of the most economic methods to minimize metallic corrosion in a hostile environment [1–4]. Environmental issues have led to an increase in the use of organic inhibitors as replacements for highly toxic inorganic inhibitors such as chromium compounds. Organic compounds containing two functionalities—heteroatoms (N, O, P, or S) of high electron density and hydrophobes of long alkyl chains—are efficient CIs. While the nucleophilic heteroatom undergoes chemisorption via coordination with the iron ions of the metal surface, the inhibitive action of the hydrophobes arises as a result of its ability to form a barrier film that shields the surface from the hostile aqueous media [5–7]. Straight chain fatty amines are usually used as inhibitors of mild steel corrosion in industrial acid pickling. These "filming amines" undergo adsorption onto the metal surface through their amino group while the hydrocarbon chains form a protective monolayer [8].

Polymers with multiple adsorption sites have been shown to undergo much stronger adsorption and exhibit greater corrosion inhibition efficiency (IE) than their corresponding monomer analogs [9–12]. Entropically, favorable displacement of many water molecules from the metal surface by a single polymer molecule along with stronger locking by many adsorption sites makes the desorption of the polymer a slower process. Availability of nonbonded-(lone pair) electrons in heteroatoms and π-electrons in alkenes, alkynes, and aromatic rings in inhibitor molecules may involve in chemisorption; the strength of the coordinate covalent bond thus formed depends upon the electron density and polarizability of the donor atom of the functional groups [13]. In the case of alkynes, it has been proposed that the alkynes undergo polymerization to form a protective film (coating) on the metal surface [14]. The film prevents transport of the corrosive electrolytes to the metal surface and thus results in inhibition of corrosion [15].

With the above discussion in mind, we would like to utilize Butler's cyclopolymerization [16] as well as cyclocopolymerization with SO_2 [17] to synthesize water-soluble polymers having all three important elements—donor atoms, hydrophobic, and alkyne moieties—imbedded in each repeating unit. Cyclopolymerization process of *N*,*N*-diallyl quaternary ammonium salts has led to the synthesis of an array of scientifically and technologically important water-soluble cationic polyelectrolytes. The polymer architecture having five-membered cyclic units embedded in the backbone has been recognized as the eighth major structural type of synthetic polymers. Over 33 million pounds of poly(diallyldimethylammonium chloride) alone are sold annually for water treatment and another 2 million pounds are used for personal care formulation [18]. 1,6-Hexanediamine-based polymers [19] prepared via Butler's cyclopolymerization process have been tested for their IE against mild steel corrosion in 1 M HCl. The polymers were found to be very good inhibitors (IE% ~90), but still there is room for further



Scheme 1 Synthesis of monomers and cyclopolymers

improvement in the IE. With this in mind we report, herein, the synthesis of a 1,12-dodecanediamine (DDA)-based new monomer **2** and their polymers via Butler's cyclopolymerization process (Scheme 1) as well as their inhibiting effects on the corrosion of mild steel in acidic and saline media. It is anticipated that polymers **4**–**7** derived from **2** with a 12 carbon spacer between the nitrogens would impart greater IE against mild steel corrosion.

Experimental

Materials

Propargyl chloride, *t*-butylhydroperoxide (70 wt% solution in water), obtained from Fluka Chemie AG, were used as received. Azobisisobutyronitrile (AIBN) from

Fluka was purified by recrystallization from a chloroform–ethanol mixture. *N*,*N*-Diallyl-*N*′-formyl-1,12-diaminododecane (**1**) was prepared as described [20]. For dialysis, Spectra/Por membrane with MWCO of 6-8000 was purchased from Spectrum Laboratories Inc. Dimethylsulfoxide (DMSO) was dried over calcium hydride overnight and then distilled under reduced pressure at a b.p. of 64–65 °C (4 mmHg). All the solvents were of hplc grade. All the glasswares were cleaned using deionized water. All the reactions were carried out under a positive atmosphere of N_2.

Physical methods

Melting points are recorded in a calibrated Electrothermal-IA9100-Digital Melting Point Apparatus. IR spectra were recorded on a Perkin Elmer 16F PC FTIR spectrometer. ^1H and ^{13}C NMR spectra were measured in $CDCl_3$ and CD_3OD using TMS o in D_2O using dioxane as internal standard on a JEOL LA 500 MHz NMR spectrometer operating at 500 and 125.65 MHz, respectively. Elemental analysis was carried out on a Carlo-Erba Elemental Analyzer Model 1106.

Viscosity measurements were made by an Ubbelohde viscometer (having viscometer constant of 0.005718 cSt/s at all temperatures). Kinetic energy corrections were made to determine the viscosity data using polymer solution in the concentration range 1.5–0.25 g/dL at 30 °C in 0.1N NaCl.

Molecular weights of the synthesized polymers were determined by GPC analysis using Viscotek GPCmax VE 2001. The system was calibrated with nine polyethylene oxide monodispersed standards at 30 °C using two Viscotek columns G5000 and G6000 in series. These polymer samples were analyzed using an aqueous solution of 0.1N $NaNO_3$ as the eluant. Refractive index and viscometer detectors were used to detect polymers.

Potentiodynamic polarisation studies were carried out in a potentiostat (Model 283, EG&G PARC).

Corrosion inhibition tests

Corrosion inhibition tests by gravimetric measurements were performed using coupons prepared from mild steel having the composition: 0.089 % (C), 0.34 % (Mn), 0.037 (Cr), 0.022 (Ni), 0.007 (Mo), 0.005 (Cu), 0.005 (V), 0.010 (P), 99.47 % (Fe). Mild steel containing 0.184 % (C), 0.070 % (Si), 0.29 % (Mn), 0.097 (Cr), 0.071 (Ni), 0.021 (Mo), 0.065 (Cu), 0.014 (V), 0.012 (P), 0.029 % (S), 99.15 % (Fe) were used for electrochemical measurements.

Solutions of 1, 4, and 7.7 M HCl and 0.5 M H_2SO_4 were prepared from reagent A.C.S. concentrated HCl and H_2SO_4 (Fisher Scientific Company) using distilled and deionized water. Inhibitor efficiency was determined at 60 °C for 6 h by hanging the steel coupon measuring $2.5 \times 2.0 \times 0.1$ cm^3 into 1 M HCl (180 cm^3) containing various amounts (from 0 to 400 ppm) of the synthesized inhibitors. (However, in 4 and 7.7 M HCl a volume of 500 cm^3, and in 0.5 M H_2SO_4 a volume of 250 cm^3 was used.) The details of the gravimetric measurements are described elsewhere [21]. Percent inhibition efficiency (%IE) was determined using the following equation

$$\%\mathrm{IE} = \frac{\text{Weight loss (blank)} - \text{weight loss (inhibitor)}}{\text{Weight loss (blank)}} \times 100$$

Weight loss (blank) and weight loss (inhibitor) represent weight loss in the absence and the presence of inhibitor, respectively. Triplicate determinations were made with each of the inhibitors and with solutions containing no inhibitor. The average percent losses were found to have a standard deviation of 0.3–2 %.

For potentiodynamic polarization studies, carbon steel coupons embedded in araldite (affixing material) with an exposed area of 2.0 cm^2 were used. The details of the electrochemical measurements are described elsewhere [21]. The %IE by Tafel extrapolation method was determined using the following equation

$$\%\ \mathrm{IE} = \frac{\mathrm{CR_{blank}} - \mathrm{CR_{inhibitor}}}{\mathrm{CR_{blank}}} \times 100$$

$\mathrm{CR_{blank}}$ and $\mathrm{CR_{inhibitor}}$ represent corrosion rate in mm per year (mmpy) in the absence and the presence of inhibitor, respectively.

Monomer synthesis

*N,N-Diallyl-N-propargyl-(12-N′-formylamino)-1-dodecylammonium chloride (**2**)*

To a solution of compound **1** (15.4 g, 50.0 mmol) in acetone (25 cm^3) was added propargyl chloride (7.45 g, 100 mmol), and the reaction mixture was heated under N_2 in a closed vessel at 78 °C for 24 h. After removal of the solvent the syrupy liquid was triturated with ether several times to remove any unreacted amine and excess propargyl chloride. The quaternary salt **2** was obtained as a thick liquid (18.2 g; 95 %); (Found: C, 68.8; H, 10.0; N, 7.2. $C_{22}H_{39}ClN_2O$ requires C, 68.99; H, 10.26; N, 7.31 %); ν_{max} (neat) 3238, 3038, 2926, 2854, 2122, 1668, 1540, 1468, 1382, 1242, 1034, 966, 846, 724 cm^{-1}; δ_H (D_2O) 1.18 (16H, m), 1.37 (2H, m), 1.64 (2H, m), 3.06 (2H, t, *J* 7.0 Hz), 3.15 (3H, m), 3.85 (4H, app d, *J* 7.3 Hz), 3.99 (2H, s), 5.63 (4H, m), 5.86 (2H, m), 7.87 (1H, s); δ_C (D_2O) 22.09, 26.40, 27.13, 29.14, 29.34, 29.51, 29.57, 29.71, 29.82, 29.84, 38.85, 49.34, 59.16, 61.59 (2 C), 71.67, 82.46, 124.42 (2C), 130.24 (2C), 164.4 (dioxane: 67.4 ppm).

*N,N-Diallyl-N-propargyl-1,12-dodecyldiammonium dichloride (**3**)*

To a solution of the quaternary ammonium salt **2** (2.09 g; 5.46 mmol) was added 10 % hydrochloric acid (5 cm^3) and stirred in a closed vessel at 50 °C for 48 h. A gentle stream of N_2 removed the solvent water. The hydrolyzed quaternary salt **3** was washed with ether several times. The insoluble residue was dissolved in minimum quantity of methanol (~2 cm^3) and again separated from the solvent by adding ether (15 cm^3). This procedure was repeated three times to ensure the removal of any unreacted starting material and formic acid. The oily liquid was dried under vacuum at 50 °C until constant weight (2.03 g; 95 %). (Found: C, 64.2;

H, 10.5; N, 6.9. $C_{21}H_{40}Cl_2N_2$ requires C, 64.43; H, 10.30; N, 7.16 %); ν_{max} (neat) 3427, 3201, 2922, 2107, 2064, 1614, 1517, 1447, 1368, 1018, 954, 831, 729 cm^{-1-}; δ_H (D_2O) 1.23 (16H, m), 1.56 (2H, m), 1.70 (2H, m), 2.89 (2H, t, *J* 7.5 Hz), 3.18 (1H, s), 3.21 (2H, m), 3.90 (4H, app d, *J* 7.3 Hz), 4.04 (2H, d, *J* 2.5 Hz), 5.68 (4H, m), 5.91 (2H, m); δ_C 22.00, 26.20, 26.41, 27.52, 28.88, 29.04, 29.27, 29.35, 29.40, 29.48, 40.38, 49.23, 59.77, 61.54 (2 C), 71.74, 82.38, 124.47 (2 C), 130.15 (2 C) (dioxane: 67.4 ppm).

*Homopolymer **4***

To a solution of monomer **2** (7.0 g, 18.3 mmol) in deionized water (1.75 g) was added *t*-butylhydroperoxide (180 mg) and heated at 50 °C for 24 h and at 80 °C for 40 h. The mixture was dialyzed against distilled water to remove the unreacted monomer. The polymer precipitated out during dialysis as it was found to be insoluble in water. The polymer was found to be soluble in methanol. The pale yellow polymer **4** was then dried under vacuum at 55 °C to a constant weight (4.34 g, 62 %). Mp. softened around 150 °C with no apparent decomposition up to 400 °C; (Found: C, 68.7; H, 10.1; N, 7.2. $C_{22}H_{39}ClN_2O$ requires C, 68.99; H, 10.26; N, 7.31 %); ν_{max} (KBr) 3444, 3038, 2926, 2855, 2120,1666, 1533, 1455, 1378, 1239 and 1033 cm^{-1}.

*Acidic hydrolysis of homopolymer **4–5***

To a solution of the polymer **4** (3.0 g, 7.8 mmol)) in methanol (24 cm^3) was added a 4.5 M HCl (20 cm^3) and the homogeneous mixture was heated at 50 °C for 48 h. The mixture was then dialyzed against distilled water to remove HCl. Polymer solution was then freeze dried to obtain polymer **5** as a white solid (2.9 g, 95 %). Mp. Turned brownish around 220 °C with no apparent decomposition up to 400 °C; (Found: C, 64.1; H, 10.4; N, 7.0. $C_{21}H_{40}Cl_2N_2$ requires C, 64.43; H, 10.30; N, 7.16 %); ν_{max} (KBr) 3442, 2926, 2850, 2120, 1635, 1461, 1384, 1106, 1028 and 718 cm^{-1}. Intrinsic viscosity (η) in 0.1N NaCl at 30 °C was found to be 0.0378 dL/g. The molecular weight ($\overline{M}_W$) and PDI of the polymer **5** were determined to be 4.5×10^4 g/mol and 2.1, respectively.

*Copolymer **6***

In a typical experiment, SO_2 (1.28 g, 20 mmol) was absorbed in a solution of the monomer **2** (7.7 g, 20 mmol) in DMSO (6.0 g). Initiator AIBN (150 mg) was then added under N_2, and the closed flask was stirred using a magnetic stir bar at 60 °C for 24 h. A further 150 mg of AIBN was added and the mixture was stirred at 60 °C for an additional 24 h. The reaction mixture, which remained transparent throughout the polymerization process, was transferred to a dialysis tube with the help of methanol, and dialyzed against deionized water for 48 h to ensure the complete removal of the unreacted monomer. The polymer **6**, which remained insoluble in water, was collected and then dried under vacuum at 50 °C to a constant weight

(5.9 g 66 %). The onset of melting point/thermal decomposition (closed capillary) 180–184 °C (melted to a liquid) and loss of SO_2 gas at around 240 °C; (Found: C, 58.7; H, 8.9; N, 6.1; S, 6.9. $C_{22}H_{39}ClN_2O_3S$ requires C, 59.10; H, 8.79; N, 6.27; S, 7.17 %); ν_{max} (KBr) 3431, 2925, 2853, 2125, 1666, 1541, 1466, 1385, 1311, 1206, 1128, and 1039 cm^{-1}.

*Acidic hydrolysis of copolymer **6***

A solution of copolymer **6** (3.5 g, 7.8 mmol) in methanol (45 cm^3) and concentrated HCl (18 cm^3) was stirred in a sealed flask at 50 °C for 48 h. The reaction mixture was then dialyzed against deionized water for 48 h. The resulting solution was freeze dried to a constant weight (3.35 g, 94 %) of the polymer **7** at 50 °C. The onset of thermal decomposition (closed capillary) 186–192 °C and loss of SO_2 gas at around 240 °C; (Found: C, 54.5; H, 9.0; N, 6.0; S, 6.8. $C_{21}H_{40}Cl_2N_2O_2S$ requires C, 55.37; H, 8.85; N, 6.15; S, 7.04 %); ν_{max} (KBr) 3426, 2930, 2854, 2131, 1629, 1463, 1311, and 1129 cm^{-1}. Intrinsic viscosity (η) in 0.1N NaCl at 30 °C was found to be 0.0327 dL/g. The molecular weight ($\overline{M}_W$) and PDI of the polymer **7** were determined to be 3.7×10^4 g/mol and 1.9, respectively.

Adsorption isotherms

Surface coverage (θ, i.e., fractional IE) values for the inhibitor molecules as determined by the weight loss measurements using various concentrations of the inhibitors in 1 M HCl are reported in Table 1. The θ values and C (the concentration in ppm, i.e., mg/L, was changed mol/L) were used to find the best adsorption isotherm between those more frequently used, i.e., Temkin ($K_{ads}C = e^{f\theta}$), Langmuir ($\theta/(1 - \theta) = K_{ads}C$), Frumkin [22] ($K_{ads}C = \theta/(1 - \theta)\ e^{-2a}\theta$), and Freundluich ($\theta = K_{ads}C^n$) [23].

Table 1 Inhibition efficiency (%IE) for different concentrations of inhibitors for the inhibition of corrosion of mild steel in 1 M HCl (6 h), 4.0 M HCl (3 h), 7.7 M HCl (2 h), and 0.5 M H_2SO_4 (6 h) exposed at 60 °C

Inhibitor	IE at concentration (ppm) of compounds in												
	1.0 M HCl							4.0 M HCl			7.7 M HCl	0.5 M H_2SO_4	
	0.5	1	2	3	5	10	200	5	10	200	200	200	400
1	–	–	–	–	40	48	81	–	–	–	–	–	–
2	50	64	69	74	79	86	97	83	94	98	88	68	77
3	48	66	71	75	80	85	97	84	93	97	87	67	78
5	63	71	74	78	82	87	98	86	94	98	91[a]	73	89
7	74	78	80	82	85	89	99	93	95	98	93[a]	91	94
DDA	–	–	–	–	–	35	57	–	–	–	–	9.0	13

DDA 1,12-Dodecanediamine

[a] Cloudy

The correlation coefficient indicated the best fit for the Temkin adsorption isotherm for inhibitors in 1 M HCl (Table 1; Fig. 6) where K_{ads} is the equilibrium constant of the adsorption process. The linear fitting slope gave the values of *1/f* (Table 4), where f is a molecular interaction parameter [24] related to the molecular interactions in the adsorption layer as well as energetic inhomogeneity of the surface [23].

The equilibrium constant of the adsorption process K_{ads} is related to the free energy of adsorption (ΔG^0_{ads}), by:

$$K_{\text{ads}} = \frac{1}{55.5}\, \mathrm{e}^{\frac{-\Delta G^0_{ads}}{RT}},$$

where 55.5 is the molar concentration of water in solution. Adsorption equilibrium constants K_{ads} and ΔG^0_{ads} that were obtained from the Temkin adsorption isotherms are summarized in Table 4.

Results and discussion

Monomer synthesis

Diallyl monoformate **1**, on alkylation with propargyl chloride, afforded the quaternary ammonium salt **2** in excellent yield (Scheme 1). The quaternary salt, on acidic hydrolysis of the formate group, led to the formation of HCl salts **3** in 95 % yields. The spectroscopic (IR and NMR) and elemental analyses confirmed the structure of the monomer. Absorption at $\sim$2,110 cm^{-1} indicated the presence of alkyne moieties in **2** and **3**. *N*-Formyl proton of **2** appeared at δ 8 ppm (Fig. 1a), while the signal was absent in ^{1}H NMR spectrum of **3** (Fig. 2b). A similar observation was made from the ^{13}C NMR spectra; the *N*-formyl carbon, which appeared at 164.4 ppm for monomer **2**, is absent from the spectrum of **3** (Fig. 3a), thereby ascertaining the complete removal of the formyl group by hydrolysis.

Synthesis, solubility, and spectroscopy of homopolymers

The monomer **2**, on cyclopolymerization in water in the presence of the initiator *t*-butylhydroperoxide, afforded homopolymer **4** which on acidic hydrolysis gave the deformylated homopolymer **5** (Scheme 1). Homopolymer **4** was found to be insoluble in water but soluble in methanol, while the amine salt **5** was water soluble. Homopolymers **4** and **5** turned brownish around 220 °C with no apparent decomposition up to 400 °C.

Careful analysis of the IR and NMR spectra revealed the presence of alkyne moiety in the polymer (absorption at 2,120 cm^{-1} indicated the presence of alkyne moieties in the polymers). Alkyne group is not known to participate in the cyclopolymerization process [25]. However, recent study by us demonstrated the participation of propargyl moiety in Butler's cyclopolymerization process [26].

The ^{1}H spectra of monomer **2**, polymers **4** and **5** are shown in Fig. 1. It is evident, after comparing the proton spectra, that the *N*-formyl proton of **4** (Fig. 1b), which

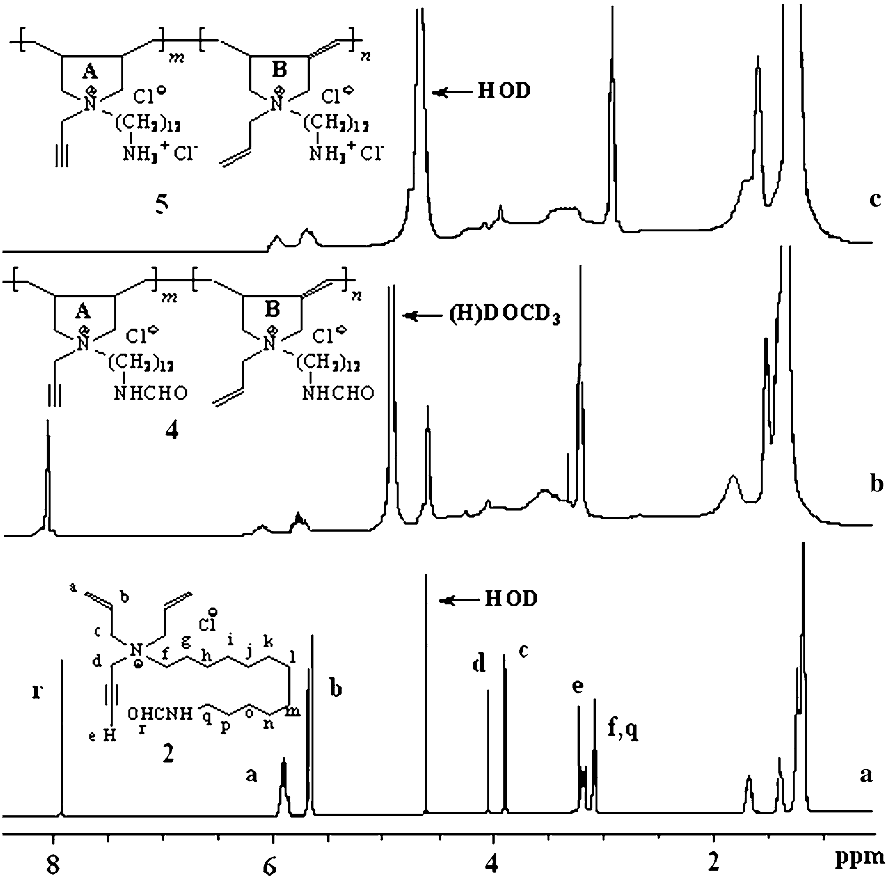


Fig. 1 ^{1}H NMR spectrum of **a** **2** (in D_2O), **b** **4** (in CD_3OD), and **c** **5** (in D_2O)

appeared at δ 8 ppm is absent in the spectrum of **5** (Fig. 1c). A similar observation is made from the ^{13}C NMR spectra (Fig. 3); the *N*-formyl carbon, which appeared at 164.4 ppm for monomer **2** ("Experimental") is present in **4** [δ_C (CD_3OD, TMS) 163.7 ppm] (not shown in the figure) while absent from the spectrum of **5** (Fig. 3b), thus indicating the complete removal of the formyl groups by hydrolysis.

Synthesis, solubility, and spectroscopy of SO_2 copolymers

Monomer **2** underwent cyclocopolymerization with sulfur dioxide in dimethyl sulfoxide (DMSO) solvent using AIBN as the initiator at 60 °C to yield the copolymer **6**, which on acidic hydrolysis was converted to polymer **7** (Scheme 1). Elemental analyses ascertained the **2**/SO_2 ratio of 1:1 thereby implying the alternate nature of the copolymer. Copolymer **6**, like homopolymer **4**, was found to be insoluble in water but soluble in methanol, while the amine salt **7** was water soluble.

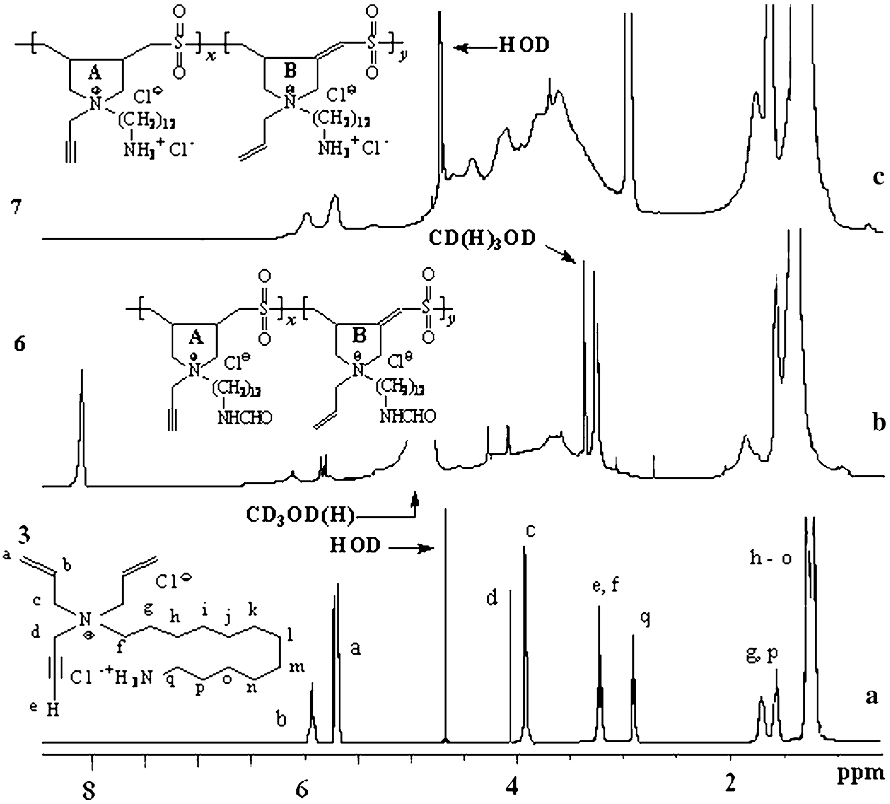


Fig. 2 ^{1}H NMR spectrum of **a** **3** (in D_2O), **b** **6** (in CD_3OD), and **c** **7** (in D_2O)

Dicationic charges in hydrolyzed copolypolymers **7** as well as in homopolymer **5** make them water soluble as anticipated.

Based on earlier reports [27, 28], the cyclopolymers have the linear backbone containing five-membered ring structure embedded on it. The IR spectrum of copolymers **6** and **7** indicated the presence of the SO_2 unit into the polymeric backbone. The two strong bands at ~1,300 and ~1,120 cm^{-1} were assigned to the asymmetric and symmetric vibrations of SO_2 unit.

The ^{1}H spectra of hydrolyzed monomer **3**, polymers **6** and **7** are shown in Fig. 2. It is evident that the *N*-formyl proton of **6** (Fig. 2b) at δ 8 ppm was absent in the spectrum of **7** (Fig. 2c). A similar observation is made from the ^{13}C NMR spectra (Fig. 3); the *N*-formyl carbon, which appeared at 164.4 ppm for the monomer **2** ("Experimental") is present in **6** [δ_C (CD_3OD, TMS) 164.2 ppm] (not shown in the figure) while absent from the spectrum of **7** (Fig. 3c), thus indicating the complete removal of the formyl groups by hydrolysis.

Copolymers **6** and **7** were stable up to 220 °C; thermal degradation appeared to happen at around 230–250 °C and is attributed to the loss of sulfur dioxide.

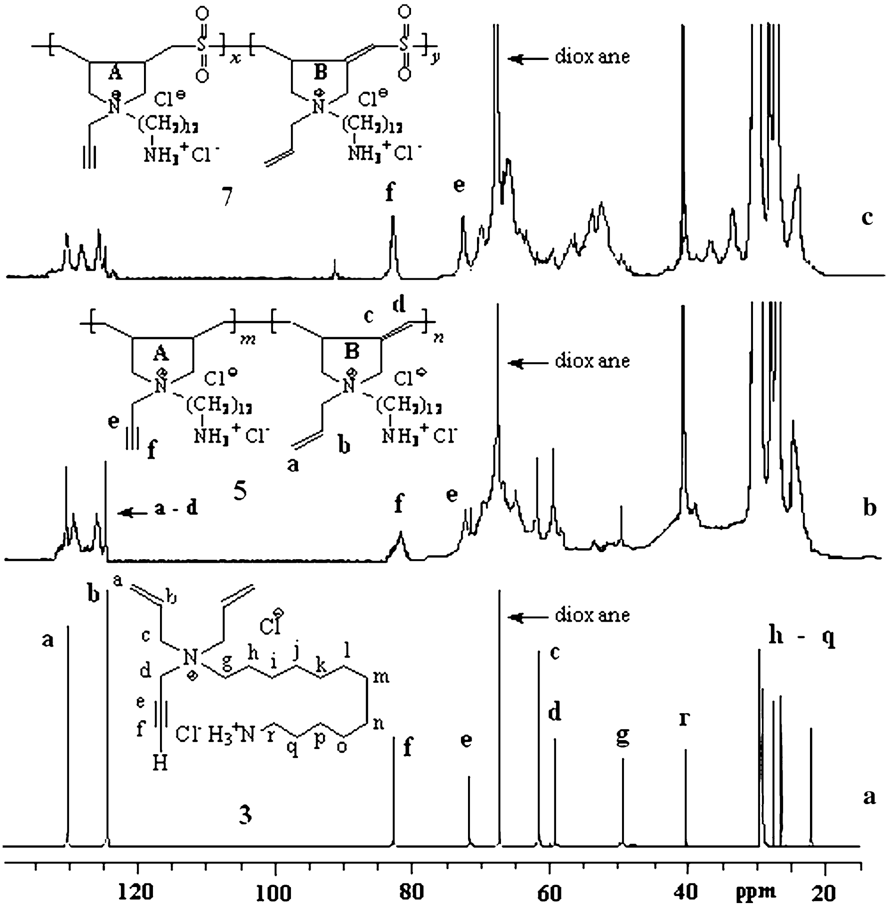


Fig. 3 ^{13}C NMR spectrum of **a** **3**, **b** **5**, and **c** **7** (in D_2O)

Polymer structure

Monomer **2** has two allyl and one propargyl groups. One of the allyl groups must undergo cyclopolymerization with either the propargyl or the other allyl group in competing pathways. Formation of ring structure **A** ascertains the participation by the two allyl groups in cyclopolymerization, while a combination of one allyl and one propargyl group would lead to the formation of ring structure **B** (Scheme 1). The presence of fragment **A** is ascertained by ^{13}C NMR spectra which displays alkyne carbons in their expected positions of around δ 71.74, 82.38 ppm (Fig. 3b, c). The presence of fragment **B** is manifested by the appearance of the alkene carbons at around δ 125 ppm in the spectra of the polymers. Ring structure **B** in polymers **4** and **6** has four alkene protons in the range δ 5–6 ppm—3 Hs in pendent allyl group and 1H in exocyclic double bond—whereas *N*-formyl proton (NC$\underline{H}$O) of both **A** and **B** appeared at δ 8 ppm (Figs. 1, 2). Percent **B** fragments, hence percent propargyl participation was calculated as 100 (P/4)/Q, where P is the area for the four alkene protons in the polymer and Q is the area of the *N*-formyl proton. The calculation revealed a 4:1 ratio for the fragments **A** and **B**, respectively, thereby confirming the faster incorporation of the allyl group in the polymer chain than the alkyne moiety of monomer **2**.

Corrosion inhibition study

Gravimetric method

The synthesized monomers and their corresponding homo- and copolymers as listed in Scheme 1 have been investigated for their IEs in arresting mild steel corrosion in several corroding environments such as 1, 4, 7.7 M HCl, 0.5 M H_2SO_4, and 3.5 % NaCl at 60 °C for 6 h in the presence of 0–400 ppm of the inhibitors. The results are included in Tables 1, 2, 3. The results of the inhibition tests by gravimetric method in 1 M HCl are corroborated by the results of the electrochemical method (Table 2). All the compounds used in this study are highly surface active and showed excellent inhibition of corrosion in 1 M HCl (Table 1); the inhibitor molecules at 200 ppm achieved inhibition efficiencies (IE%) in the range 81–99 %. Even though the parent diamine 1,12-DDA is found to be an ineffective inhibitor, its derivative monomers **2** and **3** as well as homopolymer **5** and copolymer **7** were found to be excellent inhibitors (Table 1). The polymers are adsorbed strongly on the metal surface owing to multiple adsorption centres which make the desorption process less favorable. The polymers demonstrated better IE than the monomer especially in the lower concentration range. It is interesting to note that copolymer **7** at a concentration of a meager 5 ppm gave a protection efficiency of 85 % (Table 1).

The inhibitor molecules **2**, **3**, **5**, and **7** (at a concentration of 200 ppm) exhibited IE in the ranges 97–98 % in 4 M HCl, 87–93 % in 7.7 M HCl, 68–91 % in 0.5 M H_2SO_4, and 84–92 % in 3.5 % NaCl. There are not many compounds in the literature, which reports the excellent corrosion inhibition activity both in the acidic

Table 2 Corrosion IE using gravimetric and electrochemical methods: results of Tafel Plots of mild steel sample in various solutions containing 200 ppm inhibitors in 1 M HCl at 60 °C for 6 h

Compounds	E_{corr} vs SCE (mV)	β_a (mV/dec)	β_c (mV/dec)	I_{corr} (μA/cm^2)	Corr rate (mm/year)	Tafel (IE)	Gravimetric IE, 6 h
Blank[a]	−452	59.9	131	4,140	48.23	0	0.00
1	−490	47.9	137	219	2.55	95	81
2	−462	55.4	130	65.5	2.12	96	97
3	−497	64.2	129	140	1.63	97	98
5	−485	59.7	135	182	0.763	98	98
7	−508	83.2	141	190	0.797	98	99
DDA	−484	50.5	186	1,300	15.1	69	57

DDA 1,12-Dodecanediamine

[a] The blank was a 1 M HCl solution

Table 3 Corrosion IE using gravimetric and electrochemical methods: results of Tafel Plots of mild steel sample in various solutions containing 200 ppm of the inhibitors in 3.5 % NaCl at 60 °C

Compounds	E_{corr} vs SCE (mV)	β_a (mV/dec)	β_c (mV/dec)	I_{corr} ($\mu A/cm^2$)	Corr Rate (mm/year)	Tafel (IE)	Gravimetric IE, 100 h
Blank NaCl[a]	−659	72.7	376	174.8	2.04	0	0
3	−714	30.0	76.0	33.5	0.39	81	84
5	−691	24.8	86.3	17.2	0.20	90	92
7	−724	42.9	137	24.0	0.28	86	88

[a] The blank was a 3.5 % NaCl solution

and the saline media. The current polymers performed very well in HCl, H_2SO_4 (Table 1) as well as in saline media (Table 3). The inhibitor molecules even withstood the hostile environment of 4 M HCl and 7.7 M and gave excellent performance.

Electrochemical method: polarization curves

The inhibitors were subjected to electrochemical study for the purpose of comparison with the gravimetric methods. Anodic and cathodic polarization curves for mild steel in 1 M HCl at 60 °C in the absence and the presence of 200 ppm of the inhibitors are shown in Fig. 4. The figure and results, given in Table 2, shows that in general all chemicals have reduced the corrosion rates; the I_{corr} values decrease considerably in the presence of the inhibitors thereby confirming their inhibitive nature. Tafel plots were analyzed to estimate corrosion current (I_{corr}), corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (β_a and β_c). The corrosion current was used to calculate corrosion rate in mmpy and IE [21]. Likewise, the inhibitors which are soluble in 3.5 % NaCl were tested for their IEs at 60 °C by polarization curves. The results are given in Table 3. Gravimetric method is indeed the most simple and reliable method for the determination of IEs, nonetheless the results from the electrochemical method using Tafel plots (Fig. 5) corroborated the results obtained by the gravimetric method. It is evident from (Tables 2, 3) that the inhibitor adsorption shifted the corrosion potential (E_{corr}) in the negative direction with reference to the blank in 1 M HCl or 3.5 % NaCl signifying that suppression of the cathodic reaction is the main effect of these CIs.

Monomer **3** as well as polymers **5** and **7** inhibitor molecules followed Temkin adsorption isotherm (Fig. 6). A higher f value signifies stronger forces of repulsion between the adsorbed and adsorbing molecules (Table 4) [24]. The negative values of ΔG^0_{ads} (Table 4) ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the steel surface in 1 M HCl. Generally, values of ΔG^0_{ads} up to −20 kJ/mol are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption) while those between −80 and −400 kJ/mol are associated with chemisorption as a result of sharing electrons from the inhibitor molecules to the metal surface to form a coordinate type of bond. The ΔG^0_{ads} values in the range −68 to −91 kJ/mol, obtained by analyzing the Temkin

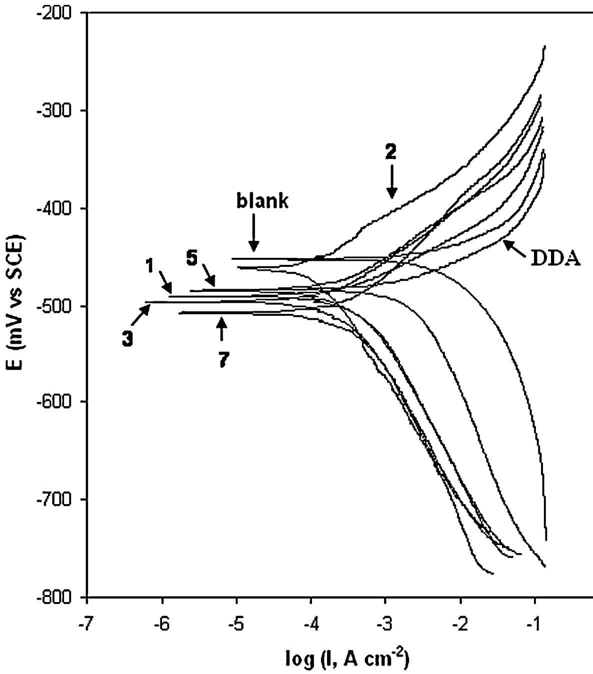


Fig. 4 Potentiodynamic polarization curves for mild steel in 1 M HCl (blank) and 1 M HCl containing 200 ppm of **1**–**3**, **5**, **7**, and DDA at 60 °C

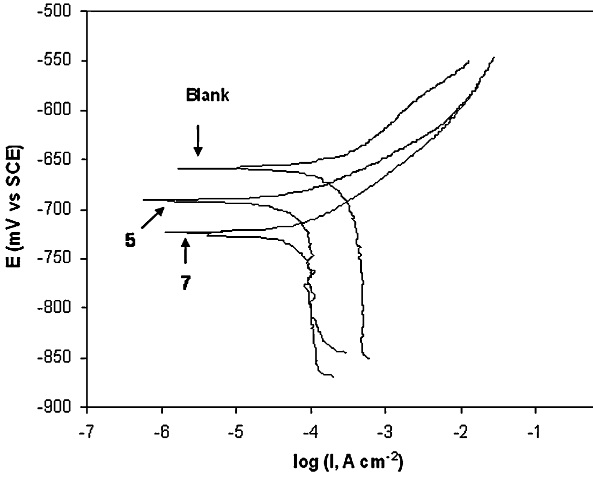


Fig. 5 Potentiodynamic polarization curves for mild steel in 3.5 % NaCl (blank) and 3.5 % NaCl containing 200 ppm of **5** and **7** at 60 °C

adsorption isotherms, are associated with both the electrostatic adsorption and the chemisorption [29]. Note that polymers **5** and **7**, especially the later, have more favorable (more negative) $\Delta G^0_{\mathrm{ads}}$ values than the monomer **3**, thereby implying the

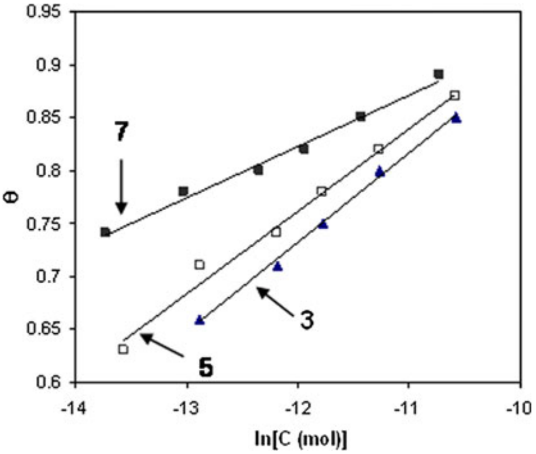


Fig. 6 Temkin adsorption isotherms of **3**, **5**, and **7** in 1 M HCl at 60 °C

Table 4 Square of coefficient of correlation (R^2) and values of interaction parameters f in the Temkin adsorption isotherms and $\Delta G^0_{\mathrm{ads}}$ in 1 M HCl at 60 °C using data from gravimetric method

Inhibitor	R^2	f	K_{ads} (L/mol)	$\Delta G^0_{\mathrm{ads}}$ (kJ/mol)
3	0.9959	12	9.16E+08	−68.2
5	0.9881	13	2.93E+09	−71.5
7	0.9884	21	3.94E+12	−91.4

stronger adsorption of the polymers onto the metal surface due to attachment via multiple adsorption sites (Table 4). The presence of π-electrons of allyl or propargyl moiety helps the inhibitor molecules to undergo adsorption through the interaction of the electron pairs with the low lying vacant *d*-orbitals of iron or deposited Fe^{2+} to provide a protective film.

Conclusions

A new 1,12-DDA-based monomer, *N*,*N*-diallyl-*N*-propargyl-(12-*N*′-formylamino)-1-dodecylammonium chloride (**2**) has been synthesized. Polymers of the quaternary ammonium salts of low molecular weights with a hydrophobic cover of pendent $(CH_2)_{12}$ spacer group have been prepared. The main objective of the study was to synthesize inhibitor molecules that would provide effective protection of corrosion of mild steel in acidic and saline media. In this respect, many important elements, which lead to inhibition of corrosion, have been successfully assembled in each repeating unit of the polymers. The polymers performed better as inhibitors than their corresponding monomers, especially in 0.5 M H_2SO_4 and 3.5 % NaCl. At a concentration of 200 ppm, the inhibitors performed excellent in HCl (IE: 97–99 %), but very good in H_2SO_4 (IE: 68–91 %), and saline media (IE: 84–92 %). The polymers even withstood the harsh corroding environment of 4 and 7.7 M HCl. The results are indeed very promising and pave the way to exploit the polymers' excellent ability to inhibit corrosion of mild steel. Further study has to be carried out to investigate the effectiveness of the inhibitor molecules exposed in acidic media for longer duration and with flowing systems using additional techniques of corrosion inhibition study. It is to be noted that polymers **5** and **7** have pH-responsive NH_3^+ groups which could be changed to NH_2. The resultant polymers having quaternary as well as trivalent nitrogens are expected to be effective in arresting CO_2 corrosion in oil- and gas-field pipelines.

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