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Synthesis and corrosion inhibition study of some 1,6-hexanediamine-based *N*,*N*-diallyl quaternary ammonium salts and their polymers

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Abstract

A variety of unsaturated *N*,*N*-diallyl compounds, capable of undergoing cyclopolymerization, are prepared from 1,6-hexanediamine. Selective monoformylation followed by allylation of the diamine afforded *N*,*N*-diallyl-*N*′-formyl-1,6-hexanediamine (DFH). The DFH was converted into quaternary ammonium monomers *N*,*N*-diallyl-*N*-carboethoxymethyl-*N*′-formyl-1,6-hexanediamine (DCFH) and *N*,*N*-diallyl-*N*-benzyl-*N*′-formyl-1,6-hexanediamine (DBFH*)*by reacting with ethyl chloroacetate and benzyl chloride, respectively. The monomer DCFH on homo- and co-polymerization (with SO_2) afforded the polyelectrolytes poly(DFCH) and poly(DFCH-SO_2), which on acidic hydrolysis of the amide and ester groups gave the corresponding polyampholytes. The monomer DBFH, likewise, on polymerization followed by acidic hydrolysis gave the corresponding polyelctrolytes.

All the synthesized materials (precursor to the monomers, monomers and the polymers containing quaternary, amide and trivalent nitrogens) and the starting 1,6-hexanediamine were used to study the corrosion inhibition of mild steel in 1 M HCl at 60°C for 6 h. The percent inhibition was found to be in the range 40–93%. There is a dramatic increase in the percent inhibition by the synthesized materials in comparison to the starting diamine. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyelectrolyte; Polyampholyte; Poly(quaternary ammonium salt)

1. Introduction

The relationship between structure dependent adsorption and corrosion inhibition is well known [1–4]. The corrosion inhibition of a metal involves strong adsorption of inhibitors to the metal surface by nitrogen, sulfur or oxygen and subsequent interference with either cathodic or anodic reactions occurring at the adsorption sites. The straight chain fatty amines adsorb through their amine group, and the hydrocarbon chain extending into the aqueous phase forms a protective monolayer at the metal surface [5]. It is known that polymers are adsorbed stronger than their monomer analogs [6], hence it is expected that polymers will be better corrosion inhibitors than the corresponding monomers. It has been shown [7] that because of multiple adsorption sites the polymers **1** and **2** are better corrosion inhibitors than the corresponding monomeric analogs **3** and **4**, respectively. Hydrocarbon-soluble alkylanilines **5** having a varying alkyl group chain length and the corresponding alkylaniline/formaldehyde oligomers **6** have been treated for corrosion inhibition of steel [8]. The oligomers are demonstrated to be far superior to their monomers in corrosion inhibition. The improved performances of the oligo- or polymeric materials are ascribed to their multiple adsorption sites for bonding with the metal surface. The polymer provides two advantages: a single polymeric chain displaces many water molecules from the metal surface, thus making the process entropically favorable and the presence of multiple bonding sites make the desorption of the polymers a slower process. Amines and their derivatives are well known corrosion inhibitors. Low molecular weight amines have the advantage over their high molecular weight analogs due to their relatively high solubility in aqueous solution [9,10]. The substitution of multiple bonds improves the adsorption and the protecting effect. Aryl groups are known to be better inhibitors than alkyl groups since the former have an aromatic π-cloud [2].

Increasing the length of the hydrocarbon chain decreases the solubility of amine inhibitors. However it is envisaged that the presence of a hydrophilic functional group in a molecule would increase the solubility of the inhibitors.

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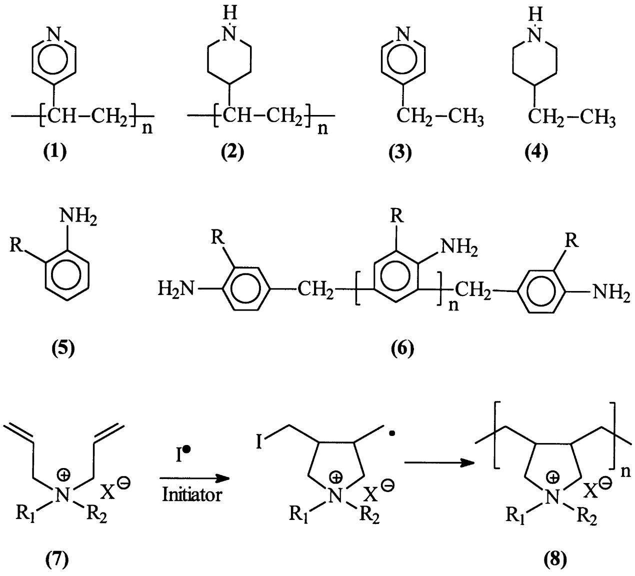
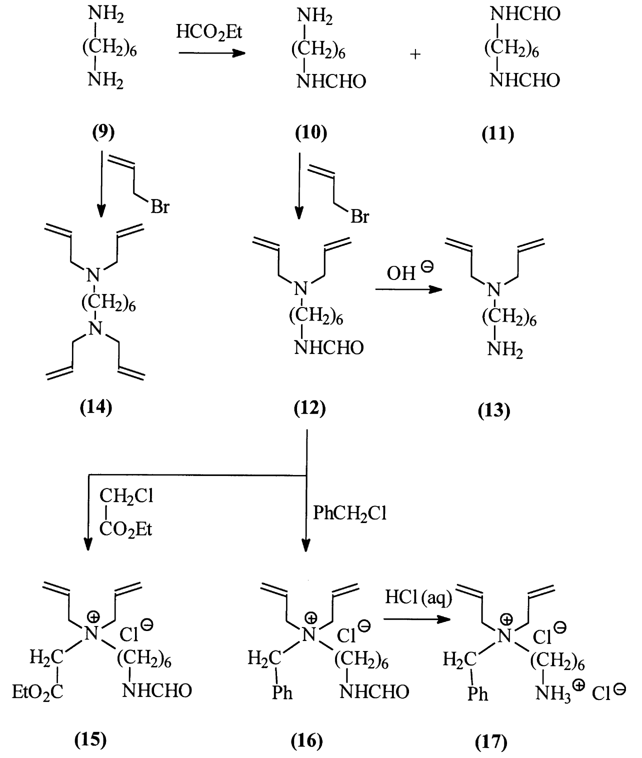
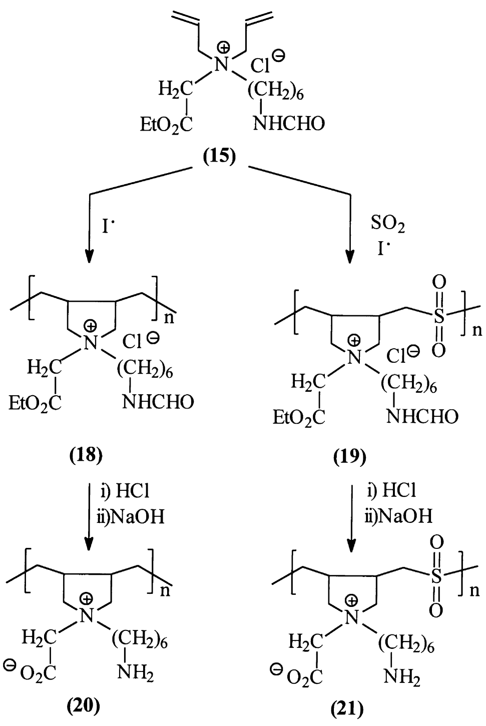


Scheme 1.

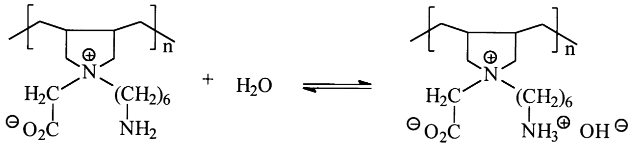
Incorporation of multiple functional groups within a molecule is expected to help the inhibitor to lock in on the metal surface strongly. With this in mind we report, herein, the synthesis of several compounds (**12–17**) (Scheme 2) and polymers (**18–23**) (Schemes 3 and 4) based on 1,6-hexanediamine (**9**) and their inhibiting effect on the corrosion of mild steel in 1 M HCl solution. The monomers **15** and **16** containing the *N*,*N*-diallyl quaternary ammonium moiety are capable of undergoing cyclopolymerization to give water-soluble polymers (Scheme 2 and 3). The pioneering works by Butler and his coworkers [11] led to the cyclopolymerization of a variety of diallyl quaternary ammonium salts **7** via an intra- and inter-molecular chain propagation through a five-membered cyclic structure [12,13] to yield linear water-soluble cationic polyelectrolytes **8** (Scheme 1). These cationic polyelectrolytes have found extensive industrial and commercial applications



Scheme 2.



Scheme 3.



(20)

Scheme 4.

[14,15]. Polydiallyldimethylammonium chloride alone accounts for over 1000 patents and publications. Polysulfones, the copolymers of the ammonium salts **7** and sulfur dioxide, are also produced commercially and used as adhesives, thickeners and paints [15].

2. Experimental

2.1. Physical methods

All m.p.s are uncorrected. Elemental analyses were carried out in a Carlo-Erba elemental analyzer Model 1102. IR spectra were recorded on a Perkin–Elmer 16F PC FTIR spectrometer (spectral resolution, 4 cm^{-1}; number of scans, 19). ^1H and ^{13}C NMR spectra of the polymers were measured in D_2O using dioxane as internal standard on a JEOL LA 500 MHz spectrometer. ^1H NMR spectra in $CDCl_3$ or CD_3OD were measured using TMS as internal standard. Viscosity measurements were made by an Ubbelohde viscometer (K 0.005718). All the reactions were carried out under a positive atmosphere of N_2.

2.2. Materials

t-Butylhydroperoxide (80% in ditertiarybutylperoxide) and 1,6-hexanediamine, allyl bromide, ethyl chloroacetate and ethyl formate from Fluka Chemie AG (Buchs, Switzerland) were used as received. Ammonium persulfate (APS) from BDH Chemical Co. (Poole, UK), was kept in the freezer and used without further purification. All solvents were of HPLC grade. Silica gel 100 was purchased from Fluka Chemie AG. All glassware was cleaned using deionized water. Dimethylsulfoxide (DMSO) was dried over calcium hydride overnight and then distilled under reduced pressure at a b.p. of 64–65°C (4 mm Hg). Sulfur dioxide gas was bubbled gently to a known quantity of DMSO and the final weight of the solution gave the wt% of the sulfur dioxide in DMSO.

2.3. Corrosion inhibition tests

Corrosion inhibition tests were performed using coupons measuring $2.5 \times 1.4 \times 0.1$ cm^3 prepared from mild steel having the composition: 0.135% (C), 0.137% (Si), 0.40% (Mn), 0.064% (Cr), 0.03 (Ni), 0.01% (Mo), 0.039% (S), 0.007% (P), 0.007% (V), 0.042% (Cu) and 99.13% (Fe). A solution of 1 M HCl was prepared from reagent A.C.S. concentrated HCl (Fisher Scientific Company) using deionized water. The mild steel coupons were polished with emery papers, then degreased with acetone and washed with deionized water. The coupons were dried and kept in a desiccator. Inhibitor efficiency was determined at 60°C for 6 h by hanging the coupon into the acid solution (50 cm^3) (in open air) containing various amounts (0 (blank), 50, 100, 200 and 400 ppm) of the synthesized inhibitors. After the time elapsed the cleaning procedure consisted of wiping the coupons with a paper tissue, polishing lightly with emery paper, washing with distilled water and acetone, followed by oven drying at 110°C. Percent inhibition (%I) was determined using the following equation:

$$\%\mathrm{I} = [(\text{weight loss (blank)} - \text{weight loss (inhibitor)})/\text{weight loss (blank)}] \times 100$$

'Weight loss (blank)' and 'weight loss (inhibitor)' represent weight loss in absence and presence of inhibitor, respectively. The results of the inhibition tests are included in Table 1.

*2.4. N,N-Diallyl-N′-formyl-1,6-hexanediamine (**12**)*

The crystalline diamine **9** (58 g, 0.5 mol) was melted in a round bottom flask fitted with a condenser by gentle heating. To the liquified diamine ethyl formate (37 g, 0.5 mol) was added dropwise with stirring at 45°C over a period of 20 min. The reaction mixture was homogeneous (due to the exothermic nature of the reaction) and was stirred at 20°C for 4 h, during which the mixture solidified. The crude reaction mixture indicated the presence of **9**, **10** and **11** in an approximate ratio of 20:60:20, as determined by integration of several proton signals in the NMR spectrum. The NMR spectrum of the pure compound **9** and the diformate **11** (prepared separately using excess ethyl chloroformate) has the following NMR signals. **9**: δ_H (CD_3OD)

Table 1
Inhibition efficiency for different concentrations of compounds for the inhibition of corrosion of mild steel in 1 M HCl exposed for 6 h at 60°C

Compound	Inhibition efficiencies (%) at concentration (ppm) of compounds			
	50	100	200	400
9	45	53	56	55
12	62	67	72	83
13	67	75	82	90
14	77	78	80	84
15	70	72	74	78
16	40	63	70	83
17	81	81	81	85
18	79	84	85	91
19	47	66	56	56
20	76	77	79	82
21	59	73	80	82
22	75	79	80	82
23	77	84	90	93

1.28–1.62 (8H, m), 2.63 (4H, t, J 7.0 Hz). **11**: δ_H (CD_3OD) 1.26–1.62 (8H, m), 2.23 (4H, t, J 7.0 Hz), 8.07 (2H, s). The signals for the monoformate **10** are deduced from the NMR spectrum of the mixture of the reaction products. **10**: δ_H (CD_3OD) 1.26–1.70 (8H, m), 2.62 (2H, t, J7.0 Hz), 3.22 (2H, t, J 7.0 Hz), 8.05 (1H, s).

To the above reaction mixture containing **9**, **10** and **11** was added methanol (200 cm^3) and to this solution allyl bromide (60.5 g, 0.5 mol) was added dropwise over a period of 30 min, maintaining the temperature around 50°C. The reaction mixture was stirred for 2 h at 50°C, then solid NaOH (20 g, 0.5 mol) was added pellet by pellet over a period of 1 h. Then another 0.25 mol of allyl bromide was added dropwise (30 min) and stirred at 50°C for 1 h, followed by addition of 0.25 mole pellets of NaOH (over 30 min). The final 0.25 mol each of allyl bromide and NaOH were added as before. The reaction mixture was then stirred at 20°C overnight, after which it was filtered and the filtrate was concentrated to remove most of the methanol. The viscous filtrate was then diluted with water (75 cm^3) and extracted with hexane (3 × 75 cm^3) to remove most of the tetraallyl derivative **14**. The aqueous solution was then extracted with liberal excess of ether (TLC, silica, checked in ether/MeOH (saturated with NH_3) 10: 1 to ensure complete extraction of the compound **12**). The combined ether layers were dried (Na_2SO_4), concentrated and chromatographed over silica using hexane, ether and dichloromethane as eluent to give **12** as a colorless liquid (43.6 g, 38.8% overall) (64.7% based on the monoformyl derivative **10**). (found: C, 69.4; H, 10.7; N, 12.35. $C_{13}H_{24}N_2O$ requires C, 69.60; H, 10.78; N, 12.49%); ν_{max} (neat) 3278, 3073, 2934, 1661, 1538, 1446, 1383, 1253, 1151, 996, 917, and 726 cm^{-1}; δ_H (CD_3OD) 1.17–1.67 (8H, m), 2.47 (2H, t, J 7.0 Hz), 3.14 (4H, d, J 6.5 Hz), 3.22 (2H, t, J7.0 Hz), 5.25 (4H, m), 5.93 (2H, m), 8.07 (1H, s).

2.5. *N,N-Diallyl-1,6-hexanediamine (**13**)*

A solution of the monoformate **12** (6.0 g, 26.7 mmol) and KOH (6 g) in methanol (15 cm^3) and H_2O (6 cm^3) was stirred under N_2 at 50°C for 6 h and then at 20°C overnight. The reaction mixture was concentrated and extracted with ether (3 × 25 cm^3). The organic layer was dried (Na_2SO_4) and concentrated to give the free amine **13** as a pale yellow liquid (4.5 g, 85.8%) (found: C, 73.2; H, 12.15; N, 14.3. $C_{12}H_{24}N_2$ requires C, 73.41; H, 12.32; N, 14.27%); ν_{max} (neat) 3319, 3076, 2930, 2858, 2800, 1642, 1572, 1470, 1388, 1320, 1152, 996, and 918 cm^{-1}; δ_H ($CDCl_3$) 1.42–2.00 (10H, m), 2.76 (2H, t, J 7.0 Hz), 3.03 (2H, t, J 7.0 Hz), 3.42 (4H, d, J 6.5 Hz), 5.46 (4H, m), 6.20 (2H, m).

2.6. *N,N,N′,N′-Tetraallyl-1,6-hexanediamine (**14**)*

To the diamine **9** (11.6 g, 0.1 mol) a solution of NaOH (0.4 mol) in water (50 cm^3) was added dropwise from a dropping funnel and allyl bromide (49 g, 0.4 mol) from another dropping funnel at 0°C over 1 h. The mixture was stirred at 20°C for an additional 3 h, and then at 20°C overnight. The mixture was taken up in water (100 cm^3) and extracted with ether (3 × 25 cm^3). The organic layer was dried (Na_2SO_4) and evaporated, and the resulting liquid was chromatographed over silica using 1:1 hexane–ether mixture to give the tetraallyl derivative **14** (13 g, 47%) as a colorless liquid. (found: C, 78.0; H, 11.5; N, 9.85. $C_{18}H_{32}N_2$ requires C, 78.20; H, 11.67; N, 10.14%); ν_{max} (neat) 3076, 3006, 2930, 2858, 2798, 1642, 1448, 1418, 1352, 1260, 1150, 1110, 994, 918 cm^{-1}; δ_H ($CDCl_3$) 1.00–1.80 (8H, m), 2.40 (4H, app. t), 3.05 (8H, d, J 6.0 Hz), 4.80–5.30 (8H, m), 5.55–6.13 (4H, m).

2.7. *N,N-Diallyl-N-carboethoxymethyl-N′-formyl-1,6-hexanediamine (**15**)*

Ethyl chloroacetate (15 g, 0.122 mol) was added to the compound **12** (10 g, 0.0446 mol) and the reaction mixture was stirred under N_2 at 60°C for 48 h. The mixture was then taken in MeOH (20 cm^3) and ether (75 cm^3) added. The separated oily salt **15** was again dissolved in methanol and separated by adding ether. The process was repeated five times to obtain **15** as a viscous liquid (15.5 g, quantitative). (found: C, 58.5; H, 9.25; N 7.8. $C_{17}H_{31}N_2O_3Cl$ requires C, 58.86; H, 9.00; N, 8.08%); ν_{max} (neat) 3214, 2936, 2861, 1743, 1673, 1538, 1469, 1383, 1218, 1019, 954, and 856 cm^{-1}; δ_H ($CDCl_3$) 1.28 (3H, t, J7.0 Hz), 1.30–1.74 (6H, m), 1.94 (2H, m), 3.26 (2H, m), 3.68 (2H, m), 4.26 (2H, q, J7.0 Hz), 4.43 (4H, m), 4.48 (2H, s), 5.82 (4H, m), 6.13 (2H, m), 8.24 (1H, s), 8.35 (1H, br).

2.8. *N,N-Diallyl-N-benzyl-N′-formyl-1,6-hexanediamine (**16**)*

A solution of the compound **12** (4.0 g) and benzyl chloride in acetone (10 cm^3) under N_2 was heated in a closed vessel at 60°C for 30 h. Addition of ether resulted in the separation of the salt **16**. The viscous liquid was dissolved in methanol and separated by adding ether. The process was repeated three times in order to remove any unreacted amine **12** and the salt was obtained as a viscous liquid in 91% yield. A saturated solution of the salt in methanol/ether was kept in the freezer and after long standing the salt crystallized as white crystals, m.p. 55–60°C. (found: C, 68.2; H, 9.1; N 7.85. $C_{20}H_{31}N_2OCl$ requires C, 68.45; H, 8.90; N, 7.98%); ν_{max} (KBr) 3486, 3400, 3212, 3037, 2935, 2853, 1670, 1542, 1498, 1474, 1458, 1384, 1240, 1220, 1042, 1006, 978, 958, 850, 794, 750 and 710 cm^{-1}; δ_H (CD_3OD, TMS) 1.40 (4H, m), 1.57 (2H, quint, J7.3 Hz), 1.92 (2H, m), 3.23 (4H, m), 3.97 (4H, m), 4.62 (2H, s), 5.74 (4H, m), 6.21 (2H, m), 7.58 (5H, m), 8.05 (1H, s); δ_C (D_2O, dioxane: 67.8 ppm) 22.66, 26.30, 26.64, 29.28, 38.99, 59.18, 62.07 (2C), 63.19, 125.60 (2C), 128.30, 129.42 (2C), 130.57 (2C), 132.03, 133.89 (2C), 165.29.

2.9. Hydrochloride salt of N,N-diallyl-N-benzyl-1,6-hexanediamine (**17**)

A solution of **16** (0.700 g) in 12% HCl (5 cm^3) was heated at 50°C for 48 h. After removal of water the residual viscous liquid was dissolved in methanol and separated by adding ether. This process was repeated three times. The resulting viscous liquid was dried under vacuum to give the salt **17** as a white solid (0.650 g, 91%). M.p. 130–140°C; (found: C, 63.2; H, 9.2; N 7.7. $C_{19}H_{32}N_2Cl_2$ requires C, 63.50; H, 8.98; N, 7.80%); ν_{max} (KBr) 3400, 2943, 2869, 1607, 1501, 1471, 1443, 1211, 1158, 1005, 960, 852, 740 and 698 cm^{-1}; δ_H (CD_3OD, TMS) 1.40 (2H, quint, *J* 7.3 Hz), 1.51 (2H, quint, *J* 7.3 Hz), 1.75 (2H, quint, *J* 7.4 Hz), 1.96 (2H, m), 2.97 (2H, t, *J* 7.5 Hz), 3.25 (2H, app. t, *J* 8.2 Hz), 4.00 (4H, d, *J* 7.0 Hz), 4.66 (2H, s), 5.74 (4H, m), 6.23 (2H, m), 7.60 (5H, m); δ_C (CD_3OD, TMS) 22.95, 26.59, 26.72, 27.98, 40.43, 59.61, 62.35, 63.72 (2C), 126.44 (2C), 128.46 (2C), 128.76, 130.41 (2C), 131.82, 133.92 (2C).

2.10. Procedure for the homopolymerization of **15** using ammonium persulfate (APS)

A solution of APS (115 mg) in water (0.30 cm^3) was injected via a syringe to a solution of the monomeric salt **15** (5.00 g) in deionized water (1.84 g) in a 10 cm^3 flask fitted with a septum (under $N_{2)}$ at 80°C over a period of 15 min (after the addition of the APS solution, the mixture becomes 70 wt% in monomer). The temperature was raised to 90°C and was stirred for 1 h. The reaction mixture was dialyzed against deionized water until the water tested negative for chloride ions as tested by $AgNO_3$ solution. The polymer solution was freeze dried and the white powder of the very hygroscopic polymer **18** was further dried under vacuum at 65°C until constant weight of the polymer was obtained (1.45 g, 29%). The intrinsic viscosity of the homopolymer 18 in 0.1 N NaCl at 30°C was determined to be 0.0464 dl/g.

Melting range: The polymer did not have a melting point upto 400°C; no color or volume change was observed. ν_{max}(KBr) 3445, 2937, 1745, 1666, 1540, 1458, 1386, 1221, 1125 and 906 cm^{-1}. The above polymerization reaction was repeated using the similar reaction conditions except that the mixture was heated at 95°C for an additional 30 min. However the polymer yield was reduced to 12.8%. The ^{1}H NMR of the crude mixture before dialysis revealed the presence of the unreacted monomer **15** as the major component in the mixture. The yield did not improve either by increasing or decreasing the monomer concentration or the amount of APS.

2.11. Homopolymerization of **15** using TBHP

TBHP (150 mg) was added to a solution of the monomer **15** (10.0 g) in deionized water (4.30 g) and heated at 50°C for 16 h and at 70°C for 32 h. The mixture was dialyzed against deionized water to remove the unreacted monomer. The polymer solution was freeze dried and the white powder of the polymer **18** was further dried under vacuum at 65°C until constant weight of the polymer was obtained (6.76 g, 67.6%). (found: C, 58.4; H, 9.3; N 7.8. $C_{17}H_{31}N_2O_3Cl$ requires C, 58.86; H, 9.00; N, 8.08%). The above polymerization carried out using 4 mg TBHP per gram of the monomer did not yield the polymer.

2.12. Hydrolysis of the polyelectrolyte **18** to polyampholyte **20**

A solution of the polyelectrolyte **18** (3.32 g, 9.60 mmol), (prepared using TBHP initiator as described above), in concentrated HCl (20 cm^3) and water (20 cm^3) was stirred under N_2 at 50°C for a period of 120 h. The resulting homogeneous solution was then dialyzed against deionized water to remove HCl (tested by $AgNO_3$ solution). The polymer solution was then basified with NaOH (1.5 g) and again dialyzed against deionized water to remove Na^+, OH^- and Cl^- ions until the $AgNO_3$ test was negative. Dialysis was continued for a further 3 h against distilled deionized water to ensure complete removal of any sodium or chloride ions. The resulting solution was then freeze dried to obtain the polyampholyte **20** as a very hygroscopic white powder, which was further dried under vacuum at 65°C until constant weight (2.35 g, 96.5%). Melting point: the polymer did not have a melting point upto 400°C; no color or volume change. (Found: C, 65.8; H, 10.5; N 10.8. $C_{14}H_{26}N_2O_2$ requires C, 66.10; H, 10.30; N, 11.02%); ν_{max} (KBr) 3430, 2939, 2865, 1626, 1437, 1390, 1323, 1248 and 902 cm^{-1}.

2.13. General procedure for the copolymerization reactions of **15** with SO_2

The required amount of the monomer **15** and DMSO–SO_2 solution (see Table 2) were taken in a flame dried 25 cm^3 round bottom flask containing a magnetic stirrer.

Table 2
Copolymerization of the monomer **15** with SO_2 in DMSO using ammonium persulfate (APS) initiator at 50°C

Entry no.	Monomer (mmol)	SO_2 (mmol)	DMSO (g)	APS (mg)	Yield (%)	$[\eta]^a$ (dl g^{-1})
1	20	20	4.20	70	46	0.480
2	20	20	7.85	70	46	0.237
3	20	40	8.40	70	37	0.234
4	20	20	4.20	120	50	0.271

[a] Viscosity was determined in a Ubbelohde viscometer (K 0.005718) in 0.1 N NaCl at 30°C.

Appropriate concentration of SO_2 was achieved by adding DMSO–SO_2 stock solution with a known wt% of SO_2. Fresh DMSO was added if needed to achieve the monomer concentrations as shown in the table. All these additions were carried out under N_2 to exclude the absorption of moisture. The required amount of initiator APS was then added (see table). The reaction mixture in the closed flask was then stirred at 50°C for the specified time. The reaction mixture was then slurried in methanol (7 cm^3) and the slurry was precipitated in acetone (50 cm^3). The precipitate was again slurried in methanol and reprecipitated in acetone two more times. The resulting pale yellow hygroscopic polymer (**19**) was dried under high vacuum 50°C for 10 h or until constant weight was obtained. The yields of the copolymers are given in the Table 2. Melting point: the polymer turned light brown at 210°C and became dark brown at 250°C. (Found: C, 49.3; H, 7.8; N, 6.55; S, 7.5. $C_{17}H_{31}N_2O_3Cl.SO_2$ requires C, 49.68; H, 7.60; N, 6.82; S, 7.80%); ν_{max} (KBr) 3438, 2938, 2862, 1744, 1662, 1553, 1532, 1466, 1446, 1407, 1386, 1311, 1276, 1222, 1126, 1049, 1020, 909 and 862 cm^{-1}.

2.14. Hydrolysis of the copolymer 19 (entry no. 4., Table 2) to 21

A solution of the copolymer **19** (3.28 g, 8.0 mmol) (entry no. 4) in concentrated HCl (20 cm^3) and water (20 cm^3) was stirred under N_2 at 40°C for a period of 120 h. The resulting homogeneous solution was then dialyzed against deionized water to remove HCl. The polymer solution was then basified with K_2CO_3 and again dialyzed against deionized water to remove K^+, CO_3^{2-} and Cl^- ions. The resulting polymer (**21**) solution was then freeze dried to obtain the polymer as a hygroscopic white powder (2.4 g, 94%). Melting point: the polymer turned light brown at 230°C and became dark brown at 270°C. (Found: C, 52.4; H, 8.5; N, 8.6; S, 9.8. $C_{14}H_{26}N_2O_2.SO_2$ requires C, 52.80; H, 8.23; N, 8.80; S, 10.07%); ν_{max} (KBr) 3424, 2938, 2854, 1630, 1580, 1478, 1392, 1316, 1130, 910 and 726 cm^{-1}.

2.15. Homopolymerization of 16 using TBHP

TBHP (60 mg) was added to a solution of the monomer **16** (5.15 g) in deionized water (2.77 g) and heated at 50°C for 24 h and at 80°C for 40 h. The mixture was dialyzed against deionized water to remove the unreacted monomer. The polymer solution was freeze dried and the white powder of the hygroscopic polymer **22** was further dried under vacuum at 65°C until constant weight of the polymer was obtained (1.67 g, 32.5 %). M.p. 160–170°C; the melted polymer did not decompose upto 400°C. (Found: C, 68.1; H, 9.2; N 7.8. $C_{20}H_{31}N_2OCl$ requires C, 68.45; H, 8.90; N, 7.98%); ν_{max} (KBr) 3429, 3253, 3033, 2935, 2865, 1666, 1534, 1456, 1382, 1245, 1124, 1038, 891, 732 and 706 cm^{-1}. The ^1H NMR spectrum confirmed the absence of olefinic protons.

2.16. Hydrolysis of the polymer 22

A solution of the polymer **22** (0.600 g) in 12% HCl (7 cm^3) was heated at 50°C for 48 h. The mixture was then dialyzed against distilled water to remove HCl. The polymer solution was then freeze dried to obtain the polymer **23** as a white solid (0.560 g, 91%). Melting point: the polymer darkened at around 250°C and did not melt upto 400°C; (found: C, 63.0; H, 9.3; N 7.6. $C_{19}H_{32}N_2Cl_2$ requires C, 63.50; H, 8.98; N, 7.80%); ν_{max} (KBr) 3412, 2931, 2853, 1624, 1459, 1381, 1206, 1044, 935 and 891, 743 and 706 cm^{-1}.

3. Results and discussion

We chose inexpensive and commercially available 1,6-hexanediamine (**9**) to elaborate upon. Successful results will pave the way to work with higher diamines. The selective protection of one of the two basic amine functional groups in the compound **9** and similar diamines has frustrated many a researcher and still poses a significant challenge. Reaction of diamines with acid chlorides, anhydrides or esters gives a mixture of mono- and di-substituted products along with the unreacted amines whose separations are most often difficult if not impossible to achieve. The situation becomes more complicated in the reaction of the diamines with alkyl halides whereby a mixture of six products differing in their degree of alkylation can be obtained. Reaction of diamine **9** with one equivalent of ethyl formate afforded a mixture of the unreacted diamine **9**, monoformyl- **10** and diformyl-diamine **11** in an approximate ratio of 20:60:20, respectively, as determined by integration of NMR signals of several protons (Scheme 2). We were unable to separate the mixture by fractional distillation under vacuum. At a high bath temperature of 125–130°C the monoformyl derivative **10** seemed to condense with itself or another molecule and the ^1H NMR spectrum indicated the gradual decrease in the intensity of the proton signals attributed to the desired compound **10**. We did not pursue the separation by distillation any further. It was decided that the separation would be carried out after conversion to the allyl derivatives in the subsequent stage. It was assumed that the 'x' moles of the diamine **9** containing $2x$ moles of amine group, on reaction with 'y' moles of the limiting reactant ethyl formate would protect 'y' moles of amine functional group to give a mixture of **9**, **10** and **11**. The remaining $(2x - y)$ moles of the unprotected amine functional group will be reacted with $2(2x - y)$ moles of allyl bromide to generate diallyl derivative **12** from **10** and tetraallyl derivative **14** from **9**. Thus a mixture of the compound **9** (0.10 mol), **10** (0.30 mol), and **11** (0.10 mol), derived from the reaction of 0.50 mol of the diamine **9** with 0.5 mol of ethyl formate, was reacted with 1 mol of allyl bromide to give the diallyl- (**12**) and tetraallyl derivative (**14**). Chromatographic separation afforded the monomer precursor **12** (obtained in 39% overall yield from **9** and 65% based on **10**). The tetraallyl derivative **14** was synthesized in a separate experiment by reacting **9** with four equivalents of allyl bromide. The NMR spectrum assured the identity of the compound.

The formate group in **12** was hydrolyzed readily on treatment with potassium hydroxide to give the amine **13**, which is also a potential candidate for corrosion study since it has two trivalent nitrogens as well as π-electrons. We were gratified that the compound **12** on treatment with ethyl chloroacetate afforded a new class of monomeric quaternary ammonium salt **15** (in almost quantitative yield). The diallylamine **12** on treatment with benzyl chloride gave the other monomer **16** also in an excellent yield. Spectral analysis confirmed the structure of the salt. The salt **16** on acidic hydrolysis afforded the diammonium salt **17** in 91% yield (Scheme 2).

Next we pursued the polymerization of the diallyl quaternary ammonium salts **15** and **16**. The polymerization reactions were carried out using the procedure described in our earlier works [16–18]. The monomer **15** underwent polymerization in aqueous solution using ammonium persulfate (APS) as an initiator at 90°C (1 h) to give the polymer **18** in only 29% yield (Scheme 3). However the polymerization carried out using TBHP as the initiator gave the polymer **18** in 68% yield.

The monomer **15** was copolymerized with sulfur dioxide in dimethyl sulfoxide (DMSO) using APS as the initiator at 50°C to give the copolymer **19** (Scheme 3). The effects of concentration of the monomers and initiator on the polymeric yields and viscosity are included in the Table 2. Entry no. 1 represents the copolymer with the highest intrinsic viscosity. Increasing the amount of the solvent DMSO decreases the viscosity of the copolymer (compare entry nos. 1 and 2). Changing the molar ratio of the monomers **15**/SO_2 from 1:1 to 1:2 also decreases the intrinsic viscosity (entry no. 3). Entry no. 1 and 4 display the effect of initiator concentration on the viscosity. All these copolymer samples have low to medium values for the intrinsic viscosity, which indicate the lower mass of the polymers.

The polyelectrolytes (**PE**), **18** and **19** (entry no. 4, Table 2), on acidic hydrolysis afforded the polyzwitterions (polyampholytes, **PA**) **20** and **21**, respectively, in excellent yields (Scheme 3).

The IR spectrum of the polymers **18**–**21** indicated their hygroscopic nature by the presence of strong hydroxyl absorption around 3440 cm^{-1}. Strong absorption at 1744 and 1662 cm^{-1} indicated the presence of ester and amide functionalities, respectively. The presence of strong bands at 1311 and 1126 cm^{-1} is indicative of the presence of the SO_2 unit in the polymeric backbone of the copolymers. The hydrolyzed polymers show a strong band around 1630 cm^{-1} indicating the presence of the CO_2^- functionality.

The ^1H (Fig. 1) and ^{13}C NMR spectra revealed the absence of the alkene moiety in the polymer structure. The proton signals due to the formyl and ethoxy groups in **PE**s **18** and **20** were absent in the spectra of the **PA**s **19** and **21** (Fig. 1). The ^{13}C signal for the methyl carbon of the OCH_2CH_3 group in the **PE**s **18** and **20** appeared as a sharp signal at ~δ14.2 ppm (dioxane: 67.4 ppm) and was free of any overlapping signal. This peak was completely absent in the **PA**s, thus ensuring the complete hydrolysis of the **PE**s.

While the polyelectrolytes (**PE**s) are usually soluble in water, the overwhelming majority of the reported polyampholytes (**PA**s) [19–21]are known to be insoluble in water. This solubility behavior is attributed [22,23] to the collapsed coil conformation of the **PA**s as a result of inter- and intra-chain interactions leading to a three-dimensional ionic network. The presence of an inorganic salt (NaCl) neutralizes the ionically cross-linked network of the **PA** and thus causes its dissolution. Unlike **PE**s, the ampholytic polymers show 'anti-polyelectrolyte behavior' [22]and have greatly enhanced solubility and extensive chain expansion, hence higher viscosity, with increasing salt (NaCl) concentration. However, both the **PE**s and **PA**s prepared in this study were found to be readily soluble in water. The viscosity curves for the **PE 18** and the corresponding **PA 20** (having the same degree of polymerization) in the absence and presence of various concentration of added salt, NaCl, are shown in Fig. 2. The plots of the reduced viscosity (η_{sp}/C) vs conc.(C) of both the polymers were found to be concave upwards in the absence of NaCl. The polyelectrolyte behavior of the **PA 20**, although less pronounced than that of the **PE 18**, can be rationalized by the partial protonation of the basic amino group thereby converting the polybetaine into a weak polycation as described in Scheme 4. The addition of the strong electrolyte NaCl suppresses the ionization of the polymers due to the common ion effect, and the viscosity behavior becomes normal as can be seen in Fig. 2. The **PE 18** and the polyampholyte **PA 20** demonstrated polyelectrolyte and antipolyelectrolyte behavior, respectively; while the addition of increasing amount of NaCl reduces the viscosity of the **PE**, the opposite trend is observed for the **PA**. The intrinsic viscosity of the copolymer **19** (entry no. 4, Table 2) and its corresponding polyampholyte **21** (having the same degree of polymerization) in 0.1 N NaCl at 30°C was determined to be 0.271 and 0.191 dl/g, respectively. In the absence of NaCl, the viscosity curves for both the **PE 19** and **PA 21** were concave upwards as in the case of the homopolymers (vide supra). The reduced viscosity of the **PE 19** and **PA 21** in the absence of NaCl were found to be 0.878 and 0.287 dl/g for 1% solutions and 2.27 and 1.11 dl/g for 0.0625% solution, respectively.

Scheme 5 describes the synthesis of the polymer **22**. The monomer **16** was polymerized using *t*-butylhydroperoxide as the initiator to afford the polymer in somewhat low yield (32.5%). The polymer on acidic hydrolysis afforded the dicationic polymer **23** in excellent yield. The intrinsic viscosity of the polymers **22** and **23**, having the same degree of polymerization, in 0.1 N NaCl at 30°C was determined to be 0.0365 and 0.0600 dl/g, respectively. The low viscosity values indicate the lower molar mass of the polymers. The

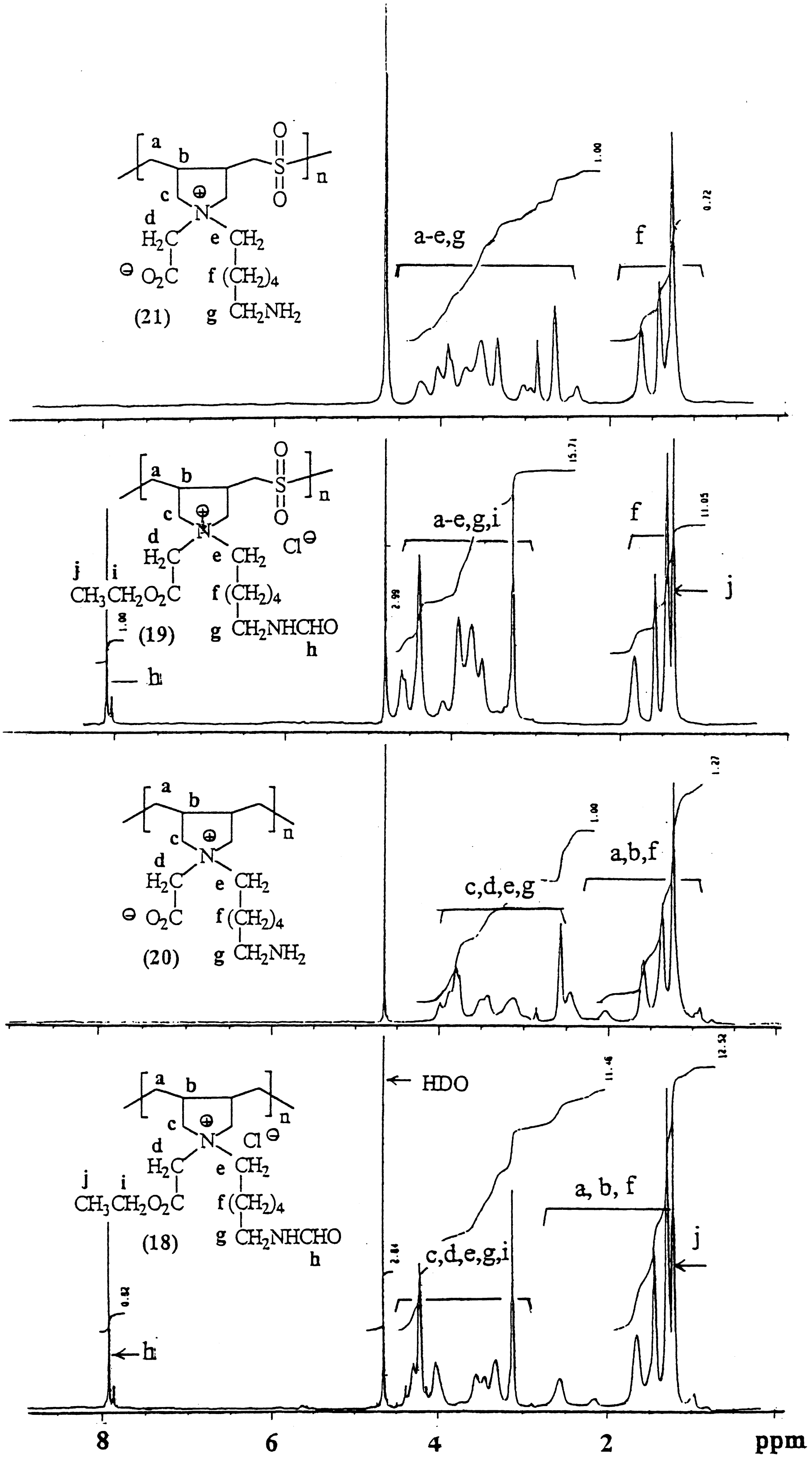


Fig. 1. ^{1}H NMR spectrum of: (a) polyelectrolytes **18**; and (b) **19**, and polyampholytes **20** and **21** in D_2O.

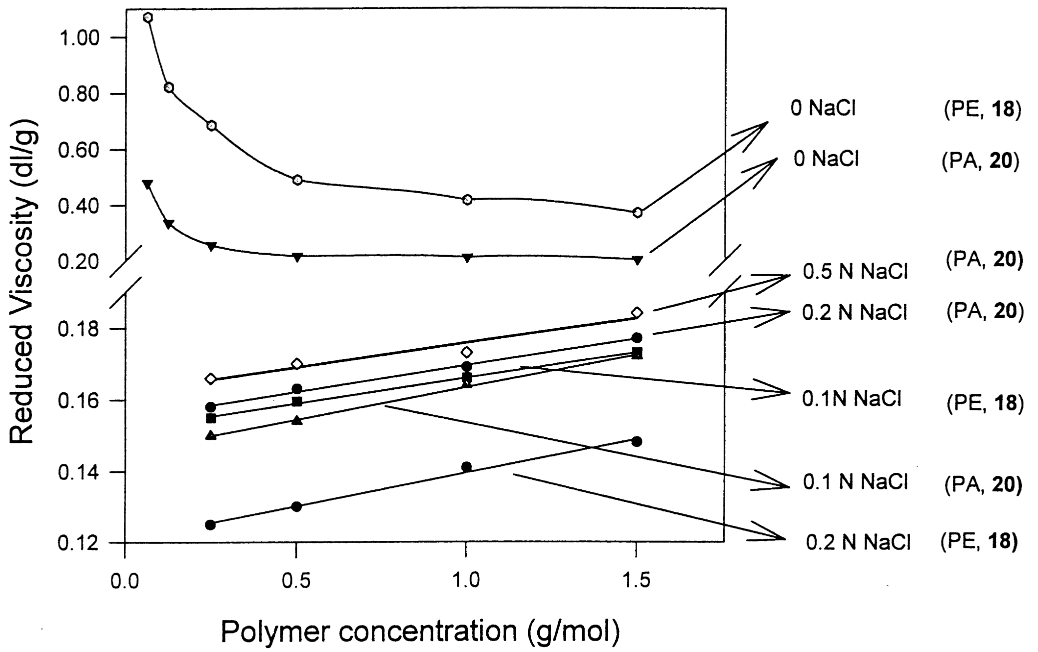
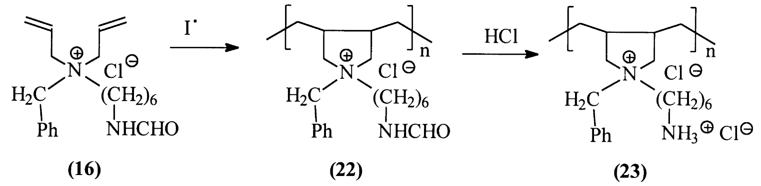


Fig. 2. Effect of added salt (NaCl) on the viscosity behavior of the polyelectrolyte **18** and polyampholytes **20** in water at 30°C using an Ubbelohde Viscometer ($K = 0.005989$).



Scheme 5.

dicationic polymer **23** experiences repulsive forces and as such has larger hydrodynamic volume, hence higher viscosity, in comparison to **22**.

The corrosion inhibition performance of the synthesized monomeric and polymeric materials **9**, **12–23** evaluated using weight loss of mild steel in 1 M HCl at 60°C for 6 hours, is shown in Table 1. As is evident from the table all the materials except the polysulfone **19** demonstrated superior inhibition effects than the parent diamine **9**. The polymers **22** and **23** were found to be more effective than their corresponding monomer **16**. The polymers **18** and **20** were also found to be better inhibitors than their monomer **15**. A kinetically slower desorption step due to the presence of multiple adsorption sites and increased entropy due to displacement of greater number of water molecules per polymer molecule make the synthesized materials better corrosion inhibitors than the parent compound 1,6-hexanediamine (**9**).

4. Conclusion

To the best of our knowledge polyquaternary amine salts of the type described here from open chain diamine have been prepared for the first time. An extensive study involving the inhibition efficiency of some of the promising synthesized materials by electrochemical measurements is currently under investigation in our laboratory. This work has paved the way to elaborate upon 1,12-dodecaneamine, an inexpensive starting material having a more extended hydrophobic cover for the metal surface than the 1,6-hexanediamine. The work is currently under way.

Acknowledgements

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