

**Synthesis, characterization and electrochemical analysis of cysteine modified
polymers for corrosion inhibition of mild steel in aqueous 1 M HCl**

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2. Experimental

2.4 Synthesis

Synthesis of methyl -2- amino -3- methylthiopropoate hydrochloride (2)

Methanol (185 mL) was transferred into a round bottom flask (250 mL), and flask was placed in ice bath at -10 °C, then thionyl chloride (SOCl₂) (48 mL) was added dropwise to methanol. *S*-methyl *L*-cysteine (**1**) (25.0 g, 185 mmol) was then slowly added to the reaction mixture in 5 minutes. The reaction mixture was taken out from the ice bath. Stirring was continued at room temperature for 4 h, then the clear solution was kept in the fume hood overnight. The solvent was evaporated pursuing with nitrogen, dissolve the resultant reaction mixture in methanol (100 mL), followed by an addition of anhydrous diethyl ether (100 mL). The solution was then filtered and methyl ester (**2**) separated as hydrochloride. Yield: 27.2 g, 79%. Elemental analysis: Calculated for C₅H₁₂NO₂S: C, 39.98; H, 8.05; N, 9.32; S, 21.34; found: C, 39.87; H, 8.12; N, 9.24; S, 21.18. ν_{\max} (neat) 3023, 2917, 1675, 1479, 1414, 1343, 1136, 1140, 912, and 844 cm⁻¹; δ_{H} (D₂O) 2.10 (3H, s), 3.06 (2H, dd), 3.16 (2H, m), 3.29 (1H, m), 3.63 (3H, s), 4.27 (2H, m), 4.37 (2H, m); δ_{C} (D₂O): 15.3 (1C, SCH₃), 35.0 (1C, C(NH₃)CH₂S), 53.6 (1C, NCH), 169.6 (1C, CO₂), 56.5 (1C, OCH₃).

Synthesis of N, N-diallyl-L-cysteine methyl ester (3)

A mixture of **2** (24.2 g, 130 mmol), K₂CO₃ (53.9 g, 390 mmol), allyl bromide (34.9 g, 286 mmol) in acetonitrile (315 mL) under N₂ was stirred at 60 °C for 28 h. The acetonitrile was removed by N₂ evaporation, dissolved the reaction mixture in de-ionized water (150 mL), extracted three times with diethyl ether (150 mL). The diethyl ether was evaporated by N₂ evaporation in water bath at 70 °C, dried and distilled using a vigreux distilling column to obtain amino methyl ester (**3**) as a colorless liquid. Yield: 24.2 g, 81%. bp (2 mbar Hg) 105 °C. Elemental analysis: Calculated for

$C_{11}H_{19}NO_2S$: C, 57.6; H, 8.35; N, 6.11; S, 13.98; found: C, 58.4; H, 8.56; N, 6.23; S, 13.87. ν_{\max} . (neat) 3489, 2932, 2862, 1679, 1477, 1341, 1160, 1271, 1208, 1176, 971, 948, and 844 cm^{-1} . δ_H ($CDCl_3$) 1.19 (3 H, t), 1.98 (1H, m), 2.05 (3H, s), 2.44 (2H, m), 2.99 (2H, dd), 3.22 (2H, m), 3.41 (1H, dd), 4.62 (2H, m), 5.01 (2H, m), 5.08 (2H, m), 5.67 (2H, m). δ_C ($CDCl_3$): 13.25 (1C, SCH_3), 32.01 (1C, CH_2S), 55.01 (2C, NCH_2), 58.89 (1C, NCH), 62.46 (1C, OCH_3), 115.22 (2C, $CH=CH_2$), 138.25 (2C, $CH=CH_2$), 171.19 (1C, CO_2), (77.00, middle C of $CDCl_3$).

Synthesis of N, N-diallyl-l-cysteine methyl ester hydrochloride (4)

Dry HCl was passed onto a solution of amine **3** (15 g, 65.4 mmol) in diethyl ether (75 mL) until the supernatant liquid does no longer become turbid due to the passage of HCl. The hydrochloride salt **4**, separated as an oily liquid, was washed with diethyl ether two times 50 mL each to obtain *N,N*-Diallyl-*l*-cysteine methyl ester hydrochloride (**4**). Yield: 16.2 g, 93%. Elemental analysis: Calculated for $C_{11}H_{20}ClNO_2S$: C, 49.7; H, 7.58; N, 5.27; S, 12.06; found: C, 49.9; H, 7.82; N, 5.62; S, 12.23. 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) 1.92 (3H, s), 2.41 (1H, m), 2.51 (1H, m), 3.02 (1H, m), 3.61 (2H, dd), 4.90 (3H, m), 5.42 (4 H, m), 5.73 (2H, m), residual H in D_2O at 4.65 ppm; δ_C (D_2O): 14.20 (1C, SCH_3), 31.21 (1C, CH_2S), 57.65 (2C, NCH_2), 63.39 (1C, NCH), 65.46 (1C, OCH_2), 125.52 (2C, $CH=CH_2$), 127.34 (2C, $CH=CH_2$), 168.69 (1C, CO_2), (67.4, dioxane).

Synthesis of cysteine residual cationic monomer (6)

A heterogeneous mixture of monomer precursor **4** (9.21 g, 40.2 mmol), CH_3OH (10 mL), H_2O (20 mL), and sodium hydroxide (1.82 g, 45.5 mmol) was stirred at 45 °C for 3 h. After concentrating the homogeneous mixture, the residual reaction mixture **5** was diluted with water (15

mL), acidified with concentrated HCl (37%) (9.42 g; 180 mmol) (i.e., two equivalents of HCl), and then freeze-dried to obtain a mixture of acid hydrochloride cysteine residue of cationic monomer **6** and NaCl. After trituration with acetone (100 mL) and filtering off the insoluble NaCl, the filtrate was concentrated to obtain monomer (**6**) as a colorless thick liquid. Yield: 9.50 g, 94%. Elemental analysis of $C_{10}H_{18}ClNO_2S$: Calculated C, 48.1; H, 7.43; N, 5.32; S, 12.6; found: C, 47.7; H, 7.21; N, 5.56; S, 12.7. ν_{\max} . (neat) 3348, 3088, 2921, 2848, 2360, 2331, 1735, 1635, 1448, 1425, 1388, 1325, 1201, 1157, 1078, 995, 946, 872, 770 and 736 cm^{-1} . δ_H (D_2O) 1.14 (3 H, t), 1.98 (3H, s), 2.12 (1H, m), 2.19 (1H, m), 2.44 (1H, m), 2.61 (1H, m), 3.79 (2H, dd), 5.47 (4 H, m), 5.78 (2H, m), residual H in D_2O at 4.65 ppm); δ_C (D_2O): 14.1 (1C, $S\underline{C}H_3$), 30.11 (1C, $\underline{C}H_2S$), 54.98 (2C, $N\underline{C}H_2$), 63.24 (1C, $N\underline{C}H$), 125.38 (2C, $\underline{C}H=CH_2$), 127.89 (2C, $CH=\underline{C}H_2$), 170.41 (1C, $\underline{C}O_2$), (67.4, dioxane).