A water-soluble alanine-derived copolymer as an effective corrosion inhibitor and its synergistic interaction (KI) for SLM 17-4 PH steel corrosion mitigation in acidified NaCl solution

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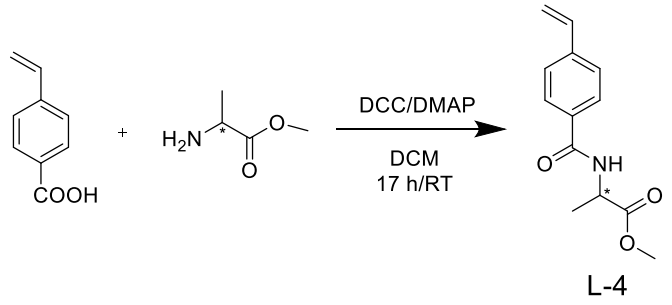
1. Synthesis of alanine-derived water-soluble copolymer

Synthesis of monomer (L-4)



Scheme S1. Synthesis of monomer **L-4**.

1-Alanine methyl ester (83 mg, 0.81 mmol), dicyclohexylcarbodiimide (DCC) (0.16 g, 0.81 mmol), and a catalytic amount of 4-dimethylaminopyridine (DMAP) were dissolved in dichloromethane (DCM) (20 mL). Then 4-vinylbenzoic acid (0.1 g, 0.67 mmol) was added to the above solution and the reaction mixture was continuously stirred at RT for 17 h. The obtained solution was filtered, washed, and extracted with DCM. Finally, the organic layer was further washed with brine, dried and the solvent was removed. The crude product was further purified by silica gel column chromatography (hexane: ethyl acetate = 2:1, *v/v*) to afford monomer L-4 (white solid, 0.13 g, 0.55 mmol, 83%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ (ppm): 7.76-7.78 (d, *J* = 8 Hz, 2H), 7.46-7.48 (d, *J* = 8 Hz, 2H), 6.71-6.77 (m, 2H), 5.82-5.87 (d, *J* = 20 Hz, 1H), 5.35-5.38 (d, *J* = 12 Hz, 1H), 4.77-4.85 (m, 1H), 3.80

(s, 3H), 1.52-1.54 (d, J = 8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ (ppm): 173.49, 166.35, 141.11, 136.10, 132.98, 127.39, 126.36, 116.08, 52.61, 48.51 ppm.

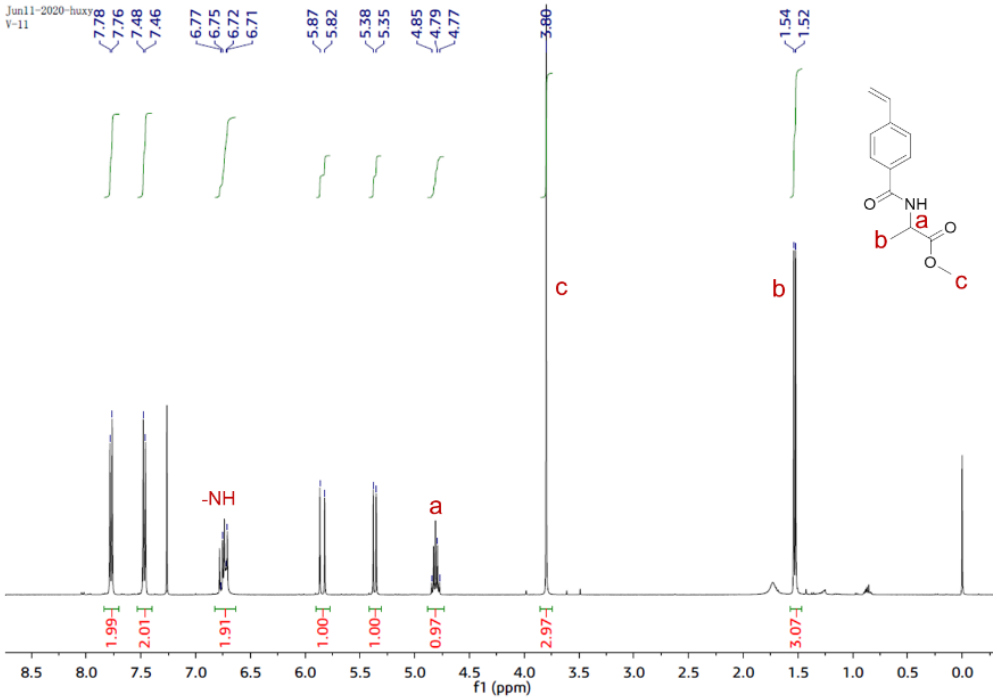


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of monomer L-4.

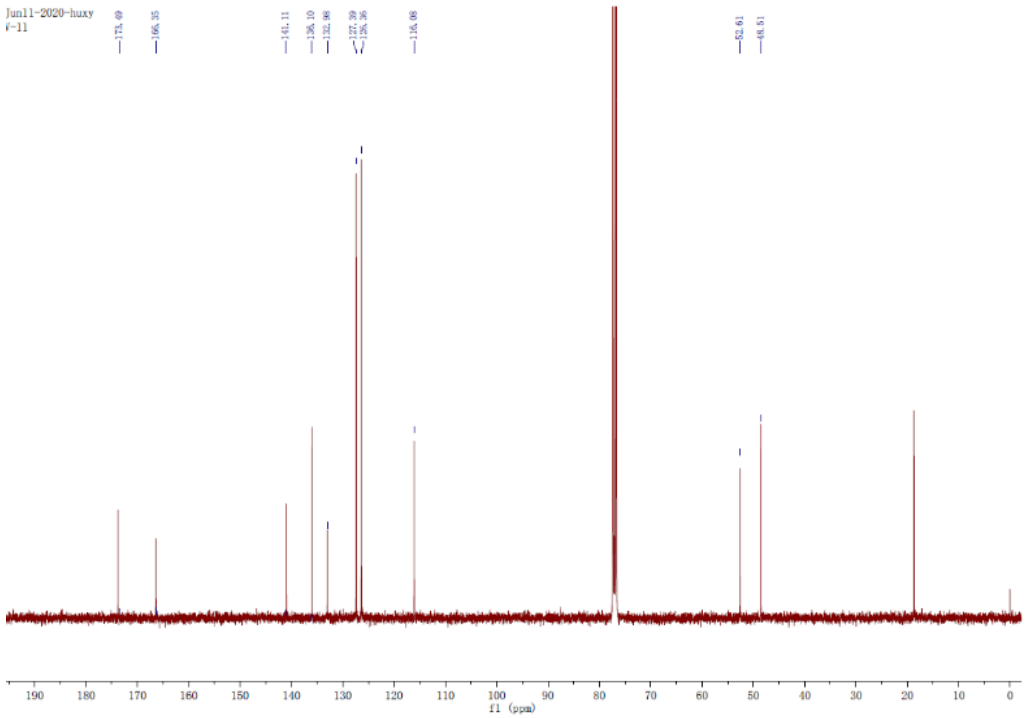
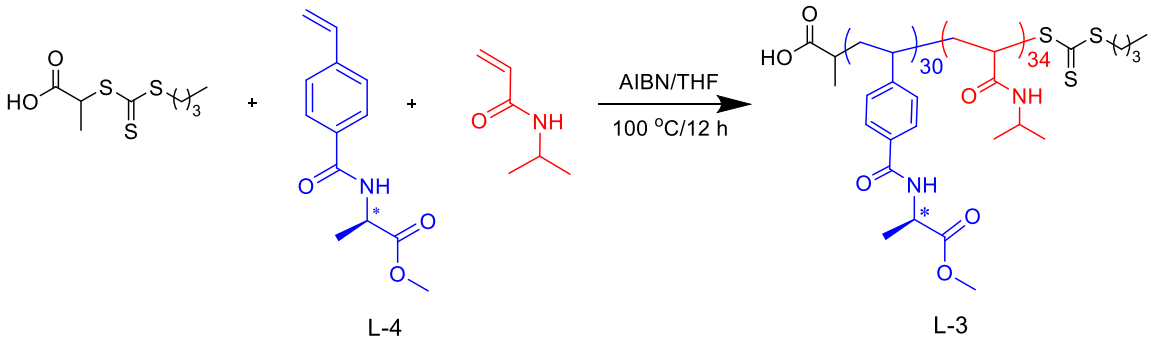


Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) spectrum of monomer L-4.

2. Synthesis of copolymer (L-3) by RAFT polymerization



Scheme S2. Preparation of copolymer L-3 by RAFT polymerization.

Monomer (L-4) (0.29 g, 1.25 mmol), 2-((butylthio)carbonothioyl)thiopropanoic acid (10 mg, 41.90 µmol) as a chain transfer agent (CTA), N-Isopropylacrylamide (NIPAM) (0.33 g, 2.90 mmol), 2,2'-azobisisobutyronitrile (AIBN) (1.3 mg, 8.30 µmol) and THF (0.7 mL) were taken in a Schlenk flask with stirring bar. This reaction mixture was degassed by three freeze-pump-thaw cycles and backfilled with N_2 and continuously stirred at 100 °C (oil bath) for 12 h. The reaction was quenched by cooling the reaction tube in an ice bath and

the mixture was precipitated by hexane. This dissolution-precipitation was further repeated three times and the obtained yellow solid was completely dried at 40 °C for 24 h. The degree of polymerization was calculated by ^{1}H NMR. ^{1}H NMR (400 MHz, CD_3OD, 298 K), δ (ppm): 7.87 (m, 120H), 6.50-7.35 (m, 124H), 3.49-3.95 (m, 188H), 0.90-2.28 (m, 435H) ppm. $M_{n,GPC}$ = 11.4 kDa, PDI = 1.13.

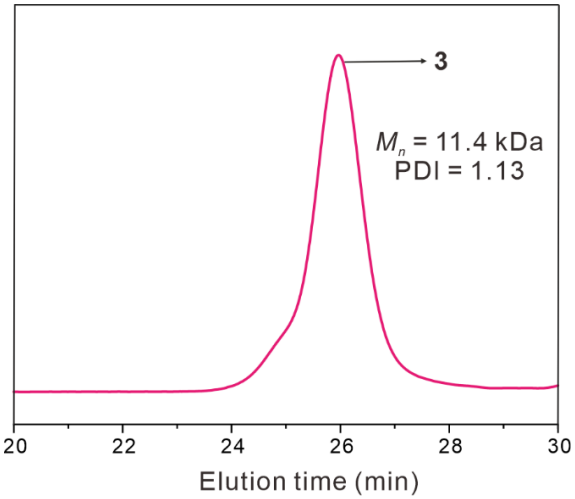


Figure S3. GPC of copolymer (L-3).

For the hydrolysis of L-3, aq. NaOH (10 mL, 2.0 M) was added into the cooled solution of **L-3** (0.1 g) in MeOH (20 mL) and the mixture was stirred at RT for 24 h. The final solution was acidified with HCl and the formed pale yellow precipitate **L-2** was filtered, washed, and dried at 40 °C for 24 h. ^{1}H NMR (400 MHz, CD_3OD, 298 K), δ (ppm): 7.33-7.96 (m, 120H), 6.24-6.98 (m, 124H), 3.96-4.70 (m, 98H), 0.60-2.78 (m, 435H) ppm.

3.0 Synthesis of alanine-derived water-soluble copolymer (L-1)

Copolymer L-2 (0.1 g) and $NH_3 \cdot H_2O$ (20 mL) were mixed and stirred at RT for 24 h. The excess ammonia and solvent were removed and dried in a vacuum. The alanine-derived water-soluble copolymer (L-1) was obtained as a yellow solid. ^{1}H NMR (400 MHz, CD_3OD, 298 K), δ (ppm): 7.49-7.69 (m, 120H), 6.78-7.12 (m, 124H), 3.52-4.31 (m, 98H), 0.84-1.93 (m, 435H) ppm.

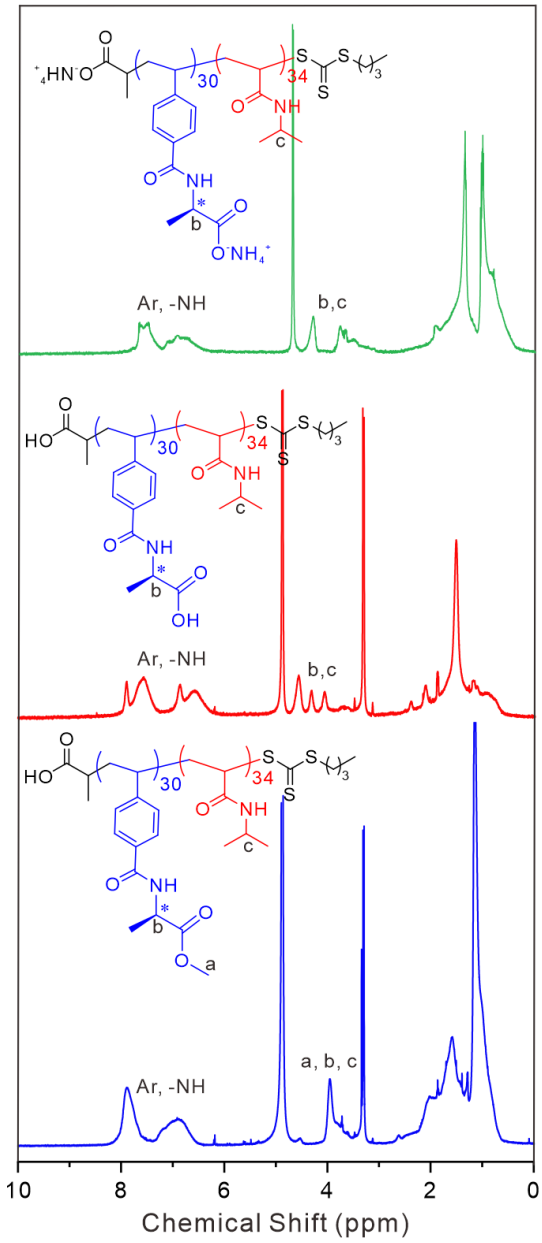


Figure S4. ^{1}H NMR (400 MHz, CD_3OD, 298 K) spectra of copolymers L-1 (D_2O), L-2, and L-3.