SUPPORTING INFORMATION

Metal-free Coumarate based poly(ionic liquid)s as Corrosion Inhibitors

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EXPERIMENTAL SECTION

1. Materials and Equipments

Materials

p-Coumaric acid, 2-(dimethyl amino)ethyl methacrylate, potassium hydroxide and Darocur (Speedcure 73) were obtained from Sigma Aldrich. 1-Bromobutane and 1-Bromohexane were obtained from Acros. Oxybis(propane-1,2-diyl) diacrylate, dipropylene glycol diacrylate, trimetylpropyl triacrylate, cyclic trimethylolpropane formal acrylate and acid based adhesion promotors were obtained from Arkema/Sartomer. Mild Steel AS1020, NaCl aqueous solution, HCl aqueous solution, MiliQ water, methanol and ethanol were used without further purification.

Equipments

Nuclear magnetic resonance (NMR)

NMR spectra were recorded on a Bruker AC-400 (for 1H-NMR, 13C-NMR, HSQC and COSY) spectrometer with the following experimental conditions: spectral width 15 ppm with 32k data points, flip angle 908, relaxation delay of 1 s, digital resolution of 0.24 Hz/pt.

Immersion test

Immersion tests were carried out in order to observe and compare the inhibition performance of the different inhibitor compounds. 24 h immersion tests of mild steel AS1020 in 0.01 M NaCl aqueous solution with and without 8mM of inhibitor monomers were carried out. Surfaces of mild steel after immersion were rinsed with MiliQ water, dried with N2 gas and dried in a dessicator for 2h.

Optical microscopy

A Leica MZ 7 optical microscope was combined with LAS V4.0 software to observe surfaces after 24 hours of immersion.

Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS)

SEM and EDS were used to observe mild steel surfaces after the immersion test. A JSM-IT300 LV SEM instrument, with an Oxford instrument X-Max 50 mm2 EDS detector at 15kV, was used with an accelerating voltage of 20 kV. EDS spectra collected for 60 s were produced using AZtec software.

UV curing conveyor

Photopolymerizations were performed on a UVC-5 UV Curing Conveyor System. The coatings were UV-cured with a intensity up to 400 mW/cm2 for 2 minutes.

Attenuated Total Reflectance – Fourier Transport Infrared spectroscopy (ATR-FTIR)

Attenuated total reflection–Fourier transform infrared spectroscopy (ATR-FTIR) measurements were performed on Bruker Alpha-P equipment. The spectra were recorded from 50 to 4000 cm -1 with a resolution of 2 cm-1.

Swelling test

Polymer coatings were immersed in MiliQ water and where weighted at time 0, after 24h, 48h and 72h.

Potentiodynamic polarisation (PP) test and Electrochemical impedance spectroscopy (EIS)

BioLogic VMP3 multi-channel potentiostat combined with EC Lab V10.44 software were used for PP experiments. A three-electrode cell was used with the steel rod as the working electrode, a titanium mesh counter electrode and Ag/AgCl reference electrode. The reference electrode was placed in a Luggin capillary that was positioned close to the working electrode surface. The Open Circuit Voltage (OCV) was monitored for 30 minutes followed by the PP scan at a rate of 0.167 mV/s, with a scan range of 150 mV below to 250 mV above OCV. Three PP curves were obtained for each test solution.
Specific icorr and Ecorr values were extracted from the PP curves using Tafel extrapolation. The curves were approximately linear over a range of 10-25 mV either side of Ecorr and so the Tafel extrapolations were made over the data in this range. A value for icorr was taken as the point where the linear section of the anodic and cathodic sections of the PP curves intersected the value for Ecorr.
From the icorr values, inhibitor efficiencies (IE) were calculated according to Equation 1:

$$IE = \frac{i_{corr\,control} - i_{corr\,inhibited}}{i_{corr\,control}} \times 100 \qquad (1)$$

The electrochemical impedance spectroscopy (EIS), over a test period of 24 hours, was carried out in order to characterize the electrochemical properties of AS1020 mild steel electrodes immersed in the control, inhibited solution or containing polymer coatings. The aforementioned BioLogic VMP3 multi-channel potentiostat was used for the EIS tests. The OCV was monitored over a frequency range from 100 kHz to 10 mHz with 6 points per decade and a sinusoidal amplitude of 10mV. Impedance responses were monitored after each hour.

2. Synthesis

Synthesis of 2-(dimethyl amino)ethyl methacrylate p-coumarate (Scheme S1.B)

2-(dimethyl amino)ethyl methacrylate and p-coumaric acid were weighed and mixed in an equimolar amount. The product was obtained in-stantly as a viscous liquid. 1H NMR (400 MHz, DMSO) δ 7.50, 7.49, 7.48, 7.45, 6.80, 6.79, 6.78, 6.78, 6.30, 6.26, 6.02, 5.66, 5.66, 5.65, 4.19, 4.18, 4.16, 3.47, 3.45, 3.43, 3.42, 2.19, 1.07, 1.05, 1.04.

Synthesis of p-butoxy coumaric acid (Scheme S1.A)

p-Coumaric acid (1 mol), KOH (3 mol) and KI (cat., 20 mol%) were dissolved in a mixture of ethanol/water (75/25) and refluxed for 1 h. Butyl bromide (1 mol) was added and the reaction mixture was refluxed for a further 24 hours. The solvent was re-moved and the precipitate was acidified with concentrated HCl. The crude product was filtered, washed with water and recrystallized from a mix-ture of ethanol/water (75/25). The final product was dried under vacuum for 48 h at 50 °C, to yield the title compound as a white powder. 1H NMR (400 MHz, D2O) δ 7.57, 7.56, 7.55, 7.55, 7.35, 7.31, 7.01, 7.01, 7.00, 6.99, 6.98, 6.40, 6.40, 6.36, 6.36, 4.85, 4.79, 4.73, 4.11, 4.09, 4.07, 1.77, 1.75, 1.74, 1.73, 1.72, 1.70, 1.48, 1.46, 1.45, 1.43, 1.41, 1.39, 0.94, 0.92, 0.92, 0.90.

Synthesis of p-hexoxy coumaric acid (Scheme S1.A)

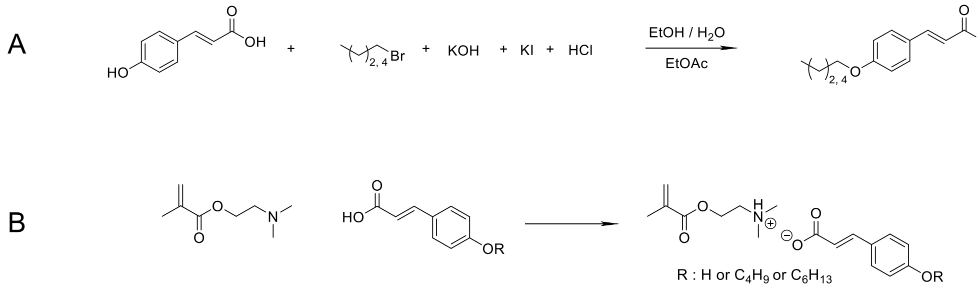
p-coumaric acid (1 mol), KOH (3 mol) and KI (cat., 20 mol%) were dissolved in a mixture of etha-nol/water (75/25%) and refluxed 1 hour. 1-Bromohexane (1 mol) was added and the reaction mixture was refluxed for a further 24 hours. The solvent was removed and the precipitate was acidi-fied with concentrated HCl. The crude product was filtered, washed with water and recrystallized from a mixture of ethanol/water (75/25%). The final prod-uct was dried under vacuum and obtained as a white powder. 1H NMR (400 MHz, D2O) δ 7.57, 7.57, 7.56, 7.55, 7.54, 7.35, 7.31, 7.01, 7.01, 6.99, 6.99, 6.98, 6.40, 6.40, 6.36, 6.36, 4.85, 4.85, 4.79, 4.75, 4.73, 4.10, 4.09, 4.08, 4.08, 4.06, 4.06, 1.78, 1.76, 1.74, 1.73, 1.71, 1.44, 1.42, 1.40, 1.38, 1.32, 1.31, 1.30, 1.29, 1.29, 1.28, 0.87, 0.85, 0.85, 0.84, 0.83.

Synthesis of 2-(dimethyl amino)ethyl methacrylate p-butoxy coumarate (Scheme S1.B)

2- (dimethyl amino)ethyl methacrylate and p-butoxy coumarate were weighted and mixed in an equimolar amount. The product was obtained in-stantly as a viscous liquid. 1H NMR (400 MHz, D2O) δ 7.84, 7.55, 7.53, 7.41, 7.34, 7.30, 7.08, 7.06, 7.04, 7.02, 6.99, 6.97, 6.39, 6.35, 5.44, 5.40, 4.99, 4.98, 4.96, 4.79, 4.08, 4.06, 4.05, 1.77, 1.75, 1.73, 1.71, 1.70, 1.43, 1.41, 1.39, 1.31, 1.30, 1.28, 0.86, 0.85, 0.83.

Synthesis of 2-(dimethyl amino)ethyl methacrylate p-hexoxy coumarate (Scheme S1.B)

2- (dimethyl amino)ethyl methacrylate and p-hexoxy coumarate were weighted and mixed in an equimolar amount. The product was obtained in-stantly as a viscous liquid. 1H NMR (400 MHz, D2O) δ 7.70, 7.66, 7.60, 7.58, 7.02, 7.00, 6.48, 6.44, 6.28, 5.72, 4.49, 4.48, 4.12, 4.10, 4.09, 3.00, 2.98, 2.97, 2.58, 2.08, 1.94, 1.93, 1.92, 1.90, 1.88, 1.59, 1.57, 1.49, 1.48, 1.47, 1.37, 1.36, 1.34, 1.06, 1.04, 1.02.



Scheme S1. Synthesis of p-butoxy coumaric acid and p-hexoxy coumaric acid (A) and 2-(dimethyl amino)ethyl methacrylate p-coumarate, 2-(dimethyl amino)ethyl methacrylate p-butoxy coumarate and 2-(dimethyl amino)ethyl methacrylate p-hexoxy coumarate (B)

Preparation of polymer coating containing 2-(dimethyl amino)ethyl methacrylate p-coumarate (Figure 3)

Oxybis(propane-1,2-diyl) diacrylate (40% w/w), di-propylene glycol diacrylate (25% w/w), trimetyl pro-pyl triacrylate (13% w/w), cyclic trimethylolpropane formal acrylate (12% w/w), acid based adhesion promotor (3% w/w), Darocur (Speedcure 73) (5% w/w) and 2-(dimethyl amino)ethyl methacrylate p-coumarate (20% w/w) were added and mixed in a vial. A mild Steel 1020 surface was prepared in order to have a rectangular gap to a depth of 62.5 µm. The gap was filled with the aforementioned mixture and then UV cured.

Preparation of polymer coating containing 2-(dimethyl amino)ethyl methacrylate p-butoxy coumarate (Figure 3)

Oxybis(propane-1,2-diyl) diacrylate (40% w/w), dipropylene glycol diacrylate (25% w/w), trimetyl propyl triacrylate (13% w/w), cyclic trimethylolpropane formal acrylate (12% w/w), acid based adhesion promotor (3% w/w), Darocur (Speedcure 73) (5% w/w) and 2-(dimethyl amino)ethyl methacrylate p-butoxy coumarate (20% w/w) were added and mixed in a vial. A mild Steel 1020 surface was prepared in order to have a rectangular gap to a depth of 62.5 µm. The gap was filled with the aforementioned mixture and it was UV cured.

Preparation of polymer coating containing 2-(dimethyl amino)ethyl methacrylate p-hexoxy coumarate (Figure 3)

Oxybis(propane-1,2-diyl) diacrylate (40% w/w), dipropylene glycol diacrylate (25% w/w), trimetyl propyl triacrylate (13% w/w), cyclic trimethylolpropane formal acrylate (12% w/w), acid based adhesion promotor (3% w/w), Darocur (Speedcure 73) (5% w/w) and 2-(dimethyl amino)ethyl methacrylate p-hexoxy coumarate (20% w/w) were added and mixed in a vial. A mild Steel 1020 surface was prepared in order to have a rectangular gap to a depth of 62.5 µm. The gap was filled with the aforementioned mixture and it was UV cured.

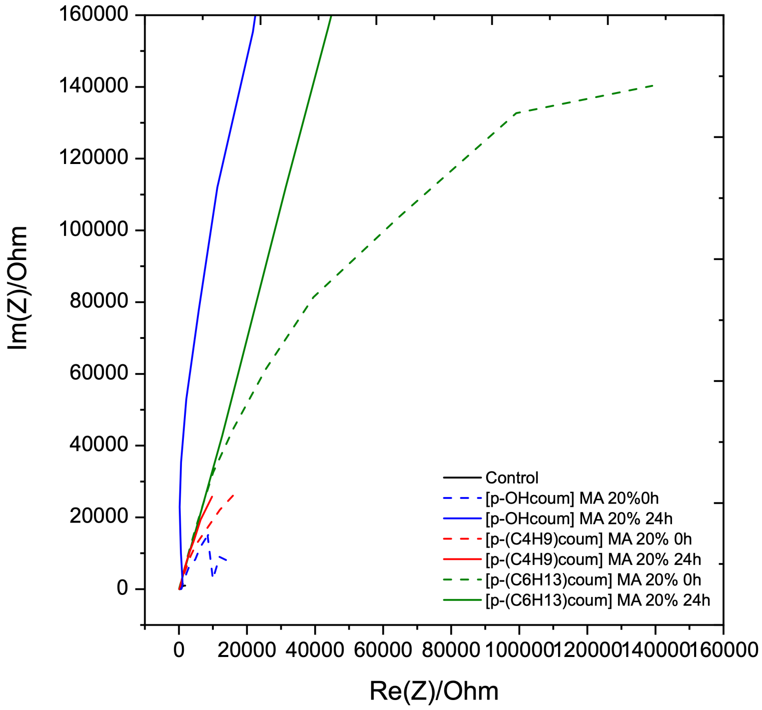


Fig. S1 Nyquist plot of AS1020 mild steel in 0.01M NaCl containing 8mM [p-OHcoum]MA (red), 8mM, [p-O(C_4H_9)coum] MA (blue), [p-O(C_6H_{13})coum] MA (green) and control (black) as a function of time (0h dots, 24h line)

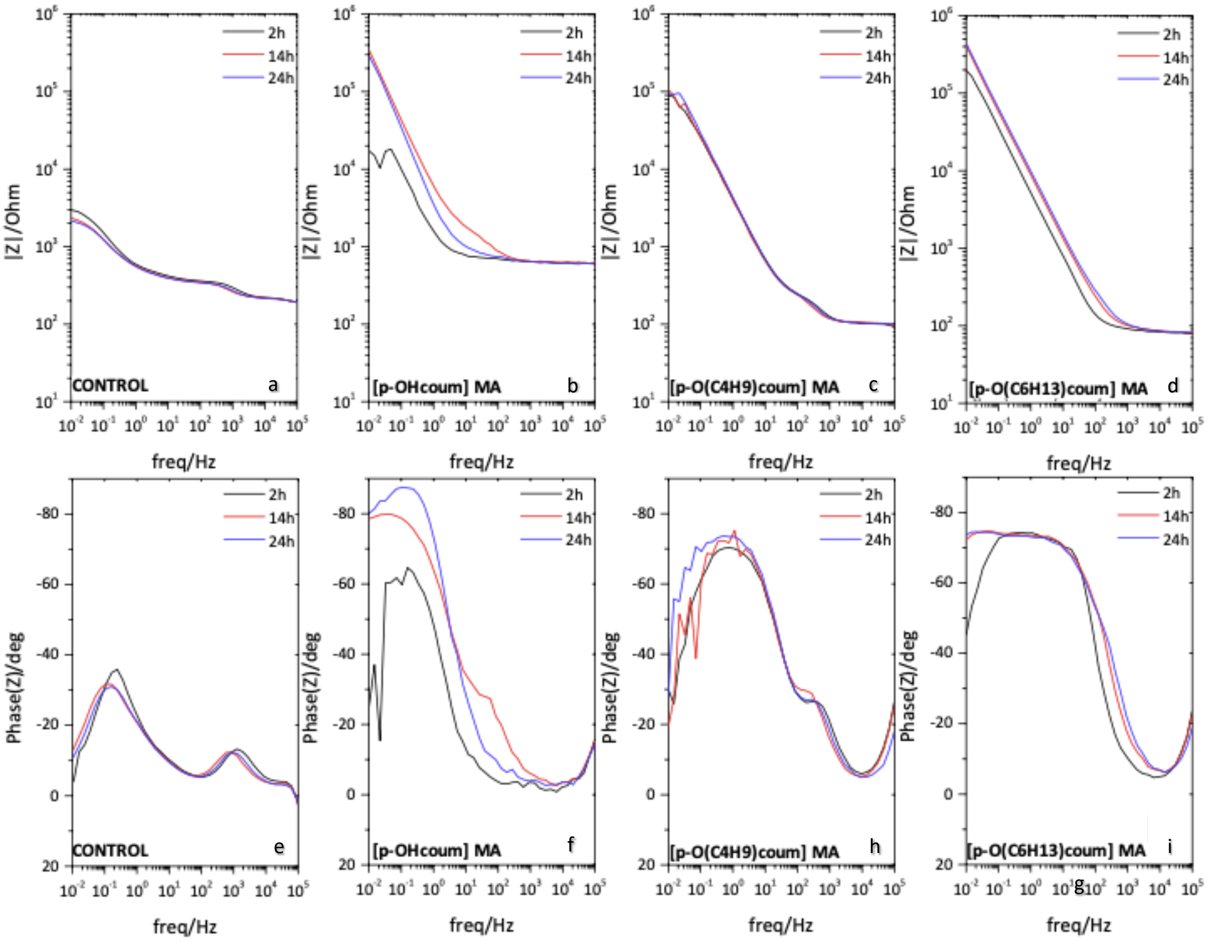


Fig. S2 Electrochemical impedance spectra for AS1020 mild steel immersed in the control and the inhibited solutions up to 24 h: impedance modulus and phase angle plots for control (a, e); inhibited solution containing [pOHcoum] MA (b, f); inhibited solution containing [p-O(C_4H_9)coum] MA (c, g); inhibited solution containing [p-O(C_6H_{13})coum] MA (d, h)

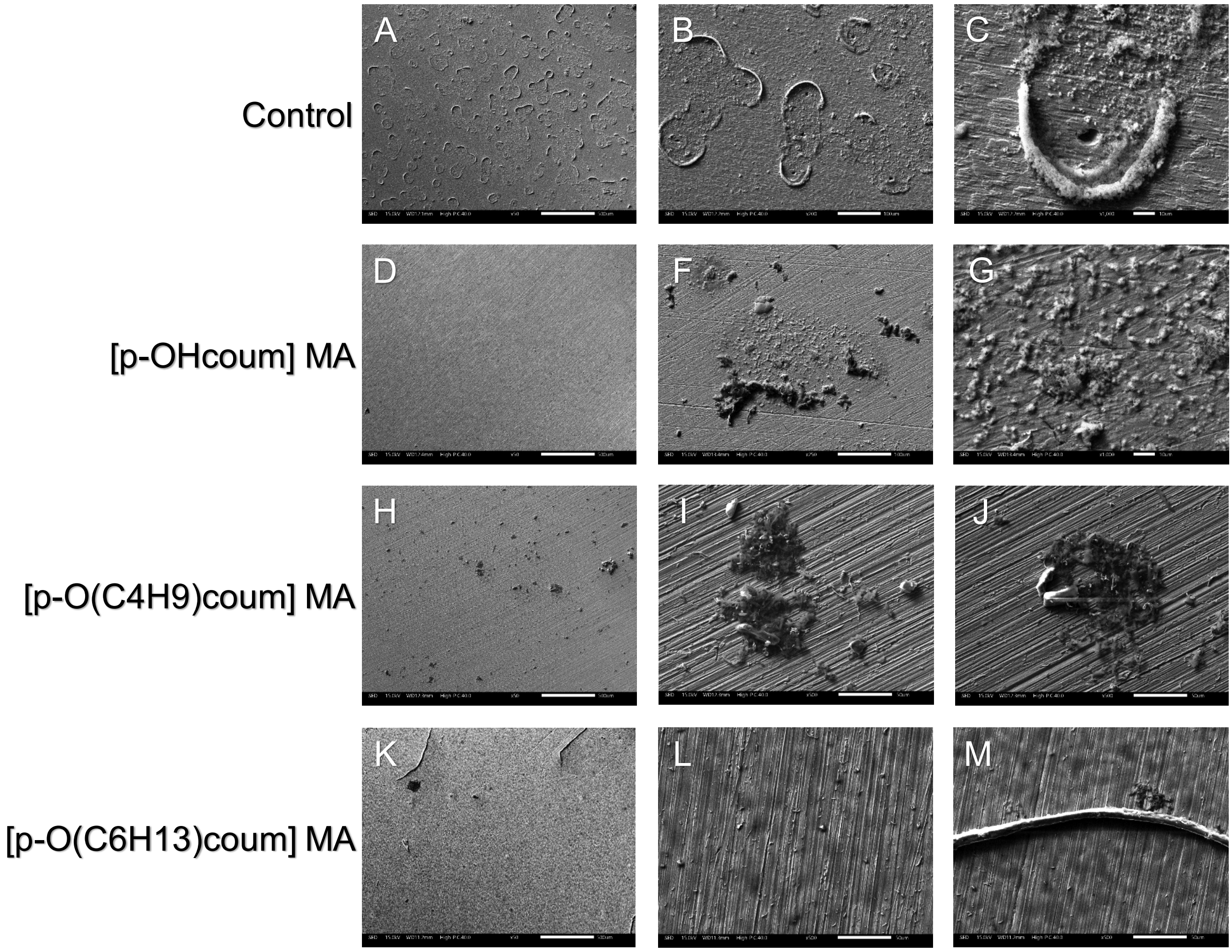


Fig. S3 SEM images (A, B, C, D, E, F, G, H, I, J, K, L and M) of mild steel samples immersed in the control and the inhibited solutions ([p-OHcoum] MA, [p-O(C_4H_9)coum] MA) and [p-O(C_6H_{13})coum] MA) for 24h

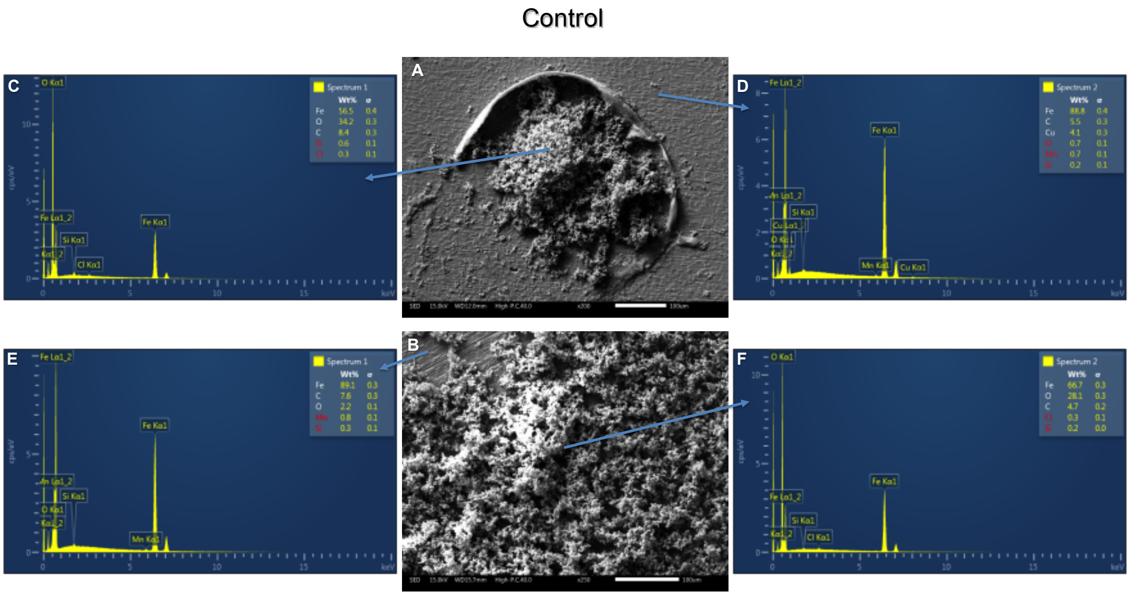


Fig. S4. SEM image and EDS spectra of bare mild steel sample exposed to 0.01M NaCl

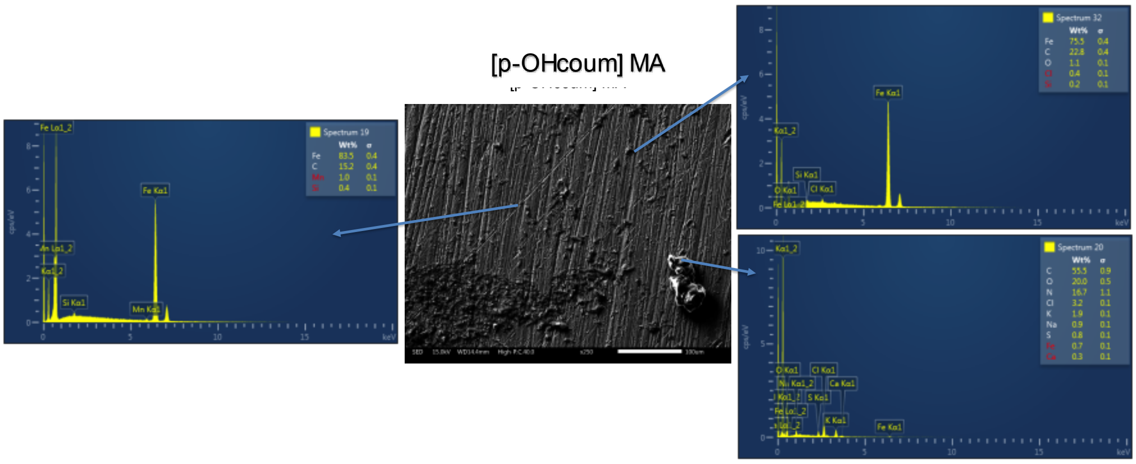


Fig. S5 SEM image and EDS spectra of mild steel sample exposed to 0.01M NaCl + 8mM [p-OHcoum] MA for 24 h for the region with heavy deposits

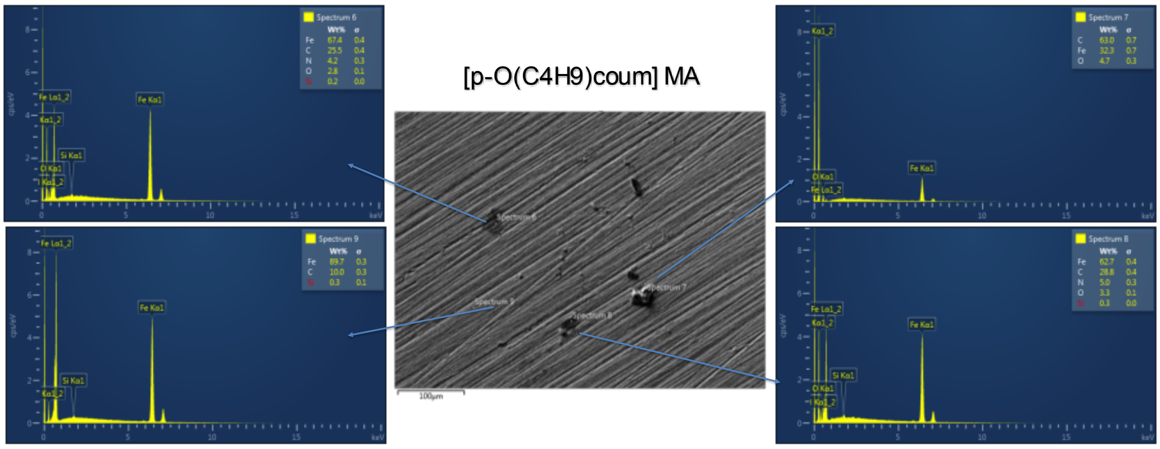
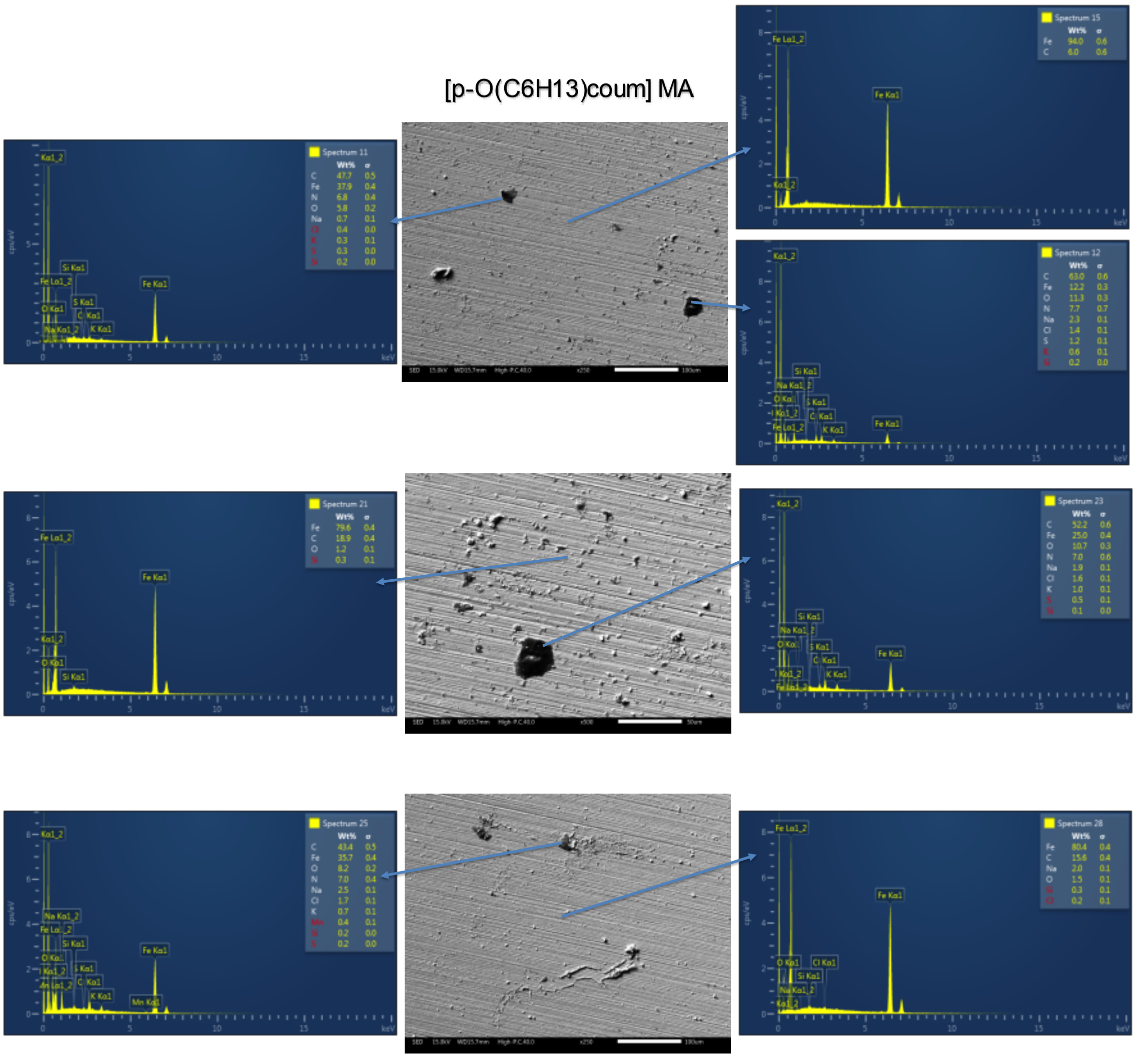


Fig. S6 SEM image and EDS spectra of mild steel sample exposed to 0.01M NaCl + 8mM [p-O(C_4H_9)coum] MA for 24 h for the region with heavy deposits



Spectrum 11

	Wt%	σ
C	47.7	0.5
Fe	37.9	0.4
N	6.8	0.4
O	5.8	0.2
Na	0.7	0.1
Cl	0.4	0.0
K	0.3	0.1
S	0.3	0.0
Si	0.2	0.0

Spectrum 15

	Wt%	σ
Fe	94.0	0.6
C	6.0	0.6

Spectrum 12

	Wt%	σ
C	63.0	0.6
Fe	12.2	0.3
O	11.3	0.3
N	7.7	0.7
Na	2.3	0.1
Cl	1.4	0.1
S	1.2	0.1
K	0.6	0.1
Si	0.2	0.0

Spectrum 21

	Wt%	σ
Fe	79.6	0.4
C	18.9	0.4
O	1.2	0.1
Si	0.3	0.1

Spectrum 23

	Wt%	σ
C	52.2	0.6
Fe	25.0	0.4
O	10.7	0.3
N	7.0	0.6
Na	1.9	0.1
Cl	1.6	0.1
K	1.0	0.1
S	0.5	0.1
Si	0.1	0.0

Spectrum 25

	Wt%	σ
C	43.4	0.5
Fe	35.7	0.4
O	8.2	0.2
N	7.0	0.4
Na	2.5	0.1
Cl	1.7	0.1
K	0.7	0.1
Mn	0.4	0.1
Si	0.2	0.0
S	0.2	0.0

Spectrum 28

	Wt%	σ
Fe	80.4	0.4
C	15.6	0.4
Na	2.0	0.1
O	1.5	0.1
Si	0.3	0.1
Cl	0.2	0.1

Fig. S7 SEM image and EDS spectra of mild steel sample exposed to 0.01M NaCl + 8mM [p-O(C_6H_{13})coum] MA for 24 h for the region with heavy deposits

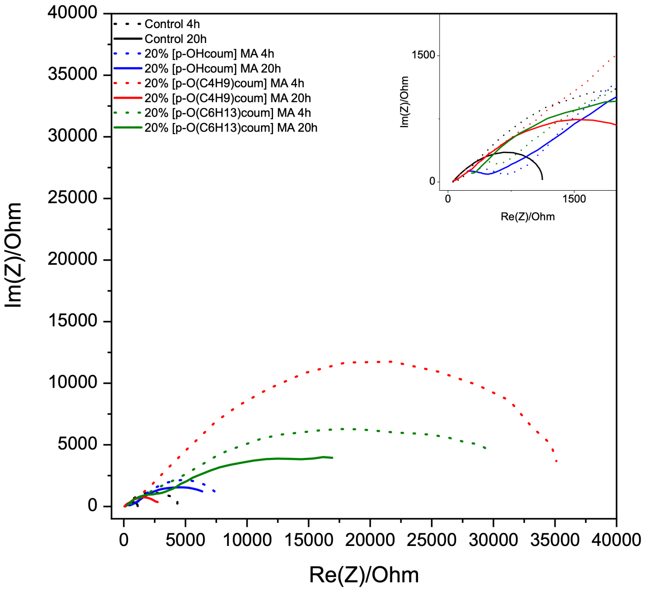


Fig. S8 Nyquist plot of polymer coating on AS1020 mild steel containing 20% of [p-OHcoum] MA (blue), 20% of [p-O(C_4H_9)coum] MA (red), 20% of [p-O(C_6H_{13})coum] MA (green) and control (black) immersed in 0.005M NaCl

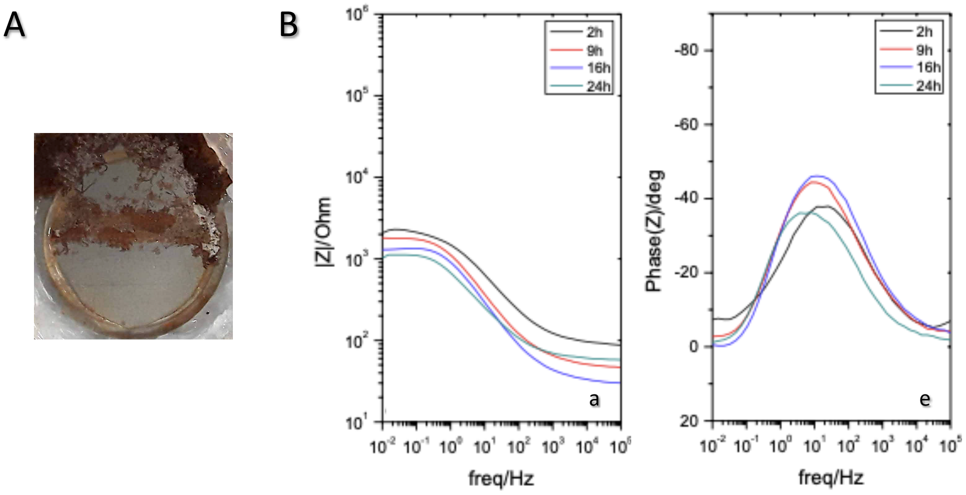


Fig. S9 Control polymer coating without inhibitor photopolymerized on AS1020 mild steel after an immersion of 20h in 0.005M NaCl after (A) and electrochemical impedance spectra of the control polymer coatings without inhibitor on AS1020 mild steel immersed in 0.005M NaCl: impedance modulus (a) and phase angle plots (b) (B).

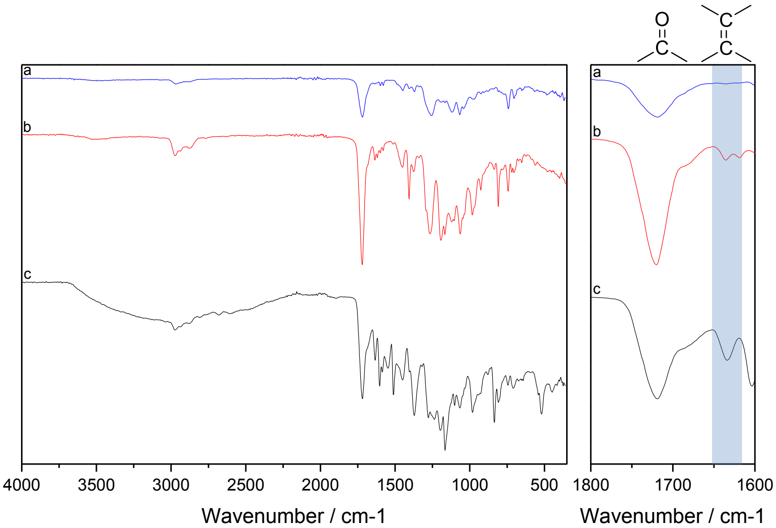


Fig. S10 FTIR of 2-(Dimethylamino)ethyl methacrylate p-coumarate protic ionic liquid ([p-OHcoum] MA) based monomer mixture and coating compared with the control coating

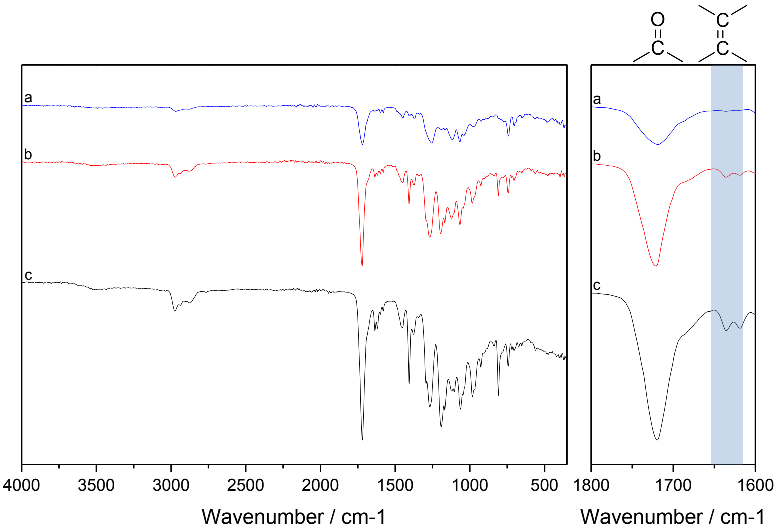


Fig. S11 FTIR of 2-(Dimethylamino)ethyl methacrylate butoxy p-coumarate protic ionic liquid ([p-O(C_4H_9)coum] MA) based monomer mixture and coating compared with the control coating

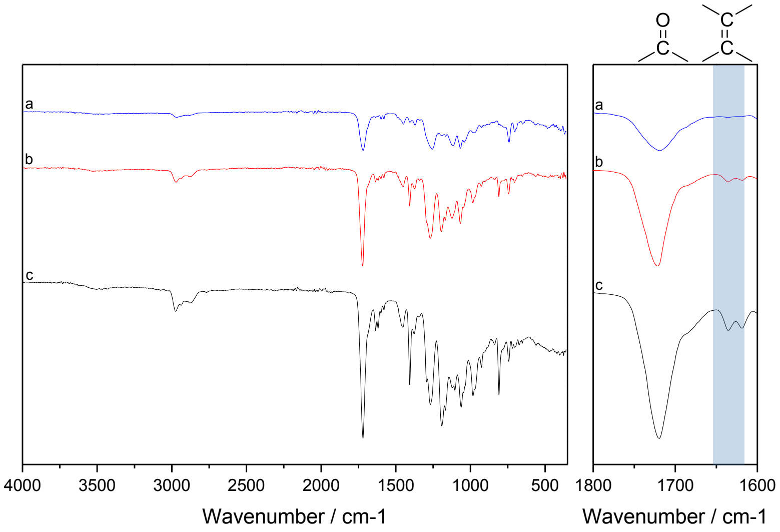


Fig. S12 FTIR of 2-(Dimethylamino)ethyl methacrylate hexoxy p-coumarate protic ionic liquid ([p-O(C_6H_{13})coum] MA) based monomer mixture and coating compared with the control coating

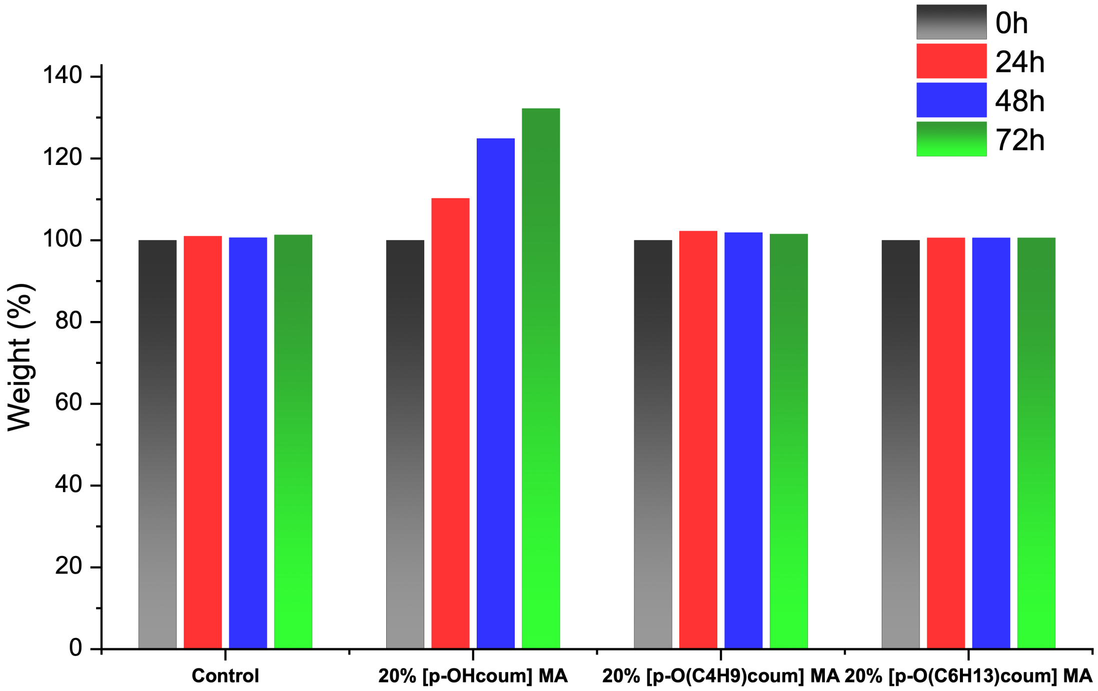


Figure S13. Weight (%) of polymer coatings at 0h and after 24h, 48h, and 72h immersed in MiliQ water

Table S1. Summary of corrosion parameters obtained from PP curves in control and 8mM inhibited solutions ([p-OHcoum] MA and [p-O(C_6H_{13})coum] MA) after 24 h immersion in NaCl 0.01M

Solution	**E_{corr} / V**	**i_{corr} / µA**	**β_a / mV/decade**	**β_c / mV/decade**	**IE /%**
Control	-0,523	0,925	21,2	28,9	-
[p-OHcoum] MA	-0,012	0,009	316,4	71,6	99
[p-O(C_4H_9)coum] MA	-0,140	0,026	20,6	46,8	97,2
[p-O(C_6H_{13})coum] MA	-0,147	0,008	162,3	62,2	99,1