

SUPPORTING INFORMATION

Simultaneous Hydrate and Corrosion Inhibition with Modified Poly(vinyl caprolactam) Polymers

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Experimental

Synthesis of Poly(VCap-co-AA) copolymers

The Poly(VCap-co-AA) copolymers were prepared by free radical copolymerization of VCap with AA in the presence of AIBN as initiator. VCap and AA (feed ratio=82.5mol%:17.5mol%) were dissolved in IPA with total monomer concentration of 33wt%. 2mol% of AIBN was then added to resulting solution. The mixture was purged with nitrogen for 30 min and then heated to 70 °C under constant stirring (1000 rpm) for 24 h under nitrogen. After this time the solvent was removed by rotary evaporation. The product was washed several times by MilliQ water to remove residual initiator and monomer and dried completely under vacuum.

Preparation of Poly(VCap-co-Na AA) copolymers

The carboxylic acid groups of Poly(VCap-co-AA) copolymers were neutralized by sodium hydroxide solution. The exact amount of NaOH used for neutralization had been calculated based on the determination and analysis of acidic comonomer units via titration and nuclear magnetic resonance spectroscopy (NMR). The pH test strips were also used to confirm the resulting solution was neutral after the reaction. The resulting polymers were then freeze dried and were prepared as a stock solution.

Preparation of modified polymers

EDC was dissolved in distilled water and added to an aqueous solution of Poly(VCap-co-Na AA) (20w/v%), and the resulting solution was mixed using a magnetic stirrer. After 3 min, NHS was dissolved in distilled water and was then added to the mixture. The reaction was left to proceed for a further 3 min, this process activated the polymers to post-synthetic modification. Then the requisite functional amine was added to the activated polymer solution. This carbodiimide-mediated coupling (CMC) reaction was carried out in open vials in the presence of oxygen at a low temperature (approx. 0°C) to ensure that the solutions were below the cloud point of the polymers. Representative synthesis conditions are shown in Table 1 for an array of structurally unique, modified PVCap polymers prepared at one polymer concentration (20w/v%) with several functional amines.

Table S1. Representative Synthesis Conditions based on 5ml of a 20w/v% Poly(VCap-co-Na AA) solution

Activated polymer (%) ^a	Activators		Primary Amines ^b										
	EDC	NHS	Taurine	Taurine	Taurine	ATC	ATC	ATC	API	API	API	AMP	AMP
	(g)	(g)	(g)	C ₁₂ (g) _c	noC ₁₂ (g) _{c,d}	(g)	C ₁₂ (g) _c	H ₁₂ (g) _{c,d}	M	M	inoC ₁₂ (g) _{c,d}	A (g)	C ₁₂ (g) _c
									(g)	(g)			noC ₁₂ (g) _{c,d}

20	0.29 46	0.1768 0.1923			0.26 91		0.19 23		0.17 06		
18			0.173	0.173	0.24	0.24	0.17	0.17	0.15	0.153	
+	0.29 64	0.1768	1	1	21	21	30	30	36	6	
2			0.028	0.061	0.02	0.06	0.02	0.06	0.02	0.061	
			4	6	84	16	84	16	84	6	

Activators (EDC and NHS) and amines are dissolved in 0.5 mL of water.

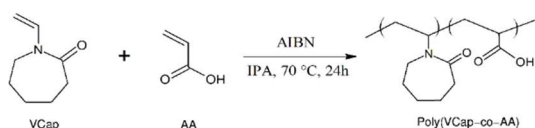
Amines: Taurine ($\geq 99\%$); (2-Aminoethyl)trimethylammonium chloride hydrochloride (ATCH); 1-(3-Aminopropyl)imidazole (APIM); (aminomethyl)phosphonic acid (AMPA); Dodecylamine (C_{12}); 1,12-Diaminododecane (Diamino C_{12})

^a mol% of polymer repeat units activated with EDC and NHS, 20 mol% is the maximum because the polymer contains 20% sodium carboxylate group (1Na AA: 1EDC: 1NHS). The reaction either with C_{12} amines or C_{12} diamines is conducted after the modification of other amines to avoid random polymers.

^b Polymers are denoted as PVCap-amine-X or PVCap-amine-X-amine-Y, where X or Y represents the theoretical modification percentage of the polymer by the requisite amine.

^c C_{12} amine and C_{12} diamine are insoluble in water so an additional 0.5 mL of THF was added.

^d excess amount of diamine was required to avoid alternative cross-linking reaction which will form hydrogel at a rapid speed.



Scheme S1. Synthesis of the base Poly(VCap-co-AA) copolymer.

Characterization

GPC

Gel permeation chromatography (GPC) was performed on a Shimadzu system equipped with a CMB-20A controller system, an SIL-20A HT auto sampler, an LC-20AT tandem pump system, a DGU-20A degasser unit, a CTO-20AC column oven, an RDI-10A refractive index detector, and 4x Waters Styragel columns (HT2, HT3, HT4, and HT5, each 300mm x 7.8 mm², providing an effective molar mass range of 100–4 × 10⁶). N,N-Dimethylacetamide (DMAc) (containing 4.34 g L⁻¹ lithium bromide (LiBr)) was used as an eluent with a flow rate of 1 mL/min at 80 °C. Number (M_n) and weight average (M_w) molar masses were evaluated using Shimadzu LC solution software. The GPC columns were calibrated with low dispersity polystyrene (PSt) standards (Polymer Laboratories) ranging from 575 to 3,242,000 g mol⁻¹, and molar masses are reported as PSt equivalents. A 3rd-order polynomial was used to fit the log M_p vs. time calibration curve, which was near linear across the molar mass ranges.

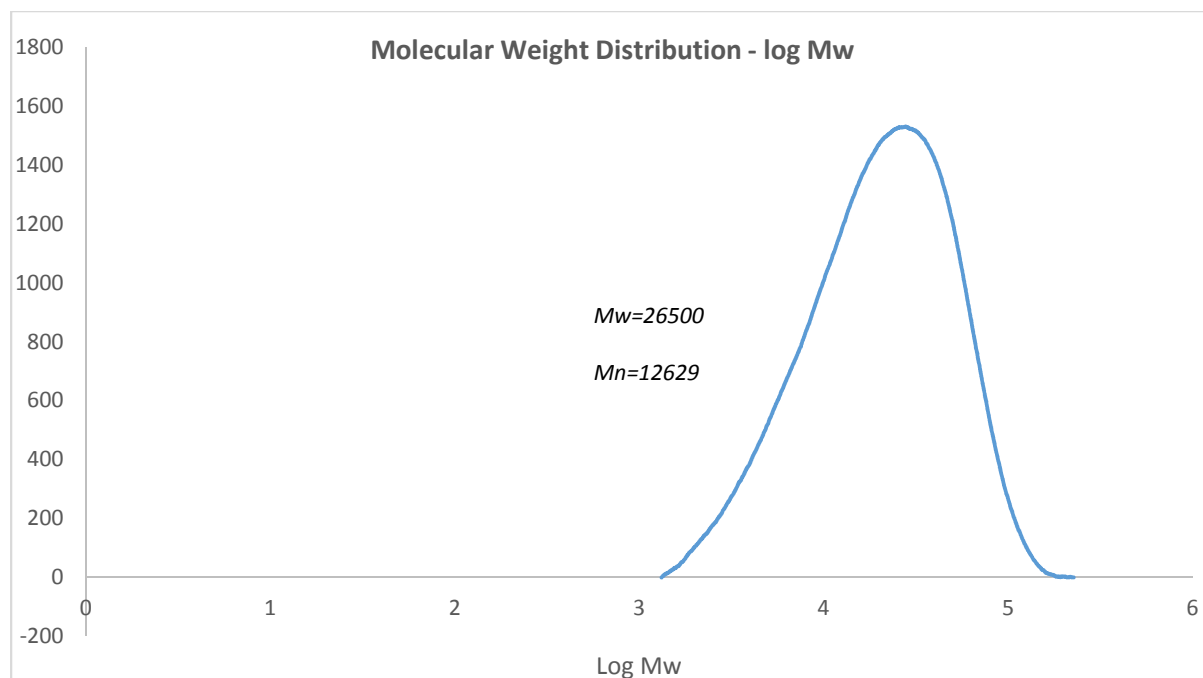


Figure S1. The molecular weight of Poly(VCap-co-AA) copolymer by GPC measurement

Titration

The copolymers (150-200mg) were dissolved in an excess of 0.1N sodium hydroxide (NaOH, 10ml) to deprotonate the carboxylic acid content. The excess of NaOH was then titrated with 0.1 N hydrochloric acid and so as to calculate the amount of the acidic comonomer units from the amount of NaOH reacted by carboxylic acid content.

Nuclear Magnetic Resonance

^1H NMR spectroscopy was performed on a Bruker Av400 NMR spectrometer using deuterium oxide (D_2O) as solvent and ^{13}C NMR spectroscopy was performed on a Bruker Av500 NMR spectrometer with a 10 mm auto tuning and matching broad band observe probe. Samples with concentration of 50wt% $\text{H}_2\text{O}/\text{D}_2\text{O}$ (9:1) were held at 50°C inside the probe. An 83° pulse was used with inverse-gated ^1H decoupling using a bilevel waltz-16 decoupling sequence. The acquisition time was 1.08 s and the relaxation delay was 10.0 s, the sum of 11.1 s being greater than 53 the longest T_1 measured using an inversion recovery sequence. The data were zero-filled once and exponential multiplication using 5 Hz line broadening was applied prior to Fourier transformation. The NMR is used for qualitative analysis because it is challenging to accurately determine composition for these polymers using NMR.

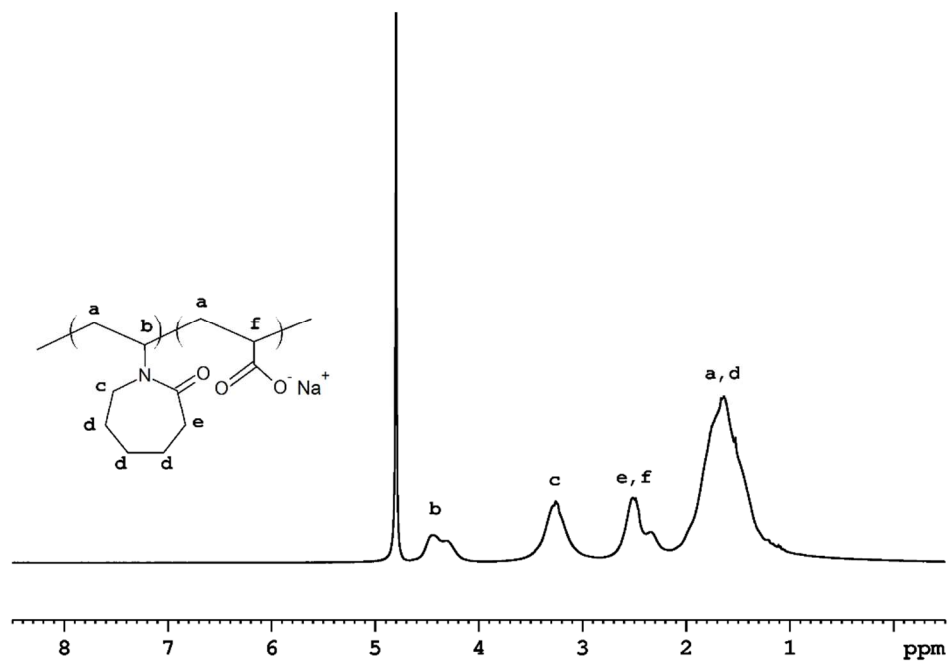


Figure S2. 1H NMR spectra of Poly(VCap-co-Na AA) copolymer in D_2O .

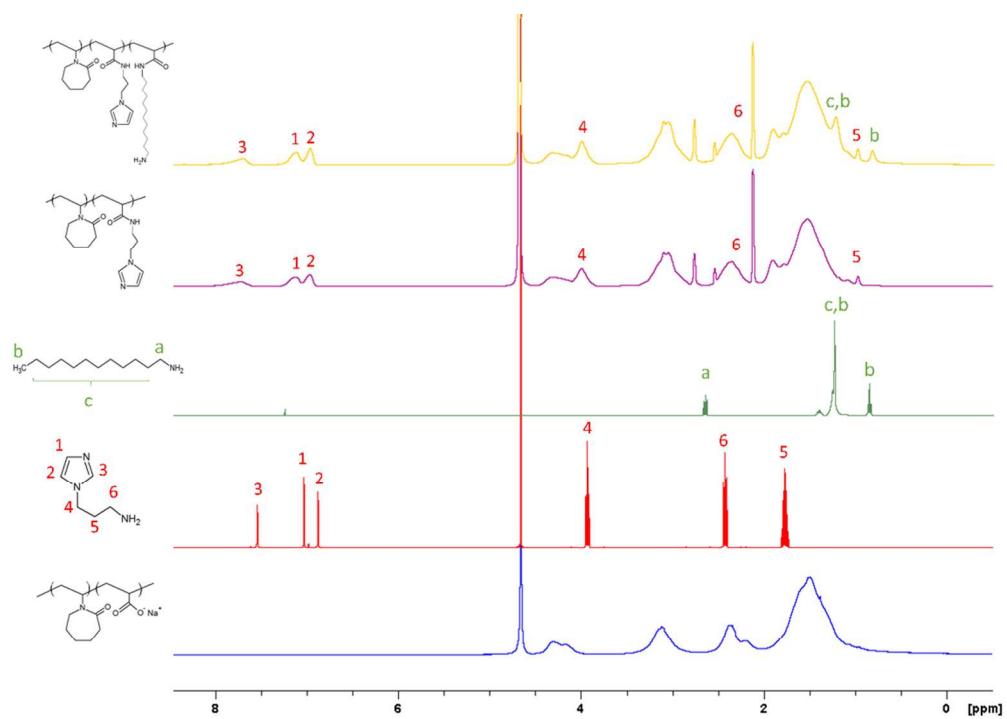


Figure S2.1. ^1H NMR spectra of PVCap-APIM-20 & PVCap-APIM(18)-C₁₂(2) in D₂O.

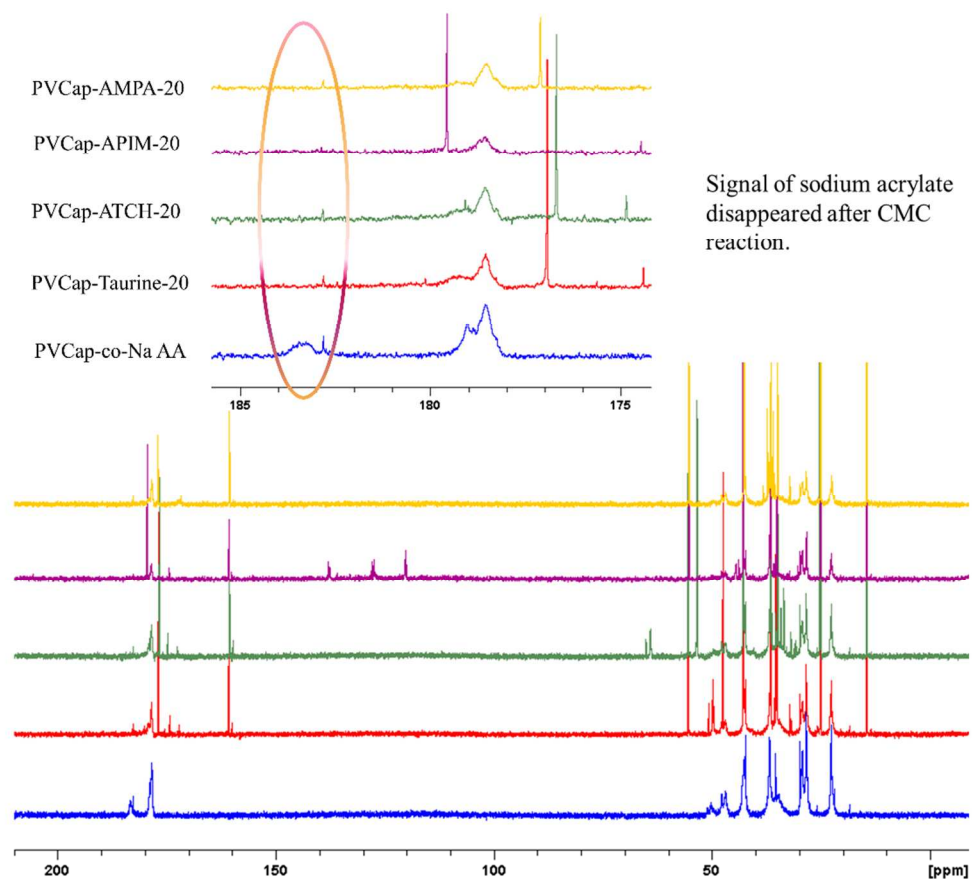
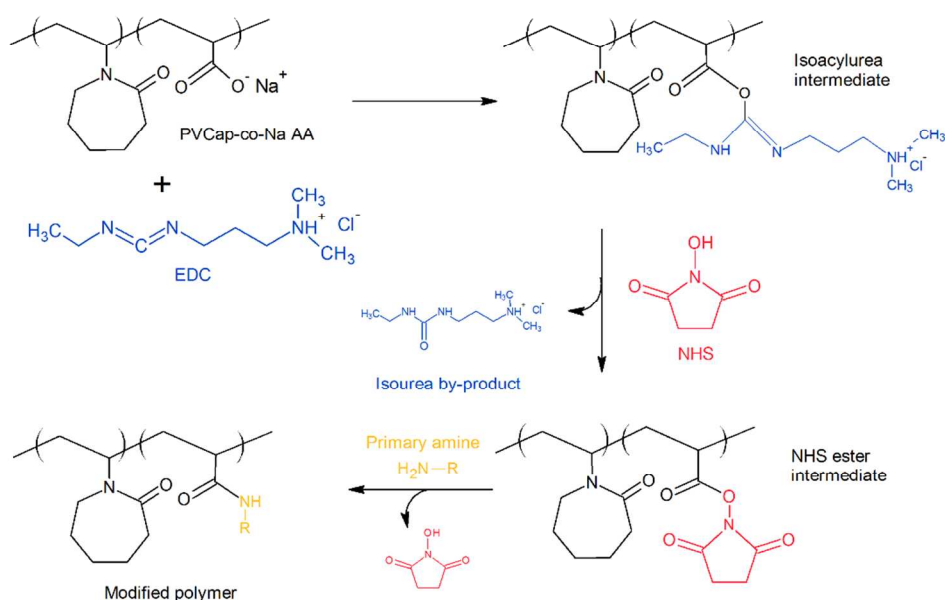


Figure S2.2. ^{13}C NMR spectra of modified polymers in D₂O, as shown in the focused area, signal of sodium acrylate disappeared after modification which confirmed the transformation of sodium acrylate to target structure was complete after CMC reaction.



Scheme S2. Reaction schematic used for the synthesis of modified polymer where the carboxylate group of Poly(VCap-co-Na AA) (shown in black) activated by EDC (shown in blue) and NHS (shown in red) forms a stable conjugation with primary amines.

Cloud point

The cloud point of KHI polymers was determined by a water bath heated at a temperature rate of 0.3 °C min⁻¹. An overall increase in cloud point of KHI polymers compared to the base polymer was observed. This result reinforces the success of the CMC modification however the trend was not significant. This is due to the nature of PVCap base polymer as can be seen in literature that high cloud point PVCap copolymers are limited and typically more than 30% (mole ration) of incorporation structure is required to achieve significant change in terms of LCST in this case. The cloud point for the majority of the KHI polymers were 3 °C degree higher than the base polymer except for two of AMPA modified polymers. Despite adding additional functionality we retain similar cloud points to other commercial KHIs which is a major advantage because the polymers have potentially more utility. Additional experiments for the base polymer with by-product in different ratio (5%, 10%, 20%) has been conducted. It suggested that by-product has no influence on cloud point temperature.

Table S2. Cloud point of KHI polymers

Polymer	T _{cp} (°C)
PVCap-co-Na AA	34
PVCap-ATCH-20	37
PVCap-ATCH(18)-C ₁₂ (2)	37
PVCap-ATCH(18)-DiaminoC ₁₂ (2)	37
PVCap-Tau-20	37
PVCap-Tau(18)-C ₁₂ (2)	37
PVCap-Tau(18)-DiaminoC ₁₂ (2)	37
PVCap-APIM-20	37
PVCap-APIM(18)-C ₁₂ (2)	37
PVCap-APIM(18)-DiaminoC ₁₂ (2)	37

PVCap-AMPA-20	39
PVCap-AMPA(18)-C ₁₂ (2)	40
PVCap-AMPA(18)-DiaminoC ₁₂ (2)	37

Table S3. Cloud point for base polymers with the presence of by-product generated in CMC reaction in different ratio (5%, 10% and 20%)

Polymer	T _{cp} (°C)
PVCap-co-Na AA	34
PVCap-co-Na AA (5% by-product)	34
PVCap-co-Na AA (10% by-product)	34
PVCap-co-Na AA (20% by-product)	34

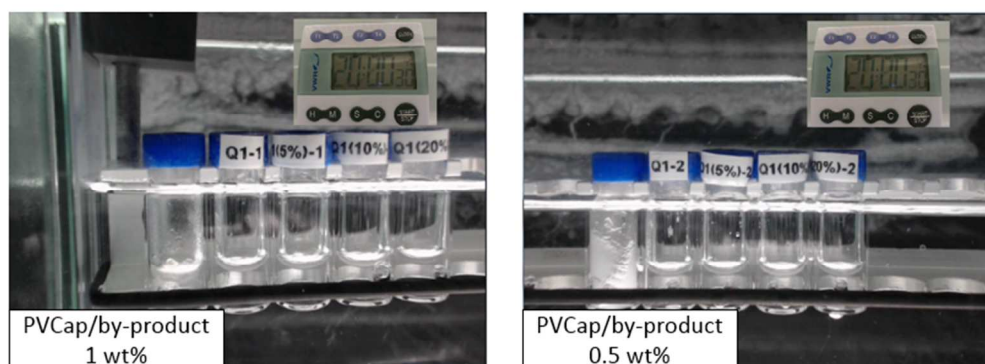


Figure S3. PVCap base polymers with or without by products (5%, 10%, 20%) were screened at 1 wt% and 0.5 wt% respectively. The threshold concentrations after a cut-off time of 20 hours remained the same at 0.5 wt%.

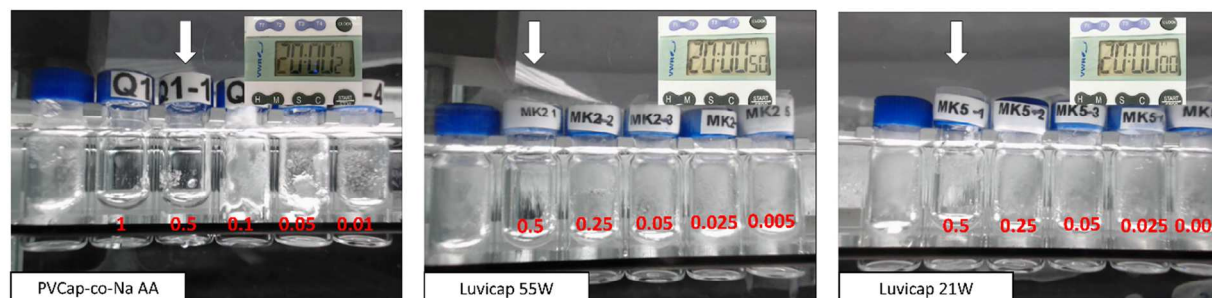


Figure S4. PVCap base polymers and commercial PVCap based polymers Luvicap 55W, Luvicap 21W were screened for comparison. The threshold concentrations after a cut-off time of 20 hours remained the same at 0.5 wt%.

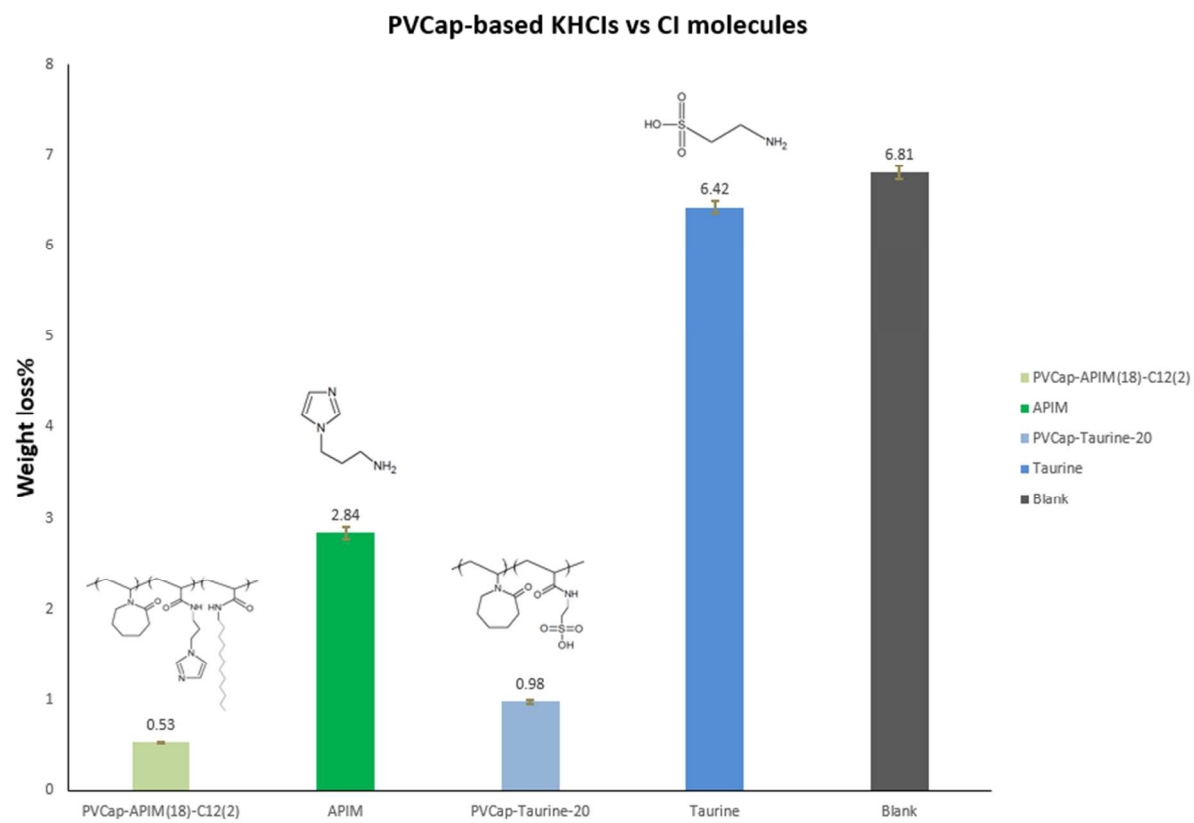


Figure S5. Weight loss percentage Comparison between two modified KHClIs and single corrosion molecules.