

Synthesis and Characterization of Oligomer 4-Vinylpyridine as A Corrosion Inhibitor for Mild Steel in CO₂ Saturated Brine Solution

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ABSTRACT

In this work, the oligomer of 4-vinylpyridine designated as O(4-VP) was synthesized by hydrogen peroxide initiated chain growth polymerization and characterized in terms of molecular weight and structure by matrix assisted laser desorption ionization time of flight mass spectroscopy (MALDI-TOF MS). The oligomer was tested as corrosion inhibitor of mild steel in brine solution saturated with carbon dioxide, with the main purpose to investigate the effect of inhibitor concentrations and temperatures on the inhibition activity defined in terms of corrosion rate and percent of protection. The inhibition tests were carried out using the methods of weight loss (WL) and linear polarization (LP). Characterization using MALDI-TOF MS revealed that the oligomer has the mass (m/z) in the range 200-2400, which corresponds to chain length of 2-22 repeating units. The results of corrosion rate measurements show that the corrosion rate with the use of oligomer is significantly lower than that without inhibitor, demonstrating that the oligomer functioned as effective corrosion inhibitor, while the 4-vinyl pyridine monomer was found to promote the corrosion. It was also found that the protection by the oligomer increased with increasing temperature and it was predicted the oligomer was chemically adsorbed by the surface of the metal.

Keywords: oligomer 4-vinylpyridine; corrosion inhibitor; CO₂ corrosion; MALDI-TOF MS

ABSTRAK

Dalam penelitian ini, oligomer 4-vinilpiridin, O(4-VP), disintesis menggunakan inisiator hidrogen peroksida untuk pertumbuhan rantai polimer dan dikarakterisasi berat molekul dan struktur molekulnya menggunakan matrix assisted laser desorption ionization time of flight mass spectroscopy (MALDI-TOF MS). Oligomer kemudian diuji sebagai inhibitor korosi baja ringan dalam larutan air garam yang jenuh dengan gas karbon dioksida, dengan tujuan utama untuk menyelidiki efek dari konsentrasi inhibitor dan suhu pada aktivitas inhibisi yang dinyatakan dalam bentuk laju korosi dan persen proteksi. Tes inhibisi dilakukan dengan menggunakan metode kehilangan berat (WL), dan polarisasi linier (LP). Karakterisasi menggunakan MALDI-TOF MS mengungkapkan bahwa oligomer memiliki massa (m/z) dalam kisaran 200-2400, yang sesuai dengan panjang rantai dari 2-22 unit monomer. Hasil pengukuran laju korosi menunjukkan bahwa laju korosi dengan penggunaan oligomer secara signifikan lebih rendah dari laju korosi tanpa inhibitor, sedangkan monomer 4-vinilpiridin ditemukan mengkatalis proses korosi baja lunak. Hasil penelitian ini menyarankan bahwa oligomer 4-vinilpiridin dapat berfungsi sebagai inhibitor korosi yang efektif. Selain itu juga ditemukan bahwa proteksi oleh oligomer meningkat dengan meningkatnya suhu dan diperkirakan oligomer itu diserap secara kimia pada permukaan logam.

Kata Kunci: oligomer 4-vinilpiridin; inhibitor korosi; korosi CO₂; MALDI-TOF MS

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INTRODUCTION

Mild steels are used extensively in the oil and gas industries because of their ideal characteristics as construction material and economic reasons [1]. However, they are generally more susceptible to corrosion than stainless steels and other high alloy steels. In general, it is found that oil and gas always contain water and acid producing gases such as carbon dioxide and hydrogen sulfide. The carbon dioxide gas dissolves in water and forms reactive carbonic acid which corrodes the pipeline [2-3]. In previous study [4], it was reported that carbonic acid is more aggressive than hydrochloric acid at the same pH [4], and for this reason, CO₂ corrosion has been a recognized problem in oil and gas production and transportation facility for many years [5-6] resulted in many accidents and economic losses. Most oil and gas wells in Australia and Indonesia are known to contain CO₂ in relatively high concentration, making the corrosion associated with this compound a major concern of oil and gas industries in both countries.

The use of corrosion inhibitors is the most effective and flexible method for controlling acid corrosion including CO₂ corrosion [7-8]. Various chemicals have been used for protection against corrosion of mild steel or metals [7-20]. For polymeric inhibitors [11], the use of polyvinylimidazoles [12], polyvinylpyrrolidone [13-14], polyvinylpyridine [15-20] has been widely examined. Poly(4-vinylpyridine), P(4-VP) has been used as corrosion inhibitor of mild steel and iron in HCl [15], of copper in 3 M HNO₃ [16], of Zinc in 1 M H₂SO₄ [17], of iron in 1 M H₂SO₄ [18-19] and of Cu60-Zn40 in 0.5 M HNO₃ [20]. Synergistic influence of P(4-VP) and Potassium iodide (KI) on corrosion inhibition of mild steel in 1 M HCl was studied by Larabi, et al. (2004). Annand, et al. [15] stated that P(4-VP) protected mild steel and iron in HCl more effective than the monomer. Based on the literature reviews, there has been no report on the use of poly(4-vinylpyridine) or oligomeric of 4-vinylpyridine as CO₂ corrosion of mild steel. However, it has been acknowledged that low molecular weight polymers or oligomers, containing between 2 and 8 units of monomers, are able to protect metal surface effectively.

Three types of monomers, namely 2-vinyl pyridine, 4-vinyl pyridine and 6-methyl-2-vinyl pyridine have general commercial importance, although a large number of other derivatives of vinyl pyridine have also been synthesized [21]. One of the monomers, 4-vinyl pyridine, was used in the present work to synthesize low molecular weight polymer known as oligomer by using hydrogen peroxide initiated chain growth polymerization [22]. In the following text the monomers 4-vinylpyridine will be abbreviated as M(4-VP), whilst the corresponding oligomer will be referred to O(4-VP) and polymer to P(4-

VP). The notations VP and PVP will be used where no specific designations are required. Some applications of PVP are useful as reviewed by Frechet and Meftahi [23]. The important application is as corrosion inhibitor [15-20]. The present study focuses on the use of low molecular weight polymer or oligomer of 4-VP for the prevention of carbon dioxide corrosion. The prepared oligomer was characterized in terms of molecular weight and molecular structure using Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS). Weight loss in brine solution with or without kerosene addition and linear polarization (LP) were used to determine the effectiveness of the oligomeric product as a CO₂ corrosion inhibitor.

EXPERIMENTAL SECTION

Materials

The corrosion electrolyte used was a brine solution prepared by dissolving sodium chloride, NaCl, at 3% (w/v) and sodium bicarbonate, NaHCO₃, analytical reagent (AR), at 100 mg.L⁻¹ in milli-Q water. The electrolyte was saturated with food grade CO₂ gas at atmospheric pressure by purging the solution with the gas at a rate of approximately 150–200 mL min⁻¹. Inhibitor solution with the concentration of 10,000 mg.L⁻¹ was prepared by dissolving the inhibitor in methanol. Mild steels (coupon and cylindrical electrode) used in this experiment were SAE/AISI Grade 1022 according to AS 1443 with the spectrographic analysis of the steel provided the chemical composition; 0.22% C, 0.74% Mn, 0.02% Si, 0.014% S, 0.02% P, 0.05% Ni, 0.04% Cr, <0.01% Mo, <0.01% Cu, <0.01% Al, and the remainder Fe.

Instrumentation

Instrumentations used were rotary evaporator, wheel oven manufactured by Detailed Design, Texas, Pine Model MSR electrode rotator, MALDI-TOF MS (Micromass, Wythenshawe, UK), Masslynx software (Micromass, Wythenshawe, UK), EG&G Princeton Applied Research Model 273A Potentiostat and EG&G Model 314 Multiplexer.

Procedure

Synthesis of oligomer 4-VP

Synthesis of 4-VP oligomer was conducted by using Scriven *et al's* method [22]. 4-VP (50 g; 0.48 mole), methanol (125 mL), water (125 mL) and H₂O₂ (37.40 mL; 0.33 mole) were poured into three-neck flash and heated to reflux for a period of time, typically

2–10 h. The solvent was removed using a rotary evaporator and, subsequently subjected to high vacuum to isolate the product.

Structure and molecular weight determination

Based on literature reviews, that method for determination molecular weight of polymer i.e. the end group titration, the freezing point depression, the light scattering, the nuclear magnetic resonance (NMR), or the viscometric cannot be used for this oligomer product.

The useful method used to determine the molecular weight and molecular structure of the synthesized oligomer was matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF MS). The analyses were carried out at Queensland University of Technology (QUT), Brisbane Australia. For measurement, a solution of the sample (10 mg.mL^{-1}) prepared in acetone/water solvent (50:50) was mixed with $1 \mu\text{L}$ of matrix solution (10 mg.mL^{-1} di-hydroxy benzoic acid in acetone). An aliquot of $1 \mu\text{L}$ of the mixture was then irradiated with laser. The spectra were acquired in reflection mode with an accelerating voltage of 20 KV.

Weight loss measurement

Coupons ($2 \times 1 \times 0.1$) cm were prepared by sand blasting a sheet of mild steel with garnet (size 0.89 mm) and cut to size using a guillotine. The coupons were degreased by placing them in a beaker filled with ethanol and sonicated for two minutes. The coupons were dried and the dimensions and weights were accurately recorded. To commence the experiments, a series of clean glass bottles (220 mL) were prepared to be used in two sets of experiment. The first set composed of two samples, each composed of 175 mL of brine solution, and one sample was added with inhibitor and another one without inhibitor. The second set consists of two samples, each contains 145 mL brine solution and 35 mL kerosene, one sample was added with inhibitor and another one without inhibitor. Each of the samples was then purged for 45 min with CO_2 gas (at about 250 mL.min^{-1}). A steel coupon was placed into the bottles and the bottles were capped with crown seals and placed in a wheel oven at $50 \text{ }^\circ\text{C}$ for 24 h. After the completion of the experiment, the bottles were removed from the oven, and the coupons were removed and immediately placed in Clarke's solution (a solution composed of 2% of Sb_2O_3 and 5% SnCl_2 , dissolved in concentrated HCl) for 45 sec in order to remove the corrosion product from the surface. The coupon was dipped into water for about 5 sec, and into ethanol for another 5 sec, and then dried and accurately weighed.

The weight loss (W), the corrosion rate (CR) and the inhibition efficiency (%P) were calculated according to the following eq. (1), (2) and (3).

$$W = W_{(i)} - W_{(t)} \quad (1)$$

$$CR = \frac{10.W.365}{A.D.t} \quad (2)$$

$$\%P = \frac{(CR_0 - CR_i)}{CR_0} \times 100\% \quad (3)$$

where W = weight loss (g), $W_{(i)}$ = initial weight, $W_{(t)}$ = end weight, CR = corrosion rate (mm.y^{-1} = millimeter per year), A = area of coupon (cm^2), D = density of metal (g.cm^{-3}), equal to 7.86 g.cm^{-3} for carbon steel, t = time of exposure (days), %P = percent protection, CR_0 = corrosion rate without inhibitor and CR_i = corrosion rate with inhibitor.

Linear Polarization (LP)

A mild steel cylinder electrode (working electrode) which has surface area of 3.02 cm^2 was prepared by polishing the surface with silicon carbide paper (grade 360, 400, 600 and 800) on a Heidolph rotator (rotated at 750 rpm), using ethanol as a lubricant. The working electrode was fitted to the end of the threaded shaft that was connected to a Pine rotator. The electrochemical cell (reaction vessel) was filled with 500 mL of brine solution and sparged with CO_2 until it was saturated (approximately 45 min). The sparging with CO_2 (100 mL.min^{-1}) was maintained during all experiments. A platinum gauze auxiliary electrode, Ag/AgCl reference electrode and thermocouple were placed in the cell. The cell was heated and regulated by a thermocouple on a digital hot plate at 30, 50, and $70 \text{ }^\circ\text{C}$. The working electrode was inserted and operated at a speed of 1000 rpm through connection to a Pine Model MSRX electrode rotator. The rotating electrode with speed of 1000 rpm was prepared for simulating turbulent flow conditions related to data obtained in real life system [24-27]. The electrochemical cell was connected for LP measurement.

LP measurements were carried out using an EG&G Princeton Applied Research Model 273A Potentiostat and EG&G Model 314 Multiplexer. The instrument was controlled using EG&G Model 352 Corrosion Software, version 2.10. The working electrode was polarized from +10 to -10 V with respect to the corrosion potential using an anodic scan of 0.1 mV s^{-1} . The polarization resistance was determined from the ensuing potential current plot, and converted to a corrosion rate by using assumed Tafel slope of $\beta = 100 \text{ mV.decade}^{-1}$. A blank measurement, with no inhibitor, was completed before inhibitor was added using a micro-pipette (0.1-0.2 mL). Eight LP measurements were completed for the blank and each inhibitor concentration, and last three readings were

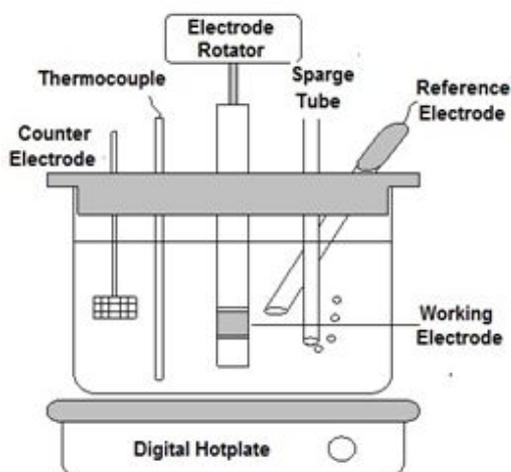


Fig 1. Cell assembly of LP Measurement

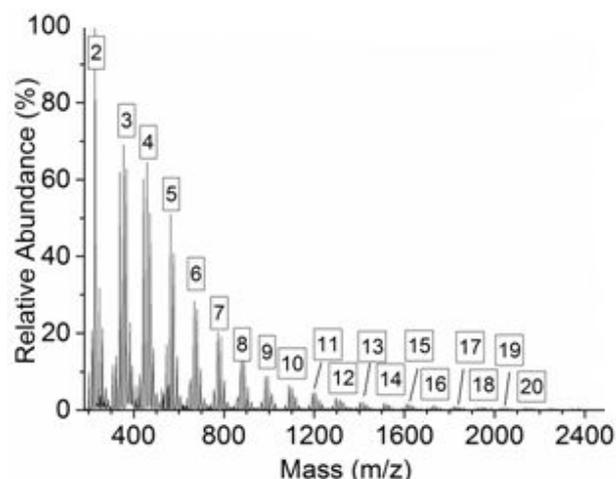
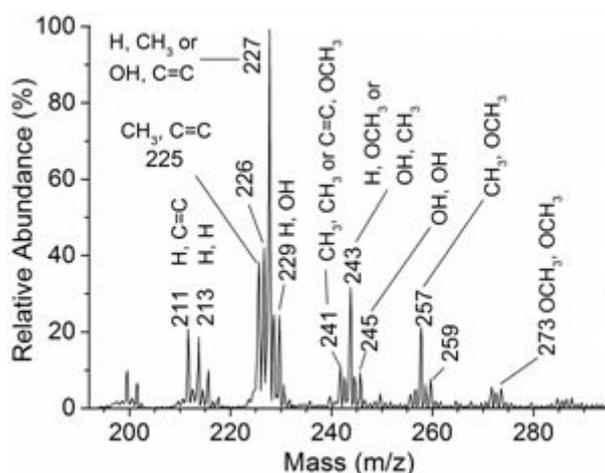
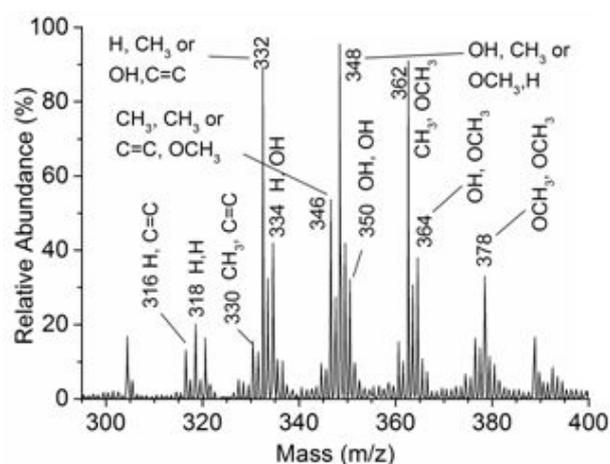


Fig 2. MALDI-TOF MS spectrum of O(4-VP)

Fig 3. Peaks and end groups of $n = 2$ of O(4-VP)Fig 4. Peaks and end groups of $n = 3$ of O(4-VP)

averaged to give a steady state corrosion rate. The experimental works were conducted at temperatures 30, 50 and 70 °C. Cell assembly for determination of the corrosion rate used is shown in Fig. 1.

RESULT AND DISCUSSION

Synthesis and Characterization of Oligomers

Monomer 4-VP, H_2O_2 and solvent, if combined in a suitable manner, will lead to polymerization. H_2O_2 can be added to the solvent-monomer mixture, monomer may be added to solvent- H_2O_2 mixture and H_2O_2 and monomer can be added to the solvent, or all can be changed simultaneously [22]. The 4-VP oligomer product existed as orange viscous liquid. The 4-VP oligomer, O(4-VP) was characterized to determine the molecular weight and molecular structure using the MALDI-TOF MS. The molecular weight distribution of 4-VP oligomer as determined by MALDI-TOF MS [28-31] is shown in

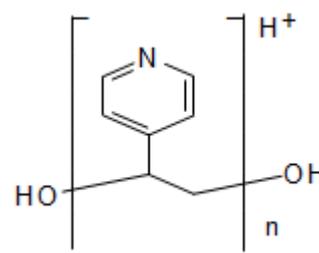


Fig 5. General structure of O(4-VP)

Fig. 2. Two expanded sections of this spectrum are reproduced in Fig. 3-4. Peaks and end groups of 4-VP oligomer can be seen for dimer ($n = 2$) in Fig. 3, and for $n = 3$ in Fig. 4.

Based on these spectra, a typical structure of the product should be the one presented in Fig. 5. This gives a molecular weight formula of: $(105)n + 32 + 1$, where 105 is the mass of repeating unit, n is the number of repeating units, 32 is the combined mass of the end groups and 1 is the mass of one proton

(attached during ionization). Using this formula, the clusters of peaks observed in the mass spectrum were correlated with their corresponding number of repeating units, and these values are marked on the main spectrum.

The clusters of peaks observed adjacent to the masses of the expected structures are most likely due to the presence of a range of alternative end groups. From the spectra, a range of alternative end groups present can be suggested, as shown in Fig. 6 with their corresponding masses.

As these end groups may occur in a number of possible combinations, a matrix was constructed (Table 1), using the expected and alternative end groups in order to determine the masses of the variety of combinations of end group that could possibly occur in this polymer. It should be noted that several of these combinations result in identical masses and are therefore indistinguishable in the mass spectra.

The masses for these end group combinations were in turn substituted into the general formula for the molecular weight of the polymer and masses calculated for a variety of chain lengths (Table 2). All of the calculated masses were observed in the mass spectrum. The peak assignments using these masses are marked on the expanded view for the first clusters of peaks ($n = 2$ and $n = 3$).

From all of the spectra, it can be summarized that oligomeric products were detected in the mass region m/z 200–2400, and this corresponds to chain lengths of 2–22 repeating units where the most abundant chain length is 2. The expected product containing 2 OH end groups appears to be present only in relatively low quantities as shown in Fig. 3 and 4. Finally, polymer chains bearing combinations end group of H + CH₃ or

OH + C=C, OH + CH₃ or OCH₃ + H, and CH₃ + OCH₃ appear to be most abundant.

Mechanism of O(4-VP)

Based on the MALDI-TOF MS results, the mechanism of O(4-VP) can be explained in terms of initiation, propagation and termination steps by free radical initiated chain growth polymerization as shown in Fig. 7. A typical initiation step is initiation reaction of 4-VP by an HO• radical shown in Fig. 7(a), followed by propagation step Fig. 7(b). The termination step can occur by disproportionation or combination, according to the usual principles of free radical chain growth polymerization. Similarly, the degree of polymerization can vary, so that n may be any value from 0 up to the highest value obtained before the reaction is terminated and the oligomer is formed. Assuming $n = 0$,

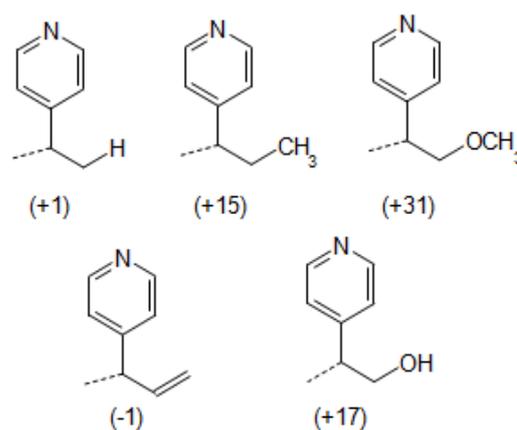


Fig 6. The end groups of O(4-VP)

Table 1. End group masses for various combinations

End Group→ Masses ↓	C=C (m=-1)	H (m=1)	OH (m=17)	CH ₃ (m=15)	OCH ₃ (m=31)
H (m=1)	0	2			
OH (m=17)	16	18	34		
CH ₃ (m=15)	14	16	32	30	
OCH ₃ (m=31)	30	32	48	46	62

Table 2. Oligomer (H+) masses for various end group combination

Units (n)	Mass of End Groups (E)										
	0	2	14	16	18	30	32	34	46	48	62
1	106	108	120	122	124	136	138	140	152	154	168
2	211	213	225	227	229	241	243	245	257	259	273
3	316	318	330	332	334	346	348	350	362	364	378
4	421	423	435	437	439	451	453	455	467	469	483
5	526	528	540	542	544	556	558	560	572	574	588
6	631	633	645	647	649	661	663	665	677	679	693
7	736	738	750	752	754	766	768	770	782	784	798
8	841	843	855	857	859	871	873	875	887	889	903
9	946	948	960	962	964	976	978	980	992	994	1008

$$\text{Oligomer mass} = n(105) + E + 1$$

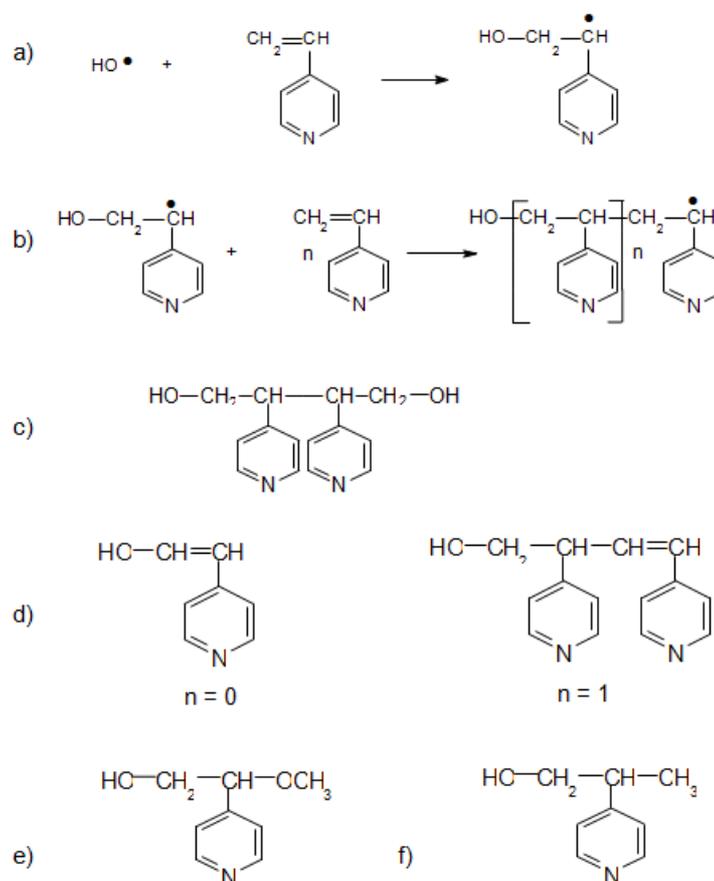


Fig 7. Mechanism of O(4-VP) in terms of initiation, propagation and termination steps. (a). Initiation reaction by an $\text{HO}\cdot$ radical. (b). Propagation reaction. (c). The structure of a O(4-VP) terminated by combination. (d). The disproportionation step of O(4-VP) for $n = 0$ and $n = 1$ (e) and (f) structures formed after chain transfer to initiator $\bullet\text{OCH}_3$ and $\bullet\text{CH}_3$ by radicals respectively in Fig. 5

the intermediate radical formed in Fig. 7(b) should be same as Fig. 7(a). If the last structure combined with an identical radical gives the structure as shown in Fig. 7(c). The disproportionation step of 4-VP oligomer for $n = 0$ and $n = 1$ could form species such as Fig. 7(d). Chain Transfer is likely to occur whereby the propagating radical is terminated by chain transfer agents such as $\bullet\text{OH}$ and $\bullet\text{OCH}_3$ formed from the initiator or solvents. Chain transfer to initiator $\bullet\text{OCH}_3$ by the radical formed in Fig. 5 gives structure as Fig. 7(e). Chain transfer to $\bullet\text{CH}_3$ by the radical formed in Fig. 5 gives structure as Fig. 7(f).

As indicated in Fig. 6, the other free radicals, which function as either initiators or chain transfer agents, are $\bullet\text{H}$, $\bullet\text{CH}_3$, and $\bullet\text{OCH}_3$. The mechanisms predicted are very similar to the $\bullet\text{OH}$ radical mechanism, and the final results are shown in Table 3. Thus, it can be seen that a complicated, but predictable, series of 4-VP oligomeric product can be formed by the hydrogen peroxide initiated chain growth polymerization of 4-VP. Chain transfer to the initiator $\text{I}\cdot$ and methanol or water used as solvents may also occur.

Weight Loss Measurement

The weight loss or wheel test was used as a screening method to evaluate potential corrosion inhibitors. As established by de Waard and Milliams (1975), this method can be used if the corrosion rate obtained for the blank (brine only) gives reasonable results. They have obtained a weight loss of 29.5 mg for a temperature of $50\text{ }^\circ\text{C}$, pCO_2 of 1 bar, gas volume of 130 mL, coupon area of 4.60 cm^2 and test period of 24 h. In our case, the average blank corrosion weight loss determined experimentally was 35.2 mg. The small difference in results between the predicted and experimental values was caused by slightly different test conditions, especially the coupon area average of 4.86 cm^2 and solution volume of 175 mL.

Based on this result, the wheel test can be used for corrosion rate study because of the reasonable corrosion rates that were obtained in controlled experiments. The wheel tests were carried out for the 4-VP product without purification in brine solution with

Table 3. Predicted products of 4-VP oligomer by the radical mechanism

End Group	Initiator	Chain Transfer Agent	Oligomeric Product	M_w
$\text{CH}_3\bullet + \text{H}\bullet$	$\text{CH}_3\bullet$	$\text{H}\bullet$	$\text{CH}_3-\text{CH}_2-\text{CH}(\text{4-VP})-\text{CH}_2-\text{CH}_2$	227.5
$\text{HO}\bullet + \text{C}=\text{C}$	$\text{HO}\bullet$	$\text{C}=\text{C}$	$\text{HC}=\text{CH}-\text{CH}(\text{4-VP})-\text{CH}(\text{4-VP})-\text{CH}(\text{4-VP})$	227.7
$\text{H}\bullet + \text{CH}_3\bullet$	$\text{H}\bullet$	$\text{CH}_3\bullet$	$\text{CH}_3-\text{CH}(\text{4-VP})-\text{CH}_2-\text{CH}(\text{4-VP})-\text{CH}_3$	227.5
$\text{CH}_3\text{O}\bullet + \text{H}\bullet$	$\text{CH}_3\text{O}\bullet$	$\text{H}\bullet$	$\text{CH}_3-\text{C}(\text{O})-\text{CH}_2-\text{CH}(\text{4-VP})-\text{CH}_2-\text{CH}_2$	243.5
$\text{CH}_3\bullet + \text{CH}_3\text{O}\bullet$	$\text{CH}_3\bullet$	$\text{CH}_3\text{O}\bullet$	$\text{CH}_3-\text{CH}_2-\text{CH}(\text{4-VP})-\text{CH}_2-\text{CH}(\text{4-VP})-\text{O}-\text{CH}_3$	257.6

Table 4. Wheel test results of O(4-VP) in presence and absence of kerosene at 50 °C

No	Compound Name	Amount Inhibitor Added (ppm)	Corrosion Rate Average (mm y^{-1})	Protection Average (%)
1	BS only	0	3.35	-
2	O(4-VP)	50	1.09	67.46
3	BS + K	0	3.46	-
4	BS + K + O(4-VP)	50	1.07	69.08

BS = brine solution, O(4-VP) = oligomer 4-vinylpyridine, K = kerosene

and without kerosene at a temperature of 50 °C. The results are shown in Table 4. A corrosion rate of 3.35 mm.y^{-1} was obtained for the blank solution corresponding to values obtained by other authors [32-34]. The addition of kerosene increased slightly the corrosion rate up to 3.46 mm.y^{-1} , but it can be deduced that the oligomeric product reduced the corrosion rate of carbon dioxide corrosion more than a factor 3. Indeed, the addition of kerosene with inhibitor does not affect the corrosion rate that remains constant at about 1.1 mm.y^{-1} . Then, we can conclude that the protection is more effective in medium containing kerosene [35].

Linear Polarization Results

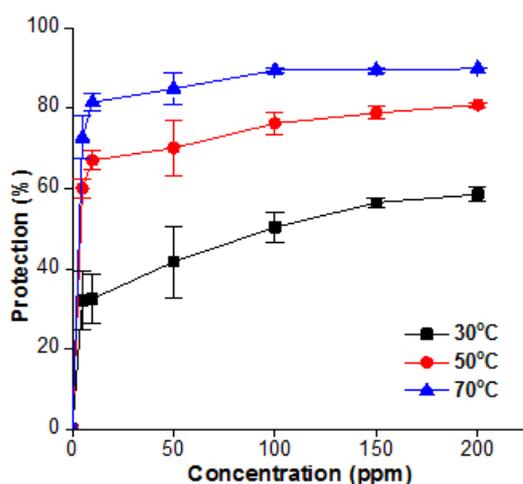
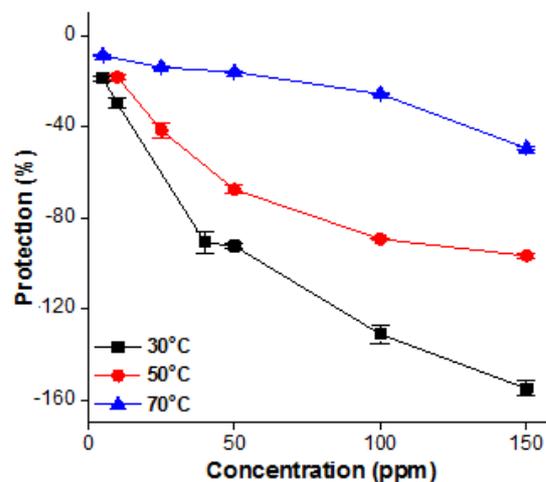
An LP measurement relies upon the determination of the polarization resistance (R_p) and calculation of the corrosion rate using the Stern-Geary approximation method. LP measurements were carried out using concentrations of 4-VP monomer ranging from 0 ppm to 150 ppm and 4-VP oligomer ranging from 0 ppm to 200 ppm at temperatures 30, 50 and 70 °C. A lot of corrosion rate measurements were conducted, and in most cases,

duplicates were also examined to assure the reproducibility of the test results. Table 5 shows the corrosion rate measurements and calculated protections of oligomer 4-vinylpyridine, O(4-VP) and monomer 4-vinylpyridine, M(4-VP) at various temperatures. The corrosion rate of blank, without inhibitor, was indicated by CR_0 and the corrosion rate of blank with inhibitor was indicated by CR_i . Inhibition efficiency (protection) was calculated using Eq. (3).

Fig. 8 presents a plot of protection (%) as a function of O(4-VP) concentration at various temperatures. The carbon dioxide corrosion protection increases with O(4-VP) concentration and the efficiency is favor by the temperature. Indeed, for the lowest oligomer concentration, the protection increases from 30% at 30 °C to 80% at 70 °C. For 30 °C and 50 °C, the protection increases progressively with the concentration and reaches a limit (55% for 30 °C and 78% for 50 °C) around 150 ppm of oligomer. At 70 °C, the protection limit (around 90%) seems reached for lower concentration (50 ppm). Then, the higher protection efficiency with increasing temperature could be suggested that the mechanism of inhibiting is a

Table 5. Corrosion rates and protections of O(4-VP) and M(4-VP) at various temperatures

Concentration (ppm)	Corrosion Rate (mm.y ⁻¹)			Protection (%)		
	30 °C	50 °C	70 °C	30 °C	50 °C	70 °C
O(4-VP)						
0	1.71±0.14	3.22±0.20	4.44±0.35	-	-	-
5	1.17±0.13	1.29±0.08	1.21±0.24	31.98±7.31	60.07 ±2.32	72.66± 5,36
10	1.08±0.09	1.05±0.08	0.82±0.10	32.55±6.01	67.07± 2.46	81.58± 2.15
50	1.00±0.15	0.96±0.23	0.67±0.17	41.75±8.87	70.10 ±7.10	84.93± 3.93
100	0.85±0.62	0.76±0.09	0.47±0.02	50.33±3.61	76.25± 2.75	89.48±0.48
150	0.75±0.02	0.68±0.05	0.47±0.02	56.49±1.09	78.83 ±1.57	89.47±0.43
200	0.71±0.03	0.62±0.02	0.50±0.00	58.55±1.83	80.88 ±0.63	89.94±0.05
M(4-VP)						
0	1.71±0.14	3.22±0.20	4.44±0.35	-	-	-
5	2.03±0.02	-	4.68±0.01	-18.62±1.11	-	-8.55±0.32
10	2.22±0.04	3.80±0.03	-	-29.61±2.12	-18.09±0.95	-
25	-	4.55±0.10	5.05±0.01	-	-41.46±3.13	-13.75±0.17
40	3.27±0.08	-	-	-90.72±4.84	-	-
50	3.30±0.01	5.39±0.06	5.14±0.01	-92.37±0.84	-67.55±1.88	-15.80±0.14
100	3.96±0.07	6.09±0.01	5.57±0.02	-131.22±4.19	-89.32±0.27	-25.47±0.37
150	4.37±0.06	6.33±0.03	6.63±0.03	-155.02±3.33	-96.65±1.00	-49.40±0.60

**Fig 8.** Plot of % protection by O(4-VP) at various concentrations and temperatures based on LP measurements**Fig 9.** Plot of % protection by M(4-VP) at various concentrations and temperatures based on LP measurements

chemisorption rather than physisorption on the metal surface. As proposed by Lopez et al. (2003) the main contribution to the formation of metal-inhibitor bonds is made by the pyridine-like nitrogen which acts as a strong base. In acidic media, the O(4-VP) are protonated and the interaction mechanism between inhibitor and the steel surface occurs through the reduction of the protonated species at the cathodic sites, which leads to the chemisorption of the reduced inhibitor species. On the other hand, the monomer of 4-VP gives a negative protection as shown in Fig. 9. It can be concluded that M(4-VP) promotes carbon dioxide corrosion, and there is less promotion at the higher temperatures. This is because lack of hydrophobicity prevents carbon dioxide from filming on to the iron of mild steel. However, M(4-VP) appears to have a higher affinity for Fe(II) than O(4-

VP). Then, Fe(II)-4VP monomer complex is formed preferentially to FeCO₃ or Fe₂(OH)₂CO₃ corrosion layer [36-38]. The high mobility of the complex due to its small size associated to a strong agitation remove from the surface Fe(II) and subsequent corrosion product that could delete the corrosion kinetic and then let the surface totally active. The corrosion continues to proceed with and an increasing active area therefore the protection efficiency decreases. Here again, the lower decrease of the protection efficiency with increasing temperature could be suggested that the mechanism of inhibiting is a chemisorption rather than physisorption on the metal surface. In the case of the monomer, temperature could bring the chemisorption on the metal surface rather than the complexion with

Fe(II) and the decrease in the protection efficiency is lower.

CONCLUSION

Oligomer of 4-vinylpyridine O(4-VP) has been synthesized using hydrogen peroxide as the initiator characterized by structure and molecular weight estimation by MALDI-TOF MS. The spectrum of MALDI-TOF MS of O(4-VP) showed that the oligomeric product was detected in the mass region m/z 200-2400 corresponding to chain lengths of 2-22 repeating units and dimers ($n=2$) were the most abundant species. The oligomers consisted of chains bearing combinations end groups of H + CH₃ or OH + C=C, OH + CH₃ or OCH₃ + H, and CH₃ + OCH₃. The first wheel test results showed that the 4-VP oligomer protected the mild steel from carbon dioxide corrosion at various levels of concentration in brine and in brine + kerosene solutions. LP measurements confirmed the efficiency of the oligomer as corrosion inhibitor. The degree of protection depends on the temperature and the concentration of oligomer. The protection afforded by the 4-VP oligomer was found to be more effective at higher temperature because it reached almost 90% for the higher temperature. The monomers of 4VP cannot inhibit the corrosion rate, and on the contrary it was found to promote carbon dioxide corrosion.

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