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Cationic Copolymer of Poly (quaternary 4-vinylpyridine) Graft Poly (n-vinylpyrrolidone): Synthesis and Characterization

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ABSTRACT

The cationic Copolymers CQGP of Quaternary 4-vinylpyridine (QVPy) Graft N-vinylpyrrolidone PVP with varied molar ratios were synthesized by radical copolymerization in solution with 2, 2-azobisisobutyronitrile as an initiator. The process of the synthesis is based on two steps, first step vinylpyrrolidone (PVP) terminated 2-Hydroxyethylmethacrylate (HEMA) is produced by cationic polymerization using HClO₄ as an initiator. The PVP product has different chain lengths of molecular weight average ranging 1500, 2000 and 3000 g/mol. The second step 4-vinyl pyridine was quaternized using Octyl bromide (C₈Br), as quaternizing reagent. The structure and composition of quaternary monomer, macromonomers and the copolymer were characterized by their FTIR, ¹H NMR and ultraviolet spectra. The molecular weight was estimated by the technical viscosity using ethanol as solvent. The corrosion inhibition of Armco steel in 0.5 M sulfuric acid in the presence of cationic Copolymers CQGP of Quaternary 4-vinylpyridine (QVPy) Graft N-vinylpyrrolidone PVP was studied by weight loss measurement the results show that inhibition efficiency increases with the increase of concentration of inhibitor, and also we compared corrosion efficiency of each component of our copolymer separately PVP macromonomers and ploy(quaternary 4-vinylpyridine) by SEM the result showed that the PVP macromonomer hasn't any corrosion inhibition properties and cationic copolymers possesses excellent corrosion inhibition.

Key words: Quaternary 4-vinylpyridine, N-vinylpyrrolidone, macromonomers, FTIR, ¹H NMR, corrosion inhibition.

INTRODUCTION

Recently graft copolymers received a lot of attention due to excellent properties of flocculation and corrosion inhibition [1]. In fact, these grafted copolymers are widely utilized in industry as surface modifiers for coatings, adhesives, dispersants and compatibilizing agents in polymer blends and also for biomedical use. In particular, the amphiphilic graft copolymers have been extensively investigated for their particular physicochemical properties and self-assembly morphologies and antibacterial behavior [2,3].

Graft copolymerization has been successfully used to alter significantly the solution properties of many polymers like starch, cellulose, synthetic polysaccharides etc. by grafting suitable acrylic polymers onto them. The viscosity, gelling characteristics, solution rheology e.g. degree of pseudo plasticity, ion compatibility etc. can be drastically altered through graft copolymerization reaction. Enhanced functionality can also be imparted to substrates which will allow them to be more effective in flocculation, dispersion and other applications such as retention aids in paper, dry strength additives etc. Polyelectrolyte side chains can be introduced into suitable substrates by either grafting an ion-containing monomer or a suitable monomer which can then be transformed to an electrolyte by a simple chemical reaction. An example of the latter is when methylmethacrylate or acrylonitrile can be grafted onto

starch and then transformed by alkaline hydrolysis to acrylic acid or methacrylic acid grafts. Vinyl pyridine or dimethyl aminoethyl methacrylate can be grafted and then subsequently quaternized [4].

Cationic polymers are a class of polyelectrolytes that derive their unique properties from the density and distribution of positive charges along the macromolecular backbone. Chain conformation and solubility of such flocculants depend on the extent of ionization and interaction with water. Cationic functional groups can strongly interact with suspended, negatively charged particles or oil droplets and are useful in many applications, including waste treatment and paper making process. Water-soluble polymers containing cationic charge can be divided into three categories: ammonium (including amines), sulfonium and phosphonium quaternaries [4].

Cationic copolymer of poly (4-vinylpyridine) and poly (N-vinylpyrrolidone) is used to improved flocculants and pigment retention aids useful in paper making of particular interest is the work Baojiao Gao et al [1] also it used to determine copper (II) trace and as a homogeneous catalyst which formed a complex with palladium [5,6].

The purpose of the present work was to produce cationic graft copolymers with two interesting monomers N-vinylpyrrolidone and 4-vinylpyridine by involvement of two methods first preparation of macromonomers using method of Fatima Zohra Sebba [2] and the second is the syntheses of cationic copolymer by following the method of Baojiao Gao et al [1].

Poly (N-vinylpyrrolidone) (PVP) has been generally studied for applications in various fields, as antibacterial for pharmaceutical applications as cancer therapy [7,8]. Homo and copolymers of N-vinylpyrrolidone (VP) are of considerable academic and industrial interest due to their unique properties, allowing the use of these polymer systems in lithography as light sensitive thin coatings for printing plates, for the preparation of separating membranes for ultra-filtration, biocompatible polymers with low toxicity and carriers of biologically active compounds, sorbents, coagulants and flocculants [9,10].

4-Vinyl pyridine (4VP) is a functional monomer and the N atom on pyridine ring is a strong donor of electrons. Thus, Polyvinylpyridine and its derivatives have been widely studied, with particular interest in inhibition of corrosion Fe, Cu, Al, Zn, and their alloys in acidic media especially when N atom on pyridine ring formed cationic copolymers [1,11]. Homo quaternized poly (4-vinyl pyridines) have been widely studied [12,13]. allowing the use of these polymer for chromium retention and inhibitor for corrosion of pure iron in molar sulphuric acid [14,15] farther more these types of quaternized 4-vinylpyridinium are used with other monomers to produce new copolymers with interesting properties [16] it used with styrene to prepare a series of membranes [17] and an interesting work of Christian Chovino, to prepare single-ion conductor with fixed cation [18].

MATERIALS AND METHODS

2.1. Materials and measurements

4-vinylpyridine VPy was purchased from Merck-Schuchardt and purified by being stirred over solid potassium hydroxide pellets for 24 h and distilled under nitrogen at a reduced pressure (68–70 °C at 15 mmHg). NVP was also a Merck-Schuchardt product and was purified by distillation before polymerization. Perchloric acid (HClO₄, Prolabo) is used as received. 2-Hydroxyethyl methacrylate was purified by vacuum distillation at 68°C/5mmHg. 2,2-Azobisisobutyronitrile (AIBN) was purified by recrystallization twice from methanol, and N,N-dimethylformamide (DMF), purchased from Wako Pure Chemical Industries, Ltd., were purified by vacuum distillation before use. Alkyl bromide with a C8 carbon chain (Aldrich) was used as quaternizing reagent.

2.2 Preparation of Quaternary 4-vinylpyridine QVPy

We applied the same protocol for quaternization as for polymer of poly (4-vinylpyridine) and that adapted by usual method to prepare amphiphilic monomers by nucleophilic substitution of tertiary amine group at low temperature and protected from light to prevent polymerization of monomers [19]. A given amount of 4-vinylpyridine (4VP) was dissolved in methanol. The quaternization reaction was carried out at room temperature under magnetic stirring. Octyl bromide (C₈Br), as quaternizing reagent, was used in five-fold excess to the pyridine units in the monomer to ensure complete quaternization reaction, was slowly added into the monomer solution. The reaction was run for 12 h at room temperature. The Quaternary monomer (QVPy) then was precipitated by THF and washed thoroughly with THF. After filtration, the product was dried under vacuum at room temperature for 24 h, and then stored in a desiccator [1,21].

2.3 Preparation of NVP macromonomers

N-Vinyl-2-pyrrolidone was dissolved in 2 mL of freshly distilled dichloromethane and then placed under nitrogen atmosphere in a three-necked flask equipped with a condenser and magnetic stirring. The flask was thermostated at

30 °C then the initiator perchloric acid was introduced into the mixture. After 02 hours, 2-hydroxyethylmethacrylate 2HEMA same concentration as initiator was added to the reaction mixture. The precipitate was filtered, washed off with ether and dried in vacuum [2].²

Table 1. Experimental conditions and cationic polymerization yields of N- vinyl-2- pyrrolidone initiated by HClO₄

Macromonomer	[monomer] mol L ⁻¹ 10 ³	[HClO ₄] mol L ⁻¹ 10 ³	[2HEMA] mol L ⁻¹	Yield %
PVP ₁	0.0057	0.0425	0.0425	91
PVP ₂	0.0058	0.0325	0.0325	93
PVP ₃	0.0060	0.0221	0.0221	92

2.4 Preparation of cationic copolymer of poly (Quaternary 4-vinylpyridine-graft 2-Nvinylpyrrolidone) CQGP

The cationic copolymer of poly (Quaternary 4-vinylpyridine graft 2-Nvinylpyrrolidone) CQGP were obtained by radical polymerization of the mixture solution of QVPy and PVP in DMF using AIBN as an initiator adapting a technique described elsewhere[1]. A fixed amount of 10 mol QVPy, 1 mol PVP and 1% of AIBN was mixed with DMF (4 cm³), and the mixture was placed in an ampule. The mixture was reacted at 70° C for 24 h. The product was dissolved with metanol, and the cationic copolymer was precipitated in excess ether. The cationic copolymer was purified three times by such reprecipitation.

The molecular weights of series of cationic copolymers (QVPy-gr-PVP) CQGP were estimated by the viscosity technique, using a ViscoClock viscometer and ethanol as solvent, in a thermostatic bath at 25 ± 0.1 °C [21] supposing the skeleton in our dominant copolymer is the 4vinylpyridine poly quaternized with C₈Br.

Threes series of CQGP were synthesized Quaternary 4-vinylpyridine graft PVP1 (CQGP1), Quaternary 4-vinylpyridine graft PVP2 (CQGP2) and Quaternary 4-vinylpyridine graft PVP3 (CQGP3), for studying the effect of grafting length in corrosion inhibitor.

Table 2. The starting Macromonomers PVP1,PVP2 and PVP3 mol% and QVPy mol% on polymerization on polymerization, the copolymers and the number average molecular weight(Mn) .To calculate the number of moles of each macromonomer we consider the number average molecular weight(Mn) (Viscosity) we take it the law for high molecular weight $[\eta] = 6.08 \cdot 10^{-4} M_w^{0.61}$ [21] see Table 3

Copolymer	[Macomonomer] mol L ⁻¹ 10 ³	[QVPy] mol L ⁻¹ 10 ³	Mn(Viscosity) 10 ⁻⁶	Yield %
CQGP1	0.0424	0.424	2.321	87
CQGP2	0.0326	0.326	2.581	85
CQGP3	0.0227	0.227	3.122	88

RESULTS AND DISCUSSION

Structure and characterization of Quaternary 4-vinylpyridine (QVPy), macromonomers (PVP) and cationic copolymer poly (QVPy-gr-NVP) CQGP

3.1 Structure and characterization of Quaternary 4-vinylpyridine (QVPy)

FTIR spectrum

The FTIR spectra of 4VP samples were evaluated and are presented in fig.1 [22]. Bands at 994 and at 1407 cm⁻¹ are due to the vibration of the vinyl group, and the vibration near 3400 cm⁻¹ is due to imines.

In the IR spectrum of QVP-C8Br (Fig.2) alkylation leads to complete disappearance of bands corresponding to alkylation leads to complete disappearance of the bands corresponding to the valence oscillations in pyridine rings at 1597 and 1415 cm⁻¹, and to the appearance of the new bonds corresponding to the valence oscillations in the quaternised pyridine rings at 1465 cm⁻¹ [20,23,24].

The quaternization degree was determined by following the shift of the 1600cm⁻¹ IR band of the pyridine ring to 1639 cm⁻¹ characteristic of the respective quaternized group it was confirmed by the work of R'ios *et al* [24,25]. The reaction was considered finished once the band at 1600 cm⁻¹ had disappeared completely. The extent of quaternization was 100% [14].

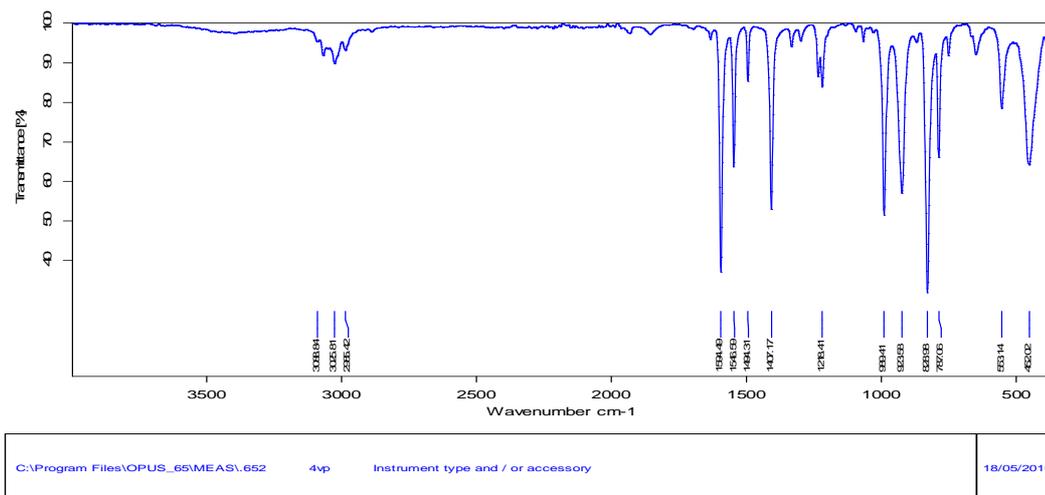


Figure 1. FTIR spectrum of 4VP monomer

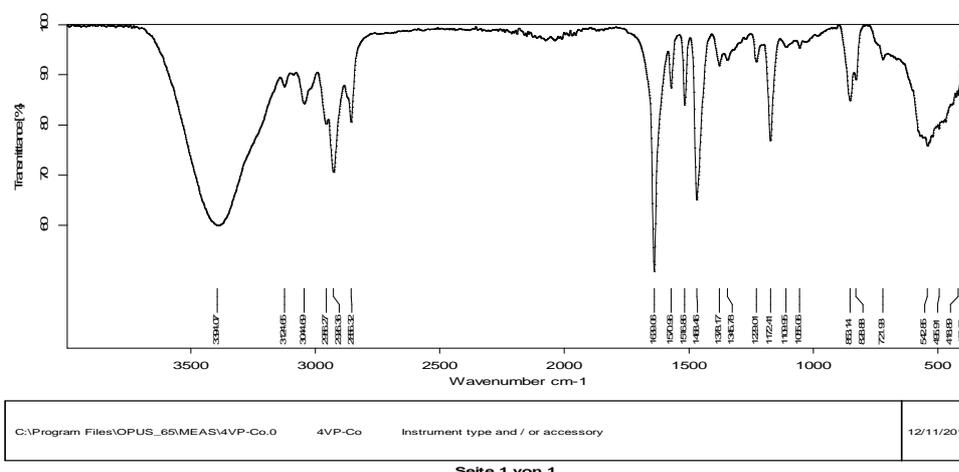
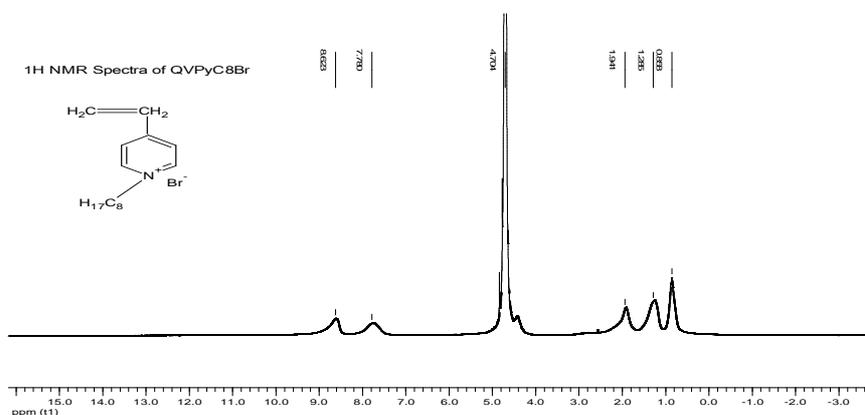


Figure 2. IR spectra of Quaternary 4-vinylpyridine (QVPy) with octyl bromide

¹H NMR spectra

Further evidence for the quaternization of the VPy with C₈Br was obtained from the ¹H NMR spectra.

Figure 2, trace a shows the ¹H NMR spectra of QVPyC₈Br. The peaks at $\delta = 8.6$ (ppm) and at $\delta = 7.7$ are ascribed to the proton at the 2, 6 sites and 3, 5 sites of alkylated pyridine rings respectively. Comparing the ¹H NMR of 4VP Fig.1 with that of the QVPyC₈Br Fig.2, a new peak at $\delta = 4.7$ is assigned to the seventeen protons of methyl group bonded with N atom in the pyridine ring [1].

Figure 3. ¹H NMR of Quaternary 4-vinylpyridine with octyl bromide

3.2 Structure and characterization of PVP macromonomer

UV analysis of chain end of PVP

UV analysis was employed to observe the fixation of the chromophoric 2HEMA group on the PVP chain end and also to determine the number-average molecular weight (M_n) of the polymer. Assuming only one chromophoric group was attached to the polymeric chain end and using molecular extinction coefficient of a molecular model, in this case the 2HEMA, the molecular weights of the samples were calculated. Thus, with the aid of a calibration curve representing the variations of the optical density according to the 2HEMA concentration in acetonitrile, a curve closely following the Beer Lambert's law (Figure1) was obtained and it allowed to determine the 2HEMA molecular extinction coefficient taken as a model ($\epsilon = 8819$ at $\lambda_{max} = 220$ nm in acetonitrile) [2].

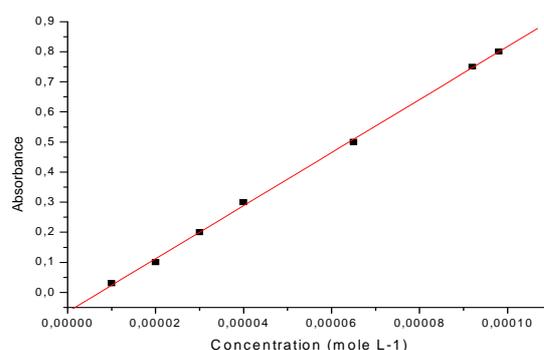


Figure 4. 2HEMA Calibration curve taken as a model (solvent:acetonitrile, $\lambda_{max}=220$ nm)

UV absorbance spectra of VP ($\lambda_{max} = 235$ nm) [2], 2HEMA ($\lambda_{max} = 220$ nm) and PVP macromonomer ($\lambda_{max} = 210$ nm), respectively.

The UV absorbance spectra shows the disappearance of the monomer double bond ($\lambda_{max} = 235$), and the appearance of a new maximum of absorbance at $\lambda_{max} = 210$ nm which characterizes the HEMA double bond. The values of the number-average molecular weights of the polymer, which were obtained from UV analysis, are listed in Table.3.

Determination of the number-average molecular weights by viscosimetry

Viscosity measurements were used to determine average molecular weights of the synthesized polymer samples. The Mark-Houwink equation was employed to calculate the viscosity average molecular weights [27,28], $[\eta] = K.M^a$. Table 3 provides the values of the average-number of molecular weights determined in three different ways: theoretically, by UV analysis and viscosity measurements.

Table 3. Number-average molecular weights of PVP polymers

Macromonomer	M_n (Theory)	M_n (UV)	M_n (Viscosity)
PVP1	1500	1600	1765
PVP2	2000	2150	2300
PVP3	3000	3200	3300

Values of the number-average of molecular weights determined by UV analysis and viscosity measurements are quite close to theoretical ones. These results suggest that the contribution of transfer reactions may be of little importance and therefore the reaction can be assimilated to a "living system" [2].

FT- IR analysis

PVP macromonomers structure and composition

Fig. 5 compares the FTIR spectra of a PVP macromonomers and the corresponding monomer VP. All PVP samples in the experimental have identical FTIR spectra.

The FT-IR spectra of the PVP macromonomer in Figure 5 shows a band absorption occurring at 1659 cm^{-1} which corresponds to the carbonyl group ($\text{C}=\text{O}$) and a peak at 2892 cm^{-1} due to C-H stretching in CH_2 and CH_3 groups. The bands appearing between 1423 and 1494 cm^{-1} correspond to the CH_2 scissor vibration of a VP unit. The peak at 1291 cm^{-1} is attributed to N-C stretching vibration.

Upon observing the FT-IR spectra, one can notice the disappearance of the characteristic bands at 1630 and 981 cm^{-1} is related to the monomer double bond and the presence of a new characteristic peak at 1374 cm^{-1} which is due to the HEMA double bond [2,22,29-30].

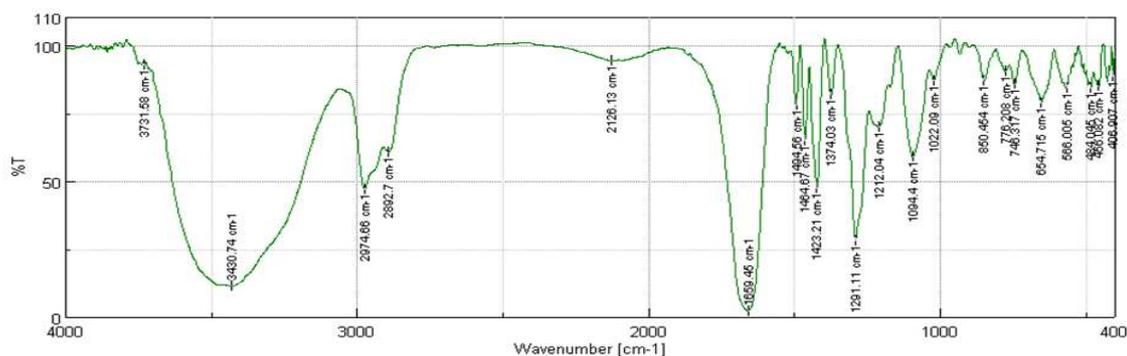


Figure 5. FT-IR spectrum of PVP Macromonomer in CHCl_3 PVP3 (3000)

$^1\text{H-NMR}$ analysis

The macromonomer $^1\text{H-NMR}$ spectrum plotted in Figure 6 shows the characteristic peaks of the PVP3 macromonomer. All PVP samples in the experimental have identical $^1\text{H-NMR}$ spectra.

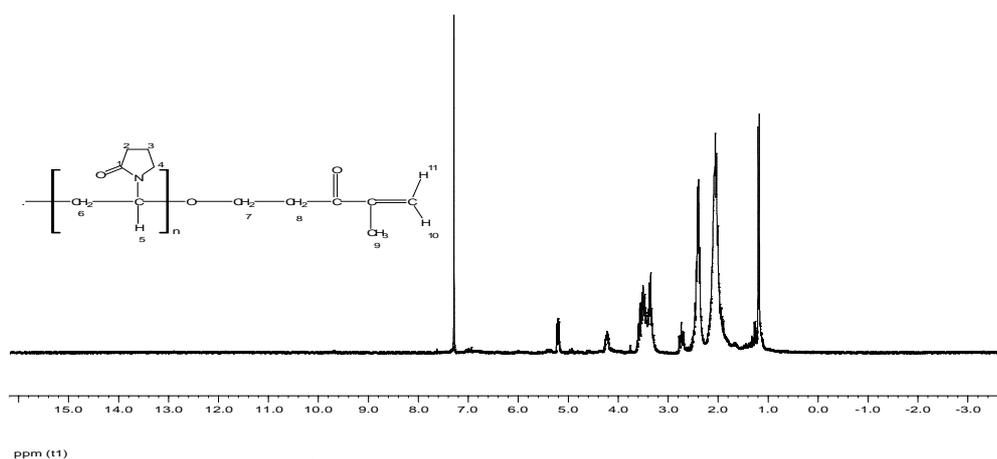


Figure 6. $^1\text{H-NMR}$ spectrum of PVP in CDCl_3 macromonomers

The resonance signals for the main chain methylene protons of NVP are at δ 2.23-2.90. The resonance signals between δ 5.2; 6 ppm correspond to protons (^{10}CH) and (^{11}CH), respectively. The methine backbone protons (^5CH) of the VP units appear as a broad peak at δ 3.5 ppm. Further, the methylene protons ($^7\text{CH}_2$), ($^8\text{CH}_2$), show resonance signals at 4.17 – 4.22 ppm whereas the ring methylene protons in NVP signals can be assigned at δ 3.5 ($^4\text{CH}_2$) δ 2.20 ($^2\text{CH}_2$), δ 1.94 for ($^3\text{CH}_2$), and δ 2.07 for ($^6\text{CH}_2$) respectively. Finally, the methane protons ($^9\text{CH}_3$), at δ 1.20 ppm [2,29,30-31].

Structure and characterization of cationic copolymer poly (QVPy-co-NVP)

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ analyses

The cationic poly (Quaternary 4-vinylpyridine – graft – PVP) CQGP copolymers were characterized by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ which generated the spectra shown in Figures 7 and 8, respectively. $^1\text{H-NMR}$ analysis of the PVP side chains confirms that the chains are capped with poly (Quaternary 4-vinylpyridine) with C_8Br backbone Figure 7. The aromatic protons of the pyridine ring appear at two different positions .the meta proton (3, 5) and ortho protons (2, 6) appear at around δ 8.08 and 9.07 ppm respectively. the resonance signal around 2.51 ppm is assigned to CH region of N-unit while the broad resonance signal resonance signal around δ 1.27 ppm is assigned the overlap of β protons of V- and N-unit, $^2\text{CH}_2$ and $^3\text{CH}_2$ proton of V-unit. The resonance signal around δ 3.38-4.54 ppm is assigned to the overlap of $^4\text{CH}_2$ and $-\text{CH}$ proton of V-unit [1,2,29,30-31].

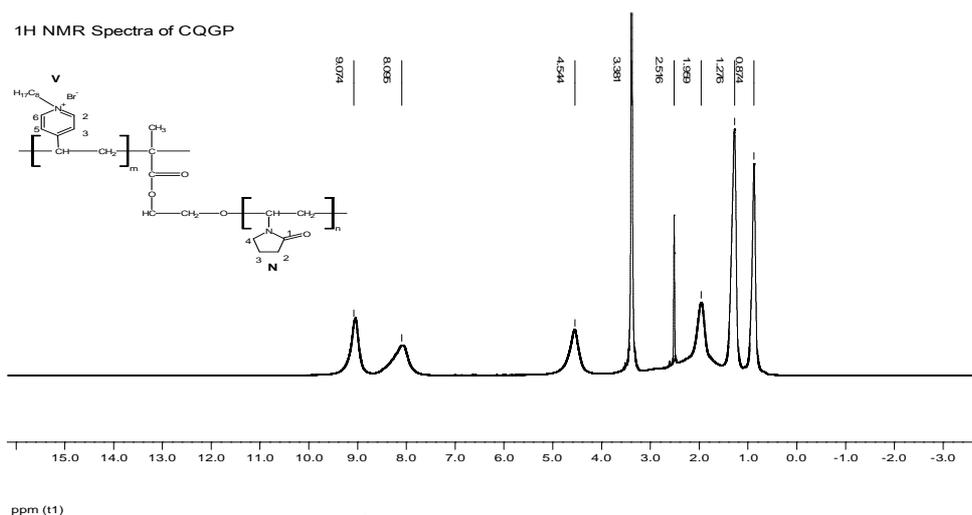


Figure 7. ¹H-NMR spectrum of CQGP in CDCl₃

The ¹³C-NMR spectrum of V/N cationic copolymer in CDCl₃ along with the complete spectral assignment in Fig.3 the carbonyl carbon and ²CH₂ carbon of V-unit appear as singlet around δ 174.93 and 31.53 ppm. The aromatic carbons of pyridine ring in N-unit appear as a set three resonance signals around 138.59, 124.23 and 47.38 ppm are assigned to C-1, C-2 and C-3, the resonance signals around 31.39, 31.05 are assigned to ⁴CH and ⁵CH₂ of pyridine ring of N-unit respectively.

The resonances signal around δ 18.05 and 14.36 ppm is assigned to ⁶CH₃ of carbon of V-unit and ⁷CH₃ of HEMA respectively.

The signal around δ 59.53, 31.39 and 45.64 ppm are assigned to ⁴CH₂, ³CH₂ and ²CH₂ of V-and N-unit .The resonance signals around δ 45.41-47.08 and 31.392 are assigned to ⁶CH and ⁵CH of V-unit [1,2,29,30-31].

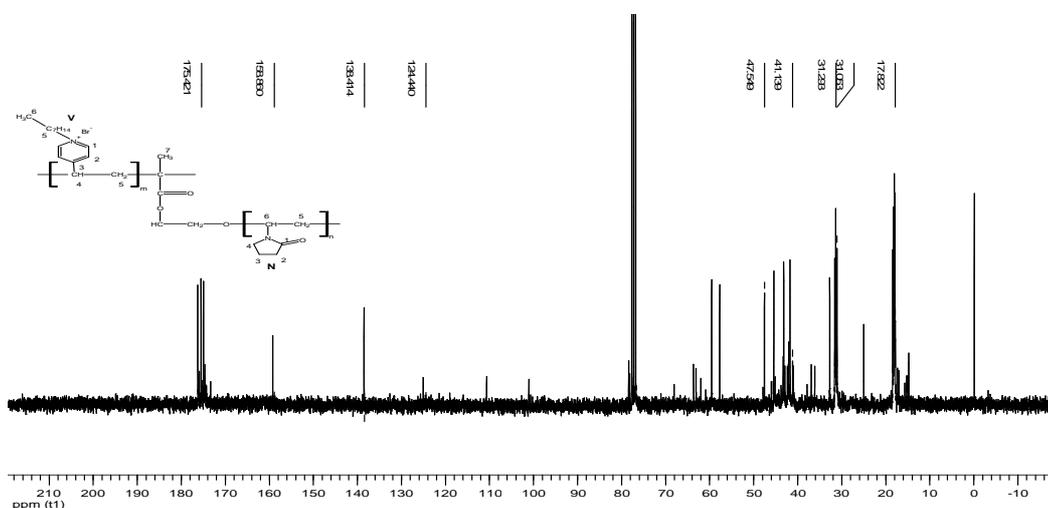


Figure 8. ¹³C-NMR spectrum of CQGP in CDCl₃

CORROSION INHIBITION

The corrosion test was carried with two methods:

4.1 Gravimetric measurements

The experiment test were executed on Armco steel of the following composition (wt.%): 0.14 % C, 0.21 % Si, 0.09 % Mn, 0.012 % S, 0.01 % Al, 0.006 % Cu, 99.532 % Fe. The samples were polished mechanically with different grades (600, 800, and 1200) silicon carbide paper, degreased in acetone, washed with distilled water and dried in warm prior to each use. The test solution was prepared from analytical-grade 98 % H₂SO₄ with bi-distilled water. The corrosion behavior was tested in 0.5 M 98 % H₂SO₄ solution in the absence and presence of different concentrations of CQGP [32,33-34].

The gravimetric tests were realized on the carbon steel specimens having as form sheets of 1 cm 1 cm 1 cm that were polished with different grades of emery papers (600, 800 and 1200) and then washed with acetone and bi-distilled water. Before and after 2h of immersion in the acidic medium with and without addition of different concentrations of CQGP (100, 50, 10, 5, and 4.0 mg/L), the samples are weighed using analytical balance of accurately [32,33,34-35].

The corrosion rate (CR) was calculated by the following equation:

$$Cr = \frac{w}{St} \quad (1)$$

Where *w* is the weight loss of carbon steel specimen, *S* was the total area of one carbon steel sheet, and *t* was time of immersion. The inhibition efficiency (IEwt %) obtained from corrosion rate can be evaluated using the following Equation:

$$IEwt\% = \frac{CR^o - CR}{CR^o} \quad (2)$$

RESULTS AND DISCUSSION

Concentration effect

Gravimetric tests

Different corrosion rates (CR) and inhibition efficiencies (IEwt %) values obtained by gravimetric measurements for natural compound tested as inhibitor on the corrosion behavior of Armco steel at different concentrations in 0.5 M H₂SO₄ are summarized in Table 4.

Table 4. Corrosion parameters obtained from gravimetric measurements for Armco steel in 0.5 M H₂SO₄ containing various concentration of CQGP at 25°C

Inhibitor	C(mg/l)	t (h)	CR (mg /h.cm ²)	IEw (%)
Blank	-	2	54	-
CQGP1	100	2	9.31	82.75
	10	2	11.90	77.96
	5	2	13.20	75.55
	1	2	14.23	73.64
	0.5	2	16	70.37
CQGP2	100	2	9.42	82.40
	10	2	12.68	76.51
	5	2	13.46	75.07
	1	2	14.52	73.11
CQGP3	0.5	2	16.43	69.57
	100	2	9.5	82.40
	10	2	12.5	76.85
	5	2	14.5	73.14
	1	2	15	72.22
	0.5	2	17	68

From **Table 4** it is clear that the decreasing of corrosion rate is accompanied to the rising of inhibition efficiency values when increasing the concentration of the tested compound. The result show that CQGP1 is best corrosion inhibition it can be explain by short length of PVP1 more accessible to charge of pyridinium ring gene steric.

We are studying also poly(Quaterny 4-vinylpyridine) with C8Br PQVC8Br with Scanning electron microscopy measurement to see the influence of quaterny alkyl bromide to corrosion inhibition because recently tow interesting work of L.Larabi and Y.Harekthe were studying the Effect of Iodide Ions on Corrosion Inhibition of Mild Steel in 0.5 M H₂SO₄ by Poly(4-Vinylpyridine) [36] and A. Chetouani et al Quaternized Poly(4-Vinylpyridine)-Graft-Bromodecane in Sulphuric Acid.³⁵ and finally the work of R. Karthikaiselvi, S. Subhashini on The water soluble composite poly(vinylpyrrolidone-methylaniline): A new class of corrosion inhibitors of mild steel in hydrochloric acid media [37] for this reason we are combined Quaternary 4-vinylpyridine (QVPy) to N-vinylpyrrolidone PVP to have an excellent compound for corrosion inhibition.

4.2 Scanning electron microscopy measurements:

The morphology of a selected example of N-vinylpyrrolidone PVP macromonomer, Poly(quaterny4-VinylpyridineC₈Br) and the cationic poly(Quaterny 4-vinylpyridine – graft – PVP) CQGP copolymer was examined by SEM(Jeol JSM-6610 LA instrument). The SEM sample was prepared by putting a cube Armco steel with 1 cm²

on solution of dilute solution of each simple in same concentration 100 mg l^{-1} on $0.5 \text{ M H}_2\text{SO}_4$ and after 2 hours we take a SEM.

The study of selected examples of derivatives using SEM measurements showed that the surfaces of cube Armco steel were more corroded with PVP3 and Poly(quaterny4-VinylpyridineC₈Br) has also inhibition properties due the presence of the charge along the chain and the cationic poly(Quaterny 4-vinylpyridine – graft – PVP) CQGP has more efficiency in corrosion inhibition.

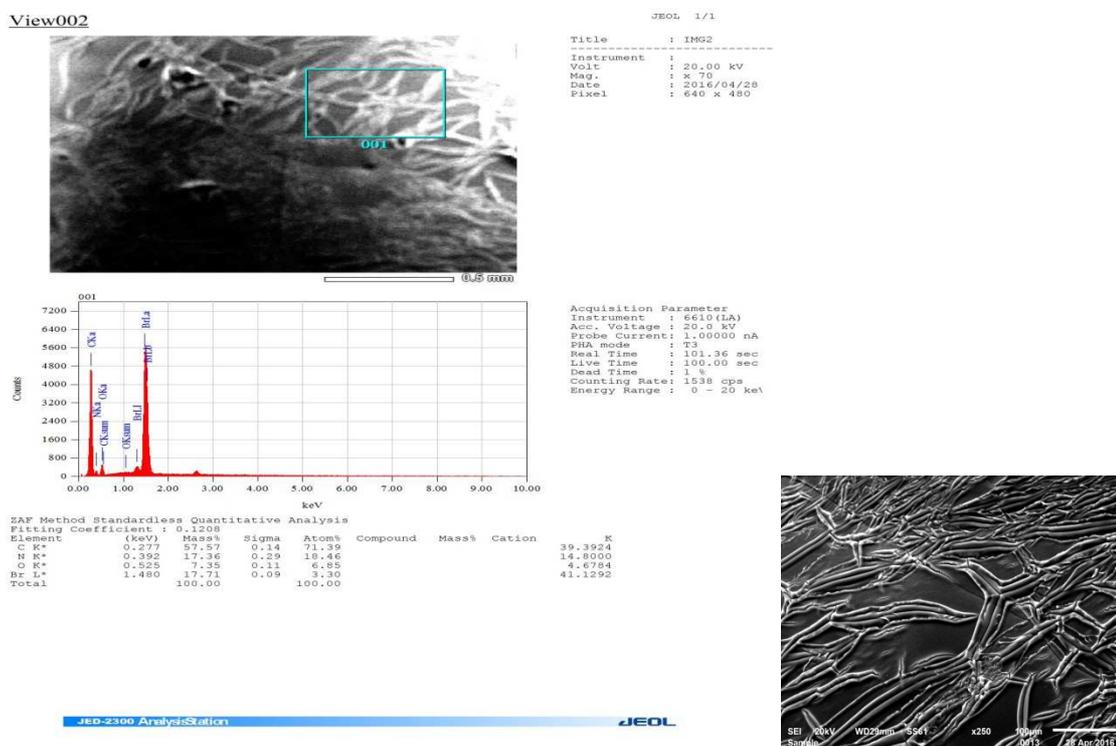


Figure 9. The SEM images of The cationic poly(Quaterny 4-vinylpyridine – graft – PVP) CQGP copolymer

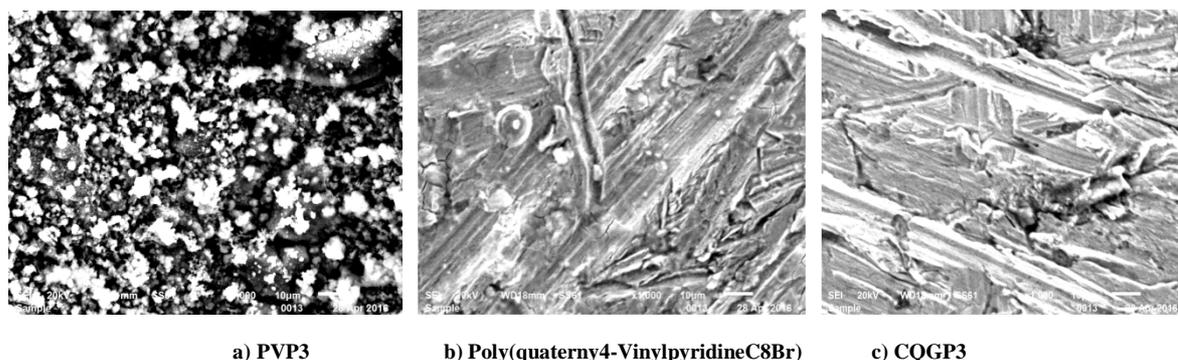


Figure 10. The SEM images of the a) N-vinylpyrrolidone PVP macromonomer , Poly(quaterny4-VinylpyridineC₈Br) and c) The cationic poly(Quaterny 4-vinylpyridine – graft – PVP) CQGP copolymer (a,b,c X=1000)

CONCLUSION

The copolymers P(QVPy-gr-PVP) CQVP of vinylpyrrolidone (PVP) macromonomers and quaterny 4-vinyl pyridine (4VP) monomers was synthesized by radical copolymerization. The process of the synthesis is based on two steps, first step vinylpyrrolidone (PVP) terminated 2-Hydroxyethylmethacrylate (HEMA) is produced by cationic polymerization using HClO_4 as an initiator.

The PVP product has different chain lengths of molecular weight averages ranging from 1500, 2000 and 3000 g/mol. The second step 4-vinyl pyridine was quaternized using Octyl bromide (C₈Br).

The structure and composition of QVPy; PVP and CQVP were characterized by their FTIR, ¹H NMR and UV spectra.

The experimental results for the Gravimetric measurements show that CGQVP1 has more inhibition efficiency than the others; it can be explained by the accessibility to positive charge due to low steric hindrance of PVPI.

The good corrosion inhibition property of CGQVP was attributed to CGQVP forming a dense and compact adsorption film on the metal surface by physical adsorption through electrostatic attraction between positive charge of CQVP polymer chain and anionic surface of the metal and by chemical adsorption through coordination of π -electrons of pyridine rings with d-orbit of Fe atoms [1]. Scanning electron microscopy measurements it confirms the presence of the Br⁻ in the copolymers Figure 10. And confirm that CQVP has more corrosion efficiency than Poly (quaternary4-VinylpyridineC8Br) and PVP macromonomers has no corrosion inhibiting property.

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