Neutralization Degree Effect on Potentiometric Behavior of Poly(N-octyl-4-vinylpyridinium Bromide)

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In this work, we synthesized poly(4-vinylpyridine) (P4VP) using radical polymerization. A pair of copolymers containing the poly(4-vinylpyridine) were quaternized using octyl bromide to get the P4VP-C_8Br with the degrees of quaternization of 48.8% and 72%. The P4VP and these two copolymers were characterized by ^{1}H NMR, IR, and ATG. Moreover, we studied the impact of the extent of quaternization and the concentration on the interaction of the P4VP-C_8Br 48.8% and P4VP-C_8Br 72% copolymers with proton H$^+$ at 25 °C within the neutralization range of (0-1). In addition, potentiometry technique was performed to evaluate the interactions at different concentrations, and a phase diagrams of solubility was established in the concentration interval of $(0.6 \times 10^{-4}$ g l^{-1}-3 $\times 10^{-4}$ g l$^{-1})$ for the two copolymers. The variation of pKa versus the concentration of copolymer and its quaternization rate was examined. In the neutralization degree range of $(0 < \alpha < 1)$, the copolymer caused a modification in the structure and conformation due to the presence of hydrophobic-hydrophilic and hydrophobic-hydrophobic interactions.

Keywords: Poly(4-vinylpyridine), Poly(N-octyl-4-vinylpyridiniumbromide), Quaternization rate, Critical neutralization degree, Conformation

INTRODUCTION

Chemical modification of synthetic polymers is important in polymer chemistry due to the growing needs for more new complexes with macromolecular structures for specific applications [1, 2]. One important class of polymers that has recently attracted the attention of researchers is the poly(4-vinylpyridines), which has shown many interesting properties due to the presence of nitrogen atom in its pyridine ring [1]. Study of the poly(4-VP) and the copolymers of 4-VP showed that the positively charged form of the poly(4-VP) can be prepared through a quaternization reaction [3]; this modification notably extended the applications of this category of macromolecules. Coleman and Fuoss [4] were the first ones

that reported the quaternization of a typical poly(vinylpyridines) called poly(4-vinylpyridine) (P4VP).

Poly(4-vinylpyridine) can be quantitatively quaternized by the addition of alkyl halides in a polar solvent; however, kinetics do not match with the simple bimolecular rate that properly describes the quaternization of a monomeric pyridine derivate. Apart from the possible side reactions, reactivity of the functional groups bound to the macromolecular chains may be different from that of small molecules counterparts. The extent to which the reactivity differs depends on various factors [5]. For example, the interfacial properties of the poly-(N-alkyl pyridinium) bromides (P4VPBr) and the quaternized poly-(2-dimethylamino) ethylmethacrylate-N-alkyl (PDAEMA) have been studied [6,7]. The study of M.D. Urzùa *et al.* showed that the interfacial tension is highly dependent on the hydrophilic-hydrophobic balance between the

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pyridinium group and the length of the polyelectrolyte side aliphatic chain [6].

P4VP homopolymer solution properties, using hydrochloric acid as protonating agent, were studied considering the pKa variation and the protonation degree (α) that depends on P4VP molecular weight. Mansri *et al.* [8] studied the weight-average molar mass, which was determined by light scattering and viscometry techniques. Tennouga *et al.* [9] reported the potentiometric and thermodynamic studies of the poly(N-octyl-4-vinylpyridinium bromide) copolymers in aqueous solutions.

There are several studies on ionic balance of the polybases such as poly(4-vinylpyridine) [10-13]. The literature data revealed that the electrostatic interactions in polyelectrolytes can generally affect the polymer properties in two ways: diminishing the degree of ionization compared to the monomer analogues, and modifying the free energies of conformation that causes altering the distribution function of the conformation set for the macromolecule.

In this paper, we studied the synthesis of the P4VP, and the quaternization of this polymer with octyl-bromide in ethanol. The obtained polymers were characterized by proton nuclear magnetic resonance (^{1}H NMR), Fourier transformation infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and conductimetry techniques. The behaviors of Copolymers in water were also examined by pH titrations of the P4VP-C$_8$Br at 25 °C. The visible dissociation constant pKa, which is a sensitive function of the electrostatic potential for protonated polymers, was estimated by changing the protonation degree and the corresponding pH values.

EXPERIMENTAL

Materials

Synthesis of poly(4-vinylpyridine). The poly(4-vinylpyridine) was synthesized by radical polymerization using benzoyl peroxide as initiators in toluene at 90 °C, taking in to consideration the described procedures [14]. First, dissolution of the poly(4-viniylpyridine) was done and then the precipitation in the solvent (ethanol/ether) was considered. We deduced the molecular weight of P4VP in absolute ethanol $\overline{M}_V = 6.1 \times 10^4$ g mol^{-1} using the following Eq. (1):

$$[\eta] = 2.35 \times 10^{-5} \times M_V^{0.68} \tag{1}$$

Synthesis of poly(N-octyl-4-vinylpyridinium bromide) copolymers (P4VP-C $_8$Br). The quaternization was completed by the refluxing of poly(4-vinylpyridine) in ethanol with octyl-bromide. The reactions were performed under nitrogen in a thermostated water batch (± 0.1 K). The quaternization rate was obtained using conductivity [15]. The kinetic study was done by taking 0.2 ml of reactional mixture against a time. Indeed, the solution was poured into the diethyl ether to get a solid that was also washed with the diethyl ether, filtered and dried under vacuum at room temperature. P4VP-C$_8$Br quaternization rate was reinforced by ^{1}H NMR and ATG. The copolymers are called P4VP-C$_8$Br1 and P4VP-C$_8$Br2, respectively (Fig. 1). Table 1 shows the obtained values of the quaternization rate.

Characterization

The molecular weights of the polymers were determined by Ubbelhode-Schott Gerat AVS400 viscometer.

Infrared (IR) spectra of the polymers were obtained using an SHIMADZU TFIR-8300, FTIR spectrometer.

The Proton Nuclear Magnetic Resonance (^{1}H NMR) of the copolymers were recorded with a Bruker 200 Mhz at room temperature (solvent methanol detred).
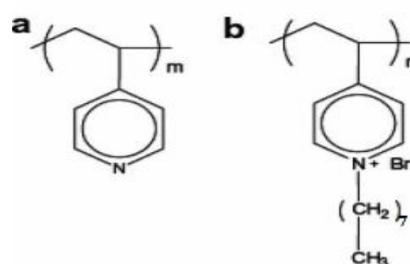
Fig.1. Structural unit of (a) P4VP and (b) P4VP-C$_8$Br.

Table 1. Values of Molar Quaternization Rate

Copolymer	Quaternization rate
P4VP-C$_8$Br 1	48.8%
P4VP-C$_8$Br 2	72%

Thermogravimetric analyses of the copolymers were conducted using TA Instruments Q Series Q600 SDT. Dynamic measurements were done at a heating rate of 5 °C min^{-1}.

Methods

Conductimetry measurements. The conversion rate of the quaternization reaction was determined by conductimetric titration of the bromide ions with AgNO$_3$ using a Mettler DL 40 RC titrator with a silver electrode.

pH Metric titrations. The pH metric titrations were achieved in a thermostated vessel at 25 °C using a "Denver Instrument" model 225, equipped with a Schott combined electrode. The system was standardized with buffers solutions at pH 4.01 and 7.02. Stabilization of the pH solutions of P4VP needed a few minutes rest time in the high pH range. Therefore, further addition of the titrant was delayed until reaching a constant value of pH.

RESULTS AND DISCUSSION

Characterization of Copolymers

FTIR Spectra. Figure 2 presents the FTIR spectra of the P4VP and P4VP-C$_8$Br samples. Bands at 994 and 1407 cm^{-1} are due to the vibrations of the vinyl group, and the vibration near the 3500 cm^{-1} is related to imines; complete disappearance of bands corresponding to the valence oscillations in pyridine rings at 1597 and 1415 cm^{-1}, and to the appearance of new bands corresponding to the valence oscillations in the quaternized pyridine rings at 1466 cm^{-1}, are due to alkylation [16]. The intensity of bands at 2924 and 2853 cm^{-1} indicates the existence of C–H bonds in –CH$_2$ and–CH$_3$ belonging to the main chain of the alkyl radicals. The small band at 2362 cm^{-1} corresponded to the ammonium salt. A band was obtained at 1638 cm^{-1} that may be related to the amine salt (–N$^+$H–binding vibration) [17, 18].

Proton nuclear magnetic resonance (^{1}H NMR). Figures 3 and 4 represent the ^{1}H NMR spectra of the P4VPC$_8$Br. Protons of alkylated pyridine rings led to signals at 8.47-8.78 ppm and 7.98-7.92 ppm. Protons of the octyl group, which are close to the pyridinium rings, led to signals at 4.58-4.58 ppm and 2.08-2.08 ppm. The signals at 3.31-3.09 ppm are due to the presence of the protons of methylene groups of the main chain. The methylene and methyl groups of the alkyl chains of octyl groups are the source of the signals at the low field 1.36-1.33 ppm and 0.94 ppm. The first spectrum proved the 48.8% alkylation of the pyridine rings; this amount was 72%in the second spectrum.
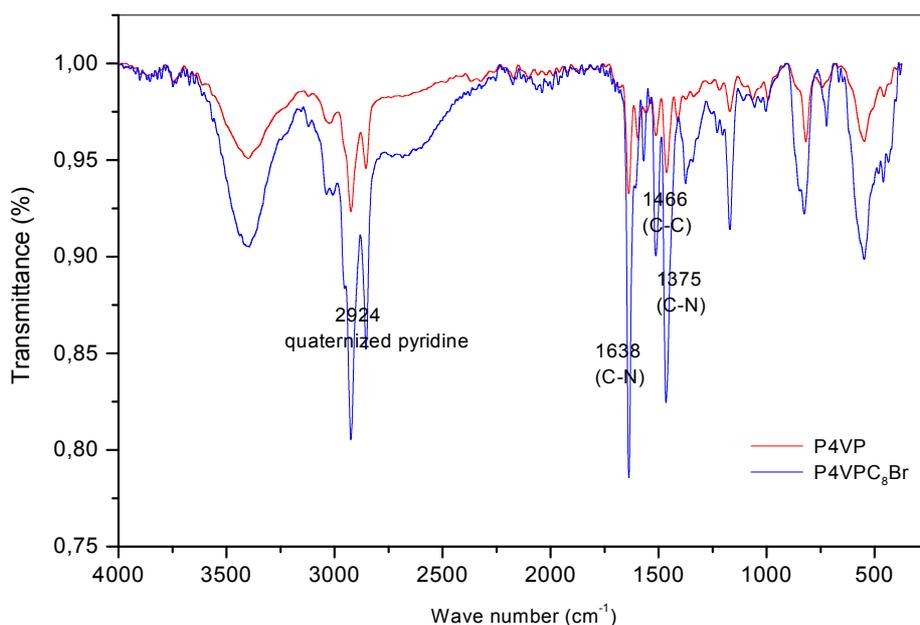
Fig. 2. FTIR spectra of P4VP and P4VP-C$_8$Br.

Fig. 3. ^{1}H NMR spectrum of P4VP-C$_8$Br 1 in CH$_3$OD.

Fig. 4. ^{1}H NMR spectrum of P4VP-C$_8$Br 2 in CH$_3$OD.

Thermogravimetric analysis. Thermogravimetric analysis is considered as the most important method for studying the thermal stability of polymers. It monitors the variation in a sample's weight as a function of temperature. We have studied the thermal stability of the P4VP-C_8Br in the temperature range between 35 and 800 °C under air. We have performed two kinds of experiments; one used a dynamic mode (35 to 800 °C, with heat ramp rate of 5 °C min^{-1}), and the other uses an isothermal mode (100 °C for 12 h). The thermogravimetric curves obtained for the P4VP-C_8Br copolymers are shown in Fig. 5. We obtained a loss of weight about 7% between 35 and 200 °C. This was due to the removal of residual water molecules from the polymer. On the other hand, for polymers with poly(4-vinylpyridinium), the loss of weight was due to the fast quaternization phenomenon resulting from the interruption of C-N$^+$ bands [19,20].

We obtained that the percentage of weight loss between 200 to 400 °C corresponded to the remained amount of the alkyl bromide C_8H_{17}Br in samples. It was at 400 °C that the degradation of the principal skeleton of the copolymer started effectively. The copolymers were stable until 200 °C. The percentage of quaternization is in accordance with the repots in the literature [21,9].

Study of (P4VP-C_8Br)/HCl interactions by potentiometric technique. We studied the interaction of the copolymer with proton H$^+$ at 25 °C by potentiometric technique using hydrochloric acid solution for potentiometric titrations.

The copolymer concentration for titrations was 0.6×10^{-4} to 3×10^{-4} g l^{-1}, that were already chosen from the phase diagram [9]; 20 ml of the solutions were titrated by HCl already prepared in water ($C_{HCl} = 10 \times C_{P4VP}$).

The potentiometric titration of the partially protonated poly(4-vinylpyridine) in aqueous medium was first studied by Fuoss and Strauss [12]. They followed the variation of pKa in accordance with the degree of neutralization in the interval of α (0-0.5) using Eq. (2). The value of pKa at $\alpha = 0.5$ was determined to be 3.0-3.2. Kirsh [11] used the complete potentiometric titration of P4VP in the ethanol/water mixtures. The results showed that both pKa at $\alpha = 0.5$ and pK_0 are notably less than pKa of the ethylpyridine. Some results were found by Satoh [22] in the presence of 0.1 M NaCl or 0.1 M of sodium benzene
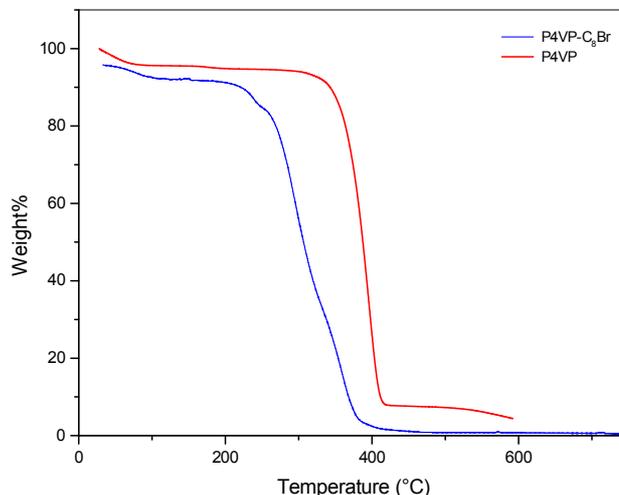
Fig. 5. Thermogravimetric curves of P4VP and P4VP-C_8Br.

sulfonate in aqueous solution as well as in 45% aqueous ethanol solution.

$$\alpha = \frac{[H_3O^+]}{[P_4VP]} \qquad (2)$$

Complete titration of polyvinylpyridines ($\alpha = 0$ to $\alpha = 1$) was performed in a water-ethanol mixture [11-23]. The titrations of P4VP and P2VP were studied by potentiometry in an ethanol-water (45-50% in weight) mixture and at ionization degree ($\alpha = 0$ to $\alpha = 1$) [11].

The pyridinc functions encircled by quaternized close groups were less reactive; this phenomenon of auto-retardation was not obtained for the simple monomers molecules. In the case of the macromolecules, the distribution of the charges is controlled by a chemical structure that defines the microstructure of the samples, and the sequence in the case of copolymer.

Mansri *et al.* [8] plotted the titration curves of the P4VP in water/methanol mixture for different concentrations and at 25 °C. For the concentrations more than 2.10^{-3} M, the pH decreased regularly. In contrast to low concentrations, the curve for 1.6×10^{-4} M was more complex, reproducing the conformational transition between $\alpha = 0.1$ and $\alpha = 0.2$. This is specific to the titration of a narrow compact conformation in which the cohesive forces maintain the pyridinium groups close together; the pKa was increased for this case.

The electrostatic repulsions in this area (α: 0.1-0.2) start to go beyond the limits of the cohesive forces, and the compact conformation deals with a diminution of the pKa. The titration curve of the molecule model ethylpyridine is specific for weak base [8].

Figures 6 and 7 represent the variation of pH as a function of neutralization degree at different concentration of P4VP-C_8Br and fixed temperature of 25 °C. For the two copolymers, the pH decreased with an increase in the concentration of the polymer. The basic order of the solution decreased according to the concentration. For α = 0, the pH of the solutions of P4VP-C_8Br 48.8% copolymers is higher than the pH of P4VP-C_8Br 72% copolymers. According to a study on the titration potentiometric of P4VP by Mansri *et al.* [8], the latter compound is more basic than the two copolymers P4VP-C_8Br 1 and P4VP-C_8Br 72%. It is known that the P4VP-C_8Br 2 is more acidic than the P4VP-C_8Br 1.

The effect of the quaternization percentage on pH variation is very obvious. Indeed, when the rate of quaternization of copolymer increases, the solution of copolymer becomes more acidic.

In the range of α = (0-0.2), the pH values of the P4VP [9] were higher than those of the P4VP-C_8Br 1. These pH values for the P4VP-C_8Br 1 were higher than those for the P4VP-C_8Br 2. The decrease in values was due to the quaternization effect which led to the reduction of the azote atom by the octyl-bromide; this is typical in the titration. Indeed, this polyelectrolyte is characterized by a balance between the hydrophilic property of the pyridinium group and hydrophobic property of the alkyl bromide, which has provided polysoap features for these copolymers [24]. The micelles formation and steric hindrance are the common causes for a decrease in pH between the polymers.

For α > 0.2 the pH decreased quickly according to the quantity of the added hydrochloric acid, and for α equal to or higher than 0.6, the pH varied very slightly.

Another usual way to plot the pH metric titration data of polyelectrolytes is to represent the apparent pKa [25]. The negative logarithm of the apparent dissociation constant, pKa, is defined by Eq. (3) [24]:

$$pK_a = pH + \log\left[\frac{\alpha}{1-\alpha}\right] \tag{3}$$
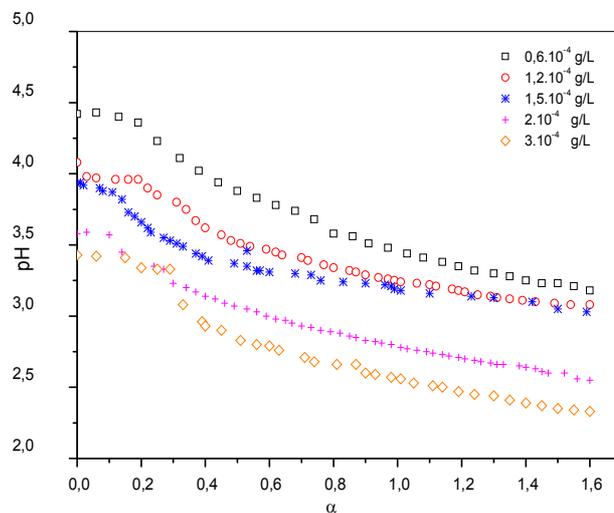
Fig. 6. Titration curves of P4VP-C_8Br 1 in water at 25° C.
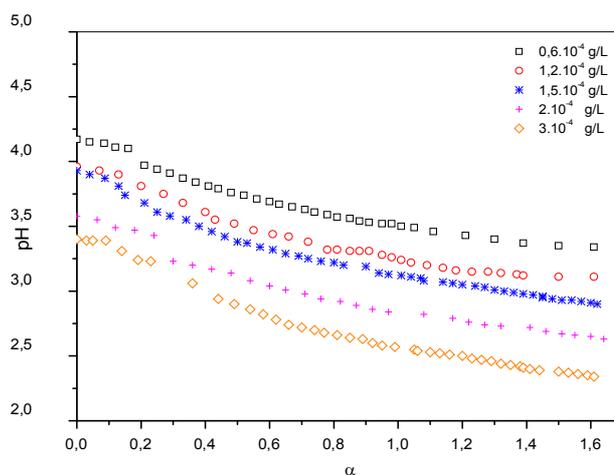
Fig. 7. Titration curves of P4VP-C_8Br 2 in water at 25 °C.

The pk$_a$ value is not constant; it increases or decreases with a change in α value of polyelectrolytes. The pK$_a$ can be expressed by a sum of two terms as shown in Eq. (4) [26].

$$pK_a = pK_{a_0} + 0.43\frac{\Delta G(\alpha)}{RT} \tag{4}$$

In above formulation, pK_{a_0} is the intrinsic dissociation constant, pH is the acidity or alkalinity of solution, α is the degree of protonation, T is absolute temperature, R is the

gas constant, and ΔG is Gibbs free energy of dissociation of one mole of protons.

To remove a molar equivalent of protons at a given α, it should be noted that the pK_a is proportional to the required free energy $\Delta G(\alpha)$.

Figures 8 and 9 show the plots of variation of pK_a *versus* α at different concentrations of the P4VP-C$_8$Br 1 and the P4VP-C$_8$Br 2, respectively.

These curves were obtained by the same results achieved from Figs. 5 and 6 using the Eq. (3).

In the interval of $\alpha = [0-0.2]$, an increase in pK_a was obtained for all concentrations of the two copolymers. Between $\alpha = 0.2$ and $\alpha = 0.6$, the pK_a was stabilized. Above $\alpha > 0.6$, the pK_a grows again for all the concentrations and increases at very low values of $0.6 \cdot 10^{-4}$ g l^{-1}.

The pK_a of P4VP [8] is higher than that of P4VP-C$_8$Br, and the pK_a of P4VP-C$_8$Br 1 is lower than that of P4VP-C$_8$Br 2. It is also observed that the pK_a values decreased with the rate of quaternization. Electrostatic interactions of the octyl bromide reduced the nitrogen atoms, which led to the disappearance of the conformation of transition in the P4VP [8]. The latter effect corresponds to the maximum active nitrogen atoms charged (N$^+$) with minimal energy [8].

The conformation of transition changes were observed at $\alpha = 0.2$ (critical neutralization degree) showing that an equilibrium exists between N and N$^+$. For $\alpha \geq 0.6$, conformation stability was obtained and the chain was not completely unfolded in an acid medium in the present system [27].

Effect of Concentration on the pk$_a$ variation of P4VP-C$_8$Br. P4VP-C$_8$Br is soluble in water because it is charged by quaternization. The superposition of the two curves of pK_a of the two polymers for the same concentration showed that the effect of polymer concentration is not visible at the concentration superior 0.6×10^{-4} g l^{-1}. The reason is that at very low concentration, the chains are scattered and thus there is no interaction between the polymer chains and the alkyl chains; the addition of HCl in the medium is mostly in low concentration. Figure 10 shows the conformation for P4VP-C$_8$Br 1; because it is less quaternized, the interactions are low, and no effect was obtained by an increase in the concentration.

The pK_{a_0} values were calculated by Eq. (3). Table 2
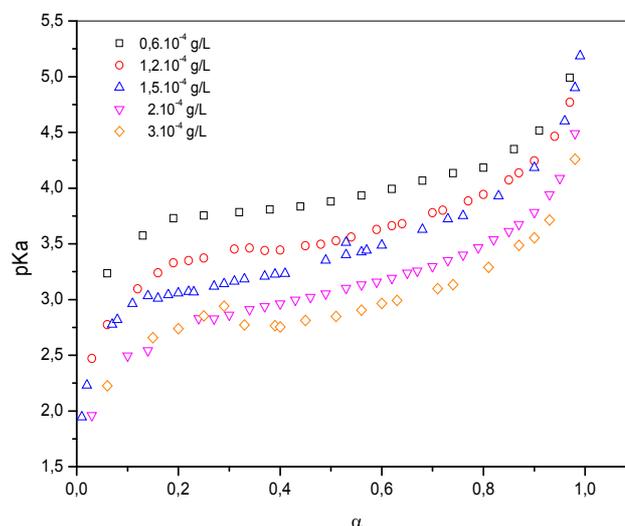
Fig. 8. pK$_a$ variation *vs.* α of P4VP-C$_8$Br 1 in water at 25 °C.
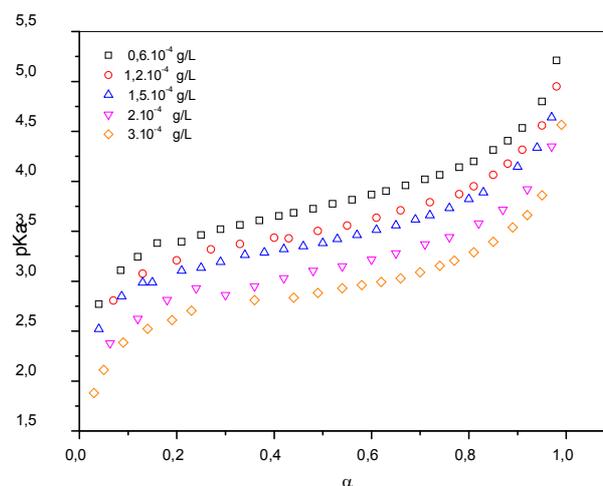
Fig. 9. pKa variation *vs.* α of P4VP-C$_8$Br 2 in water at 25 °C.

Table 2. pK_{a_0} Values of: -P4VP in Water/Methanol at 25 °C. - P4VP-C$_8$Br 1 in Water at 25 °C. - P4VP-C$_8$Br 2 in Water at 25 °C

Monomer, Polymer, Copolymers	pK_a
4VP	5.09
P4VP	4.04 - 4.64
P4VPC$_8$Br 1	2.94 - 3.23
P4VPC$_8$Br 2	2.47 - 2.76
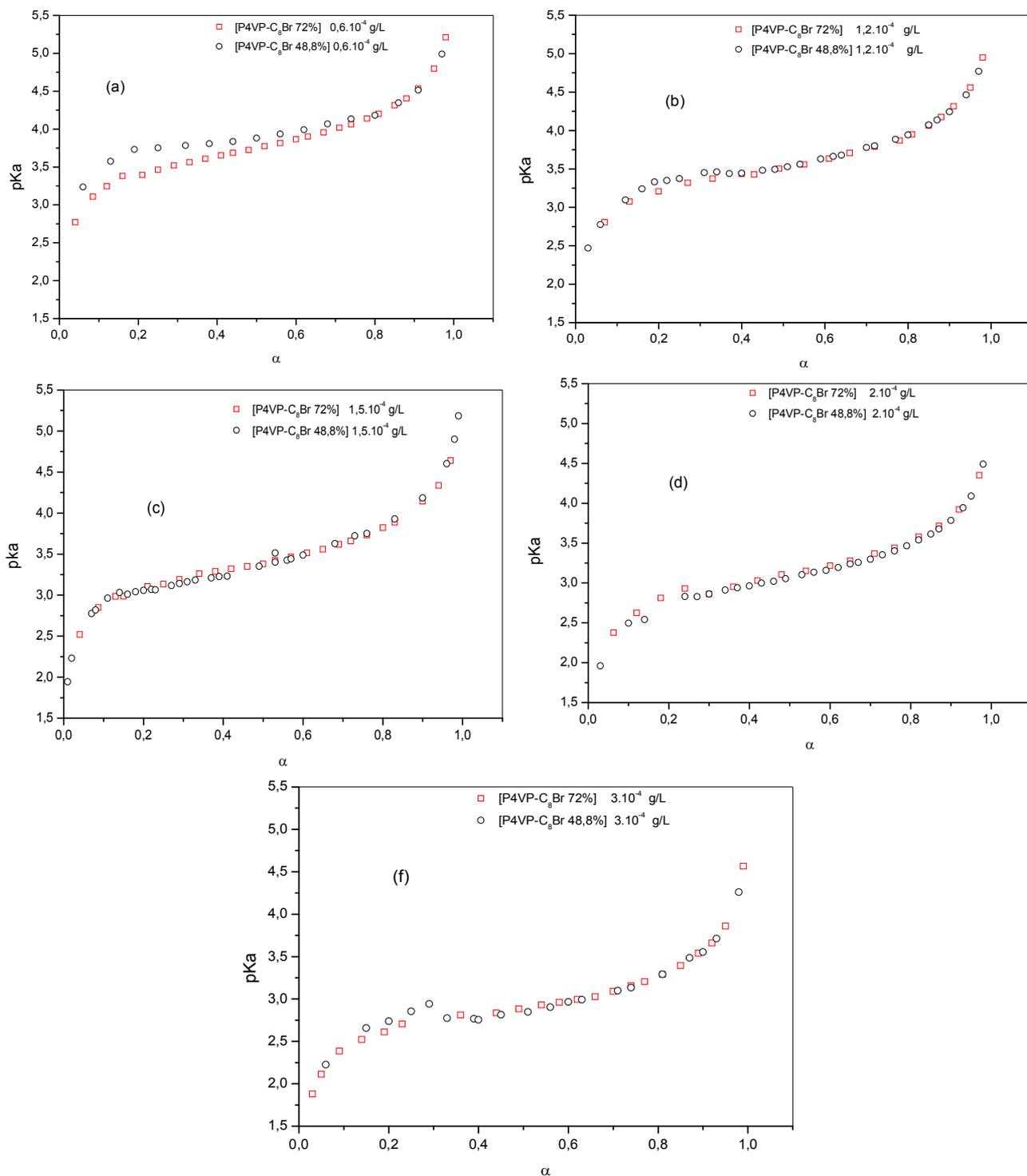
Fig. 10. Ajustement of pKa polynomial Mandel equation for P4VPC8Br 1 and P4VPC8Br 2: (a) $C_{P4VP-C8Br} = 0.6 \times 10^{-4}$ g l^{-1}; (b): $C_{P4VP-C8Br} = 1.2 \times 10^{-4}$ g l^{-1}; (c): $C_{P4VP-C8Br} = 1.5 \times 10^{-4}$ g l^{-1}; (d): $C_{P4VP-C8Br} = 2 \times 10^{-4}$ g l^{-1}; (f): $C_{P4VP-C8Br} = 3 \times 10^{-4}$ g l^{-1}.

shows that pK_{a_0} of the monomer analogue were higher than those of the P4VP, the P4VP-C$_8$Br 1, and the P4VP-C$_8$Br 2 for a concentration in range of (3×10^{-4} g l^{-1} and 0.6×10^{-4} g l^{-1}).

The pK_{a_0} of the copolymers increased by a decrease in the concentration. The dissociation constant of the pyridine function of copolymers in the absence of electrostatic interaction similarly reduced with the octyl bromide nitrogen's atoms. Coupling between the external rate of quaternization and the internal pK_a is an intriguing phenomenon with implications beyond the rate of quaternization and concentration.

CONCLUSIONS

In this work, a poly(4-viniylpyridine) was synthesized by a free radical polymerization and characterized by the ^{1}H NMR and IR. The macromolecular weight was determined by viscometry. The quaternization kinetics of the P4VP was studied using octyl bromide. Two copolymers were obtained: P4VP-C$_8$Br 1 and P4VP-C$_8$Br 2. The characterization of these copolymers was accomplished by conductimetry, ^{1}H NMR, IR and ATG. The interaction between HCl and P4VP-C$_8$Br was studied at 25 °C by potentiometric in water solution to get the total ranking of neutralization (0-1). The impacts of the quaternization percentage and the concentration on the potentiometric behavior were examined. pK$_a$ and pK_{a_0} depend on both concentration and the rate of quaternization . The effect of the quaternization percentage on pH variation was very clear. In fact, when the rate of quaternization of copolymer increased, the solution of copolymer became more acidic. The pK$_a$ decreases with the rate of quaternization. Electrostatic interactions of the octyl bromide reduced the nitrogen atoms, which caused the disappearance of the conformation of transition in the P4VP. The pK_{a_0} of the copolymers increased by a decrease in the concentration. The dissociation constant of the pyridine function of copolymers in the absence of electrostatic interaction similarly reduced the nitrogen atoms with the octyl bromide.

The augmentation of the proton H$^+$ caused an augmentation of the pyridinium group and a loss of the conformation of transition. This changes in the conformation of transition were observed at α = 0.2 (critical neutralization degree), showing that an equilibrium exists between N and N$^+$. For α ≥ 0.6, there was conformation stability and the chain was not completely unfolded in an acid medium in system.

ACKNOWLEDGMENTS

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