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Copolymers of acrylamide (AM) and 4-vinylpyridine (4-VP) containing quaternary alkyl bromides, synthesis, quaternization, characterization

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ABSTRACT

The copolymer P(AM-co-4-VP) (PAV) of acrylamide (AM) and 4-vinylpyridine (4-VP) was synthesized by conventional radical copolymerization, and then the copolymer was quaternized by alkylbromides chains with a number of carbon atoms varying (C2,C4,C8 and C10) to product cationic (CPAV), a cationic polyacrylamide containing quaternary pyridine alkylbromide chains varying. Two copolymers series have been synthesized, first PAV and second CPAV. Many techniques have been used to characterize the structure and composition of the copolymer PAV and the cationic copolymer CPAV, FTIR, HNMR spectra.

Key words: Cationic copolymer of acrylamide, Quaternary pyridinium, Alkyl bromides chains, Synthesis, Characterization

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INTRODUCTION

The chemical modification of natural or synthetic polymers is an important part of macromolecular chemistry for new structures, complex and variable. However, the reactivity of a functional group present in a polymer can be quite changed from what it is in a single molecule which often leads to lower conversion rates. More recently, Dizman and al. [1], an interesting example, these are polyacrylamides with lateral pyridine rings which are then quaternized by different alkyl bromides (C12, C14, and C16). Operating in a highly polar mixture acetonitrile-methanol at 60 ° C, the degree of quaternization exceeds 90%. Damas and al. [2, 3] have developed a series of copolymers poly (N-alkylacrylamide bromide-co-1-methyl-4-vinylpyridinium), obtained by quaternization of the copolymer precursor poly (N-alkylacrylamide-co-4-vinylpyridine). The latter is synthesized by radical copolymerization in the presence of AIBN or ADVN. Then, the quaternization by methyl bromide, conducted in chloroform, methanol or chloroform / DMF achieves almost quantitative conversion (97%). According to their hydrophobicity (number of carbon atoms in the chain N-alkylacrylamide), these polymers formed in aqueous micro-domain structure with a more or less compact. In the context of our work, a typical example is the quaternization of poly (vinylpyridine). Baojiao and al. [4] involve polymer structure quite similar to those discussed in this paper. Those are poly (acrylamide-co-4-vinylpyridinium) quaternized by dimethyl sulfate. Among the many water-soluble polymers available, copolymers and homopolymers based on acrylamide (AM) are widely used in many fields and in the past few years the study of copolymerization of acrylamide with functional monomers has attracted increasing attention [5]. Cationic and multiple-function polyacrylamide (PAM) is an important reagent in industry for wastewater treatment due to the excellent flocculation function originating from synergistic effects of charge neutralization and bridging adsorption .It has also been studied that the cationic polymer of quaternary salt-sulfur possesses fine corrosion inhibition and sterilization functions. The synthetic process involved two reactions. First, acrylamide(AM) and 4-vinylpyridine (4VP) were copolymerized and second , the copolymer was quaternarized using quaternarizing reagent. In this way, not only polyacrylamide was cationizated but also pyridine quaternary was introduced into the copolymer chains (4). In our work the copolymer of AM and 4VP, poly(acrylamide-co-4-vinylpyridine) was synthesized by radical copolymerization in solution, and the cationic polyacrylamide of pyridine quaternary alkylbromide was prepared by quaternarization of P(AM -co- 4VP) by different alkyl bromides chains (C2,C4,C8 and C10), many techniques have been used to characterize structure and composition of the copolymers and the cationic copolymers .The inhibitive power of the polymers is related structurally to the various active centers of adsorption such as cyclic rings and heteroatom's as oxygen, nitrogen and sulfur, which are the major active centers of adsorption. Polyvinyl pyridine and derives has been widely examined, has received particular attention and has been applied to the inhibition of Fe, Cu, Al, Zn and their alloys in various acidic media [6]. Recently, the encouragement result obtained by addition of poly (4-vinylpyridine) (P4VP) derivatives on the corrosion of pure iron in 1M H_2SO_4 has incited us to modify the molecular structure by introducing the poly-3-oxide ethylene group [7]. P4VP and its derivatives, the poly (4-vinylpyridine poly-3-oxide ethylene) (P4VPPOE), obtained good results [8] and Poly (4-vinylpyridine isopentyl bromide) P4VPIPBr on the corrosion of pure iron in 1M H_2SO_4 [9]. The aim of work is to investigated how the poly (4-vinylpyridine isopentyl bromide) (P4VPIPBr) inhibits the pure iron corrosion in 1M H_2SO_4 by using electrochemical impedance spectroscopy (EIS) and adsorption models of (P4VPIPBr) on the pure iron surface [10]. Kaoru and al. [11] were newly synthesized poly (N-isopropyl-acrylamide-co-4-vinylpyridine) improved the time for dissolving the deposited polymer absorbent in water as well as extractability of tris (1, 10-phenanthroline) iron (II) per chlorate. Ashish and al. [12] were Grafted the poly (MA), poly(MA-co-4VP), poly(MA-co-Aam) and poly(MA-co-AA) onto sabdariffa stem fiber in the presence of initiator yielded novel regenerated graft copolymers. It is evident from the characterization and evaluation studies of the graft copolymers through different technique that grafting resulted in the morphological transformation that improved the various physico-chemical properties of the fiber and the mechanical strength of the composites when used as reinforcement. Physico-chemical resistance, hydrophobicity and miscibility with the organic solvents acquired by the fiber after graft copolymerization innovates to utilize the renewable waste biomass in various scientific and industrial applications like in aerospace, transportation, packaging and insulators. El-Hamshary and al. [13] were synthesized new chelating hydrogel polymers containing varied AM/4-VP contents and different crosslink ratios and examined for heavy metal removal from aqueous solutions, the hydrophilic nature of the hydrogel copolymer is enhanced by increasing the amount of acrylamide.

The application of CPAV water-soluble polymers as corrosion inhibitors of metals in aggressive media with AC impedance technique takes more attention; the experimental results showed that the cationic polyacylamide containing quaternary pyridine with alkylbromide chains varying will be reported in another paper, corrosion inhibition of CPAV.

MATERIALS AND METHODS

2. 1. Monomers and Alkyl bromides

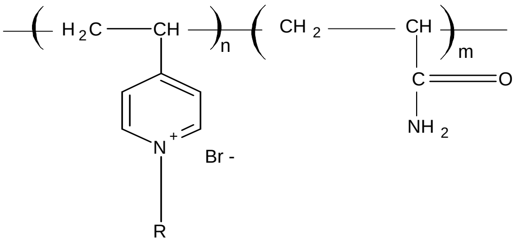
Acryl amide (company Chemika) Mw: 71.08 g / mol, 4VP (Aldrich, 98%) washed with 0.1 N NaOH to remove inhibitor and dried over $CaCl_2$. The 4VP was distilled under reduced pressure (68 to 69 ◦C at 15mmHg), just before use. Ammonium per sulfate (Aldrich, 98%) $(NH_4)\ _2S_2O_8$ is used as initiator, very soluble in cold water. This is a very powerful oxidizing agent, used to catalyze the polymerization of 4VP and acryl amide. Alkyl bromides chains (Aldrich) with a number of carbon atoms varying (C2, C4, C8 and C10), as quaternarising reagent. N, N-dimethylformamide (DMF) as a solvent of acryl amide and 4VP. Tetrahydrofuran (THF) used to precipitate the CPAV. The absolute ethanol is used as solvent for copolymers PAV and CPAV. It is supplied by Aldrich. A flask equipped with a magnetic stirrer, a flow of inert gas (nitrogen) and a thermometer to check temperature.

2. 2. Synthesis of P (AM-co-4VP)

The copolymers PAV and CPAV are synthesized by adapting a procedure described in [6]. The polymerization was carried in a bottle under a hot plate bubbling with nitrogen and a thermometer to check the temperature with magnetic stirring. A quantity of AM (5g) and 4VP (5g) was dissolved in N, N-dimethylformamide (DMF), the mixture was bubbled by (nitrogen) for 30 min then $(NH_4)\ _2S_2O_8$ (APS) was added as initiator in mixture, the mixture was heated to 45°C for 06hrs.The copolymer P (AM-co-4VP) was precipitated in distilled water twice nine times the volume of our solution and then washed several times with distilled water and methanol within 24hrs in order to eliminate monomers of AM and 4-VP that have not reacted. The product was then dried under vacuum at room temperature to constant weight and stored in desiccators.

2. 3. Synthesis of cationic P (AM-co-4VP)

A given amount of P (AM-co-4VP) was dissolved in methanol or in a mixture of methanol and glycol, depending on the composition of the copolymer. The cationization reaction was carried out at room temperature under magnetic stirring. Alkyl bromides chains with a number of carbon atoms varying (C2,C4,C8 and C10), as quaternarising reagent , was used in five-fold excess to the pyridine units in the copolymer to ensure complete quaternarization reaction ,was slowly added into the copolymer solution. The reaction was run for 11hrs at room temperature. The cationic copolymer (CPAV) was precipited by THF then was washed thoroughly with THF .After filtration, the product was dried vacuum at room temperature for 24hrs and then stored in a desiccators .The structure formula of CPAV is illustrated in Scheme 1.



R: Alkyl (C2; C4; C8; C10)

Scheme 1: Structure of CPAV

2. 4. Characterizations

IR spectroscopy of the copolymer P(AM-co-4VP) was performed using the FTIR spectrometer SHIMATZU8300.UV-visible spectroscopy. The pyridine unit in the copolymer showed an intense absorption at 258 nm, whereas the acrylamide unit has not absorption in this wavelength region, so we can measure the composition of the copolymer by determining the content of pyridine unit in the copolymers chains using the 4VP homopolymer as standard. As the quaternary reagent, was in excess and the pyridine cationic polyacrylamide containing pyridine and alkyl bromides chains (Aldrich), with a number of carbon atoms varying (C2, C4, C8 and C10), as quaternarising reagent. Ring in the copolymer was quaternized completely (this is confirmed by H^1NMR spectra) using spectrometer Brucker Advanced AM300 with D_2O and CD_3OD, so that the mol percentage of the pyridine unit in the copolymer P (AM-co-4VP) was also the cationic degree of the cationic copolymer CPAV. The conductimetric measurements were made using a (Radiometer, Meter Lab CDM 210).

RESULTS AND DISCUSSION

Bernas and al. [14] were studied isomerization of linoleic acid over supported metal catalysts and have showed that catalyst mass affected both conversion and isomerization selectivity. Sandrine Thibaud-Dartigues [15] had been made several attempts to develop conditions to obtain a 100% conversion in the poly (styrene-co-4-[3-(chlorodibutylstannyl)-propanoxy]-styrene) synthesis. While had optimizing equivalents reagent number, varying reaction time and mass concentration polymer. In Table 1, conversion rate of PAV at different degrees of APS

Table 1: Conversion rate of PAV at different degrees of APS

APS %	0.2	0.5	1	1.5
4VP (g)	5	5	5	5
AM (g)	5	5	5	5
m(g) P(AM-co-4VP)	9.3	9.7	9.8	9.2
Conversion %	93	97	98	92

3. 1. Characterization copolymer and cationic copolymer

As the spectra of quaternized CPAV (C2; C4; C10) are similar, we were simply represented in this paper IR and ^{1}H NMR only spectrum CPAVQC8.

3. 1. 1. FTIR spectrum

FTIR spectra of P(AM-*co*-4VP) and cationic P(AM-*co*-4VP) are shown in Fig. 1. In the copolymer spectra, the intense absorptions at 3459.67cm^{-1} and 1676.8cm^{-1} were assigned to the stretching vibration of N-H and C=O of -$CONH_2$ groups. The asymmetry double peak at 1676.8cm^{-1}and 1599.66cm^{-1} came from C=N stretching vibration and the absorption peak at 1451.17cm^{-1} and 1417.42cm^{-1} arise from the C=C stretching vibration of pyridine unit. Because the unreacted monomers and the homopolymers of AM and 4-VP had been removed, the above-mentioned characteristic peaks indicated the copolymer of AM and 4VP. Comparing the FTIR spectra of cationic copolymer Fig. 2 CPAV with that of copolymer Fig. 1 PAV, it can seen that the peaks between 1417cm^{-1} and 1221.68cm^{-1} basically disappeared, whereas another peaks disappeared at 2136.14 cm^{-1} came from C=N stretching vibration and 2797.24cm^{-1} assigned to -CH_2 and CH- chains, which is assigned to the absorption of quaternarized pyridine units, showing that the pyridine ring has been quaternarized.

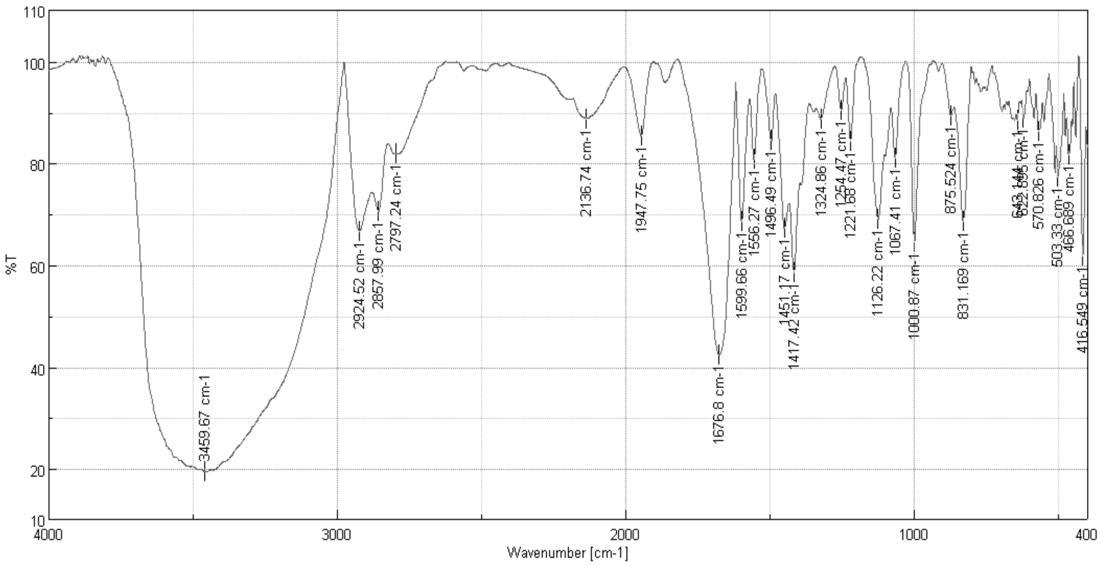


Fig.1: FTIR Spectrum of P(AM-co-4VP), APS 1%

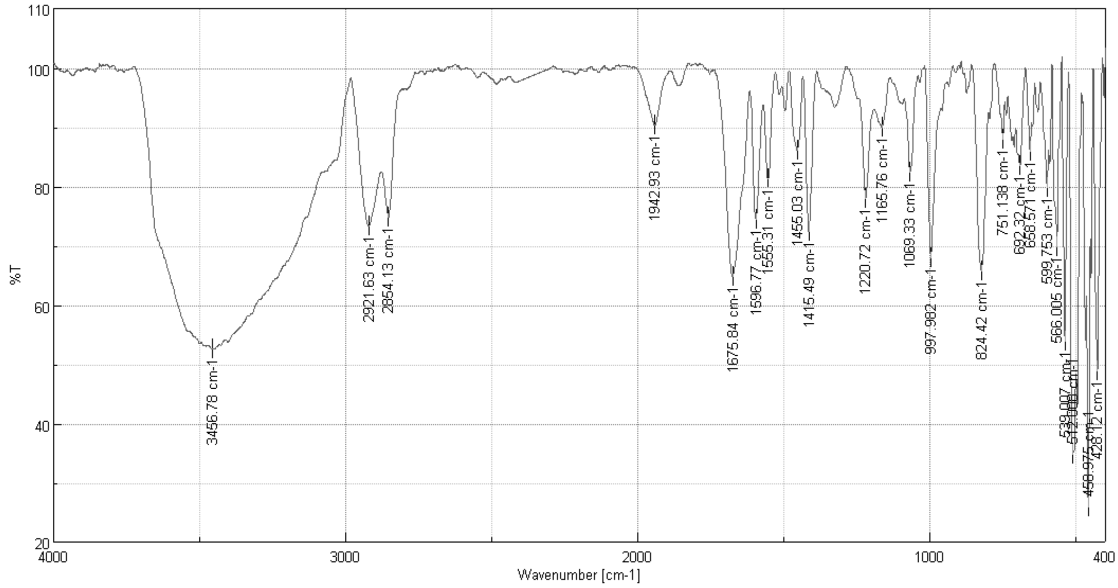


Fig. 2: FTIR Spectrum of quaternized P(AM-co-4VP), CPAVQC8

3.1. 2. ^{1}H NMR spectra

Further evidence for the quaternarization of the copolymer was obtained from the ^{1}H NMR spectra. Fig. 3, trace shows the ^{1}H NMR spectra of CPAV.

The peaks at δ = 6.55 (ppm) and at δ = 5.07 are ascribed to the proton at the 2, 6 sites and 3, 5 sites of the pyridine ring respectively. The chemical shift values are consistent with those described by Baojiao and al. (4).Comparing the ^{1}H NMR of cationic copolymer with that of the copolymer (Fig. 3), a new peaks at δ = 6.61and δ =5.17 are assigned to the proton at the 2, 6 sites and 3, 5 sites of the sequentially pyridine quaternized or not quaternized ring respectively, another peaks appears at δ = 2.86 and δ =0.31 are assigned to the fourteen protons and three protons respectively of methyl group (CPAVQC8) grafted with N atom in the pyridine ring. This result shows that the pyridine units in the copolymer were quaternized completely because of quaternary reagent being present in large excess, so that the content (mol percentage) of 4VP in the copolymer P(AM-*co*-4VP) determined by the UV spectrum method was also the cationic degree of CPAV.

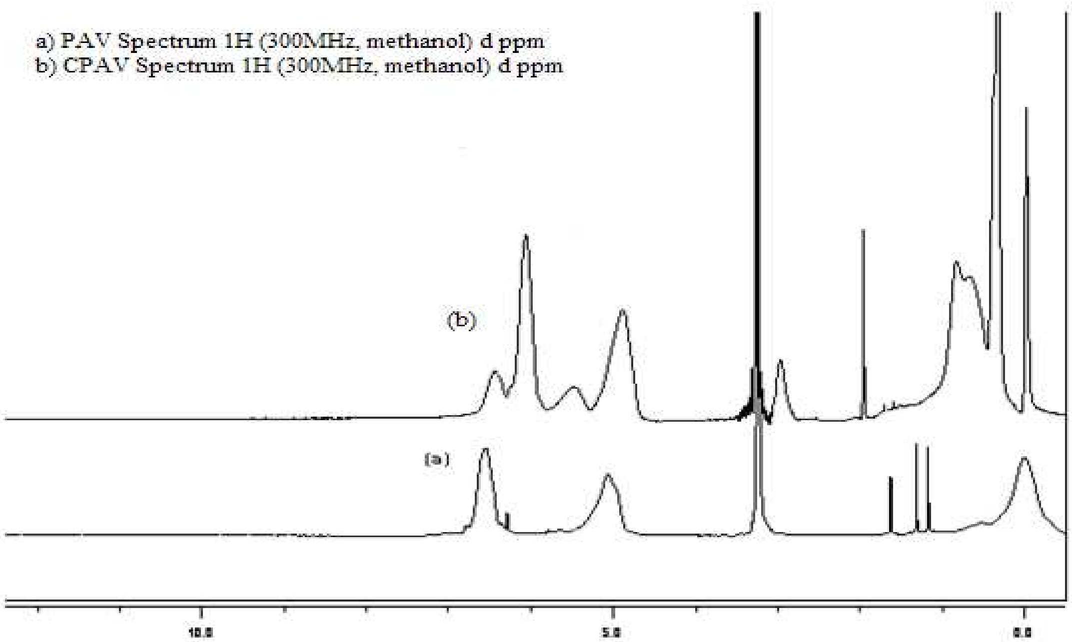


Fig. 3: ^{1}H NMR spectrum: (a) PAV; (b) CPAVQC8

3. 1. 3. Determination percentage of quaternization

During the quaternization reaction, the percentage of alkylated groups was determinated by conductimetric titration of bromide ions with $AgNO_3$ in methanol. An aliquot 1ml was taken with a pipette and diluted with 20ml of methanol. So, the alkylation was stopped and the bromide ions were titrated using a (Radiometer, Meter Lab CDM). The results Table2 of conversion rates are consistent with those cited by Damas and al. (2, 3).

Table 2: Quaternization percentage of CPAV at different degrees of APS

PAV (g/mol)	240	268	352	380
Quaternization %	60	38.91	32.64	12
Copolymers	CPAVQC2	CPAVQC4	CPAVQC8	CPAVQC10

CONCLUSION

The copolymer P (AM-*co*-4VP) of acrylamide (AM) and 4-vinyl pyridine (4VP) was synthesized by radical copolymerization, and then it was quaternarized by different alkyl bromides chains (C2, C4, C8 and C10) to produce the cationic P(AM-*co*-4VP) (CPAV). The structure and composition of P(AM-*co*-4VP) and CPAV were characterized by the FTIR and ^{1}HNMR spectra. We can measure the composition of the copolymer by determining the content of pyridine unit in the copolymers chains using the 4VP homopolymer as standard. As the quaternary reagent, was in excess and the pyridine cationic polyacrylamide containing pyridine and alkyl bromides chains by a number of carbon atoms varying (C2, C4, C8 and C10), as quaternarising reagent.

These polymers are suitable for multiple uses in metal removal, corrosion inhibitors and can be applied for environmental cleanup. The results show that a polymeric material with specific swelling properties can be obtained by proper adjustment of the optimizing equivalents reagent number, varying reaction time mass concentration polymer to be used in a specific application.

Floating microspheres have been utilized to obtain prolonged and uniform release of drug in the stomach for development of once-daily formulations. A controlled-release system designed to increase residence time in the stomach without contact with the mucosa was achieved through the preparation of floating microspheres by the emulsion solvent diffusion technique, using calcium silicate (CS) as porous carrier; (ii) Atenolol, an oral antihypertensive agent; and (iii) udragit® S as polymer [16]. The anti-solvent technique used in their study produced microcrystals that exhibited significantly faster dissolution rates than the pure Diacerin (DCN) crystals. The improved solubility and dissolution are attributable to the modification of DCN by microcrystallisation due to specific interactions between the drug and the polymers [17]. So it would be very interesting to introduce our synthesized polymer for pharmaceutical, capsule or as microsphere drug.

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