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Novel water-soluble polyelectrolytes with arsonic acid group for flocculation application

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Abstract

Novel polyelectrolytes, *o*- and *p*-methacryloylaminophenylarsonic, (*o*-MAPHA and *p*-MAPHA) in their acid and salt forms were obtained from a promising aromatic monomer class with the functional group $-AsO(OH)_2$. These were characterised and some physico-chemical properties were determined. Reduced viscosity measurements at different pH showed a minimum suggesting that macromolecules have their minimum electrostatic repulsion conformation at pH 4. The flocculation capacities of both polymers in their salt form were determined. Wastewater of the UAM-I University was used for the tests. Results are reported in terms of the residual turbidity variation versus polymer concentration and pH. Conformational changes of the polymer as a function of pH might be related to the flocculation of suspended solids in water-treatment operations. The novel polymers have advantages over other polymers, for instance 90% turbidity removal is achieved especially at low pH. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Water-soluble polyelectrolytes; Arsanilic acids; Arsonic acids

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1. Introduction

Water-soluble polymers have shown many interesting properties leading to a wide variety of industrial and environmental applications. For example, the water-soluble polymeric materials are used in areas such as paper products, film coating, membranes and flocculation [1–3].

Water-soluble macromolecules can be considered among the most efficient flocculants in water clarification, mainly with industrial and municipal wastewater. There are two possible mechanisms for the induced coagulation and flocculation phenomena of polyelectrolytes. One is attributed to particle bridging and the other to neutralisation of particle surface charge. The addition of polyelectrolytes with opposite charge to suspended particles can cause flocculation due to charge neutralisation [3–5]. The presence of ionic groups in the macromolecules makes them particularly suitable for flocculation purposes.

Therefore, it is important to prepare new polymeric structures with the ability to flocculate and precipitate a vast number of different cationic colloidal species in today's wastewater treatment.

Free radical polymerisation of monomers with methacryloyl moieties is a convenient way to obtain oligomers of linear homopolymers with arsonic acid groups $-AsO(OH)_2$ attached. The polymers produced may have striking features, which come from the union of the properties of $-AsO(OH)_2$ arsonic group embedded in a polymeric matrix. Such polymers have polyelectrolytic properties due to the presence of arsonic acid ($-AsO(OH)_2$) groups. Besides, $-AsO(OH)_2$ group is known as an excellent chelating agent in analytical chemistry for heavy metal atoms.

Hirsch et al. [6] have reported highly selective ion-exchange resins based on polystyrene–divinylbenzene, chemically modified to contain arsonic acid groups $-AsO(OH)_2$ as the ion-exchanging site and which find use in diverse analytical procedures. The arsonic acid resins showed an enhanced selectivity to metal cations in the order $Mg^{2+} < Ca^{2+} < Mn^{2+} < Co^{+2} < Ni^{+2} < Zn^{+2} < Cu^{+2}$.

On the other hand Fritz et al. [7] have reported $-AsO(OH)_2$ resins for the concentration and separation of trace metal ions from hard water and seawater. The effects of pH and complexation sites on the recovery of metal ions were studied.

In particular, benzenearsonic acid [8] and its analogues react with various metal ions at different pH to form

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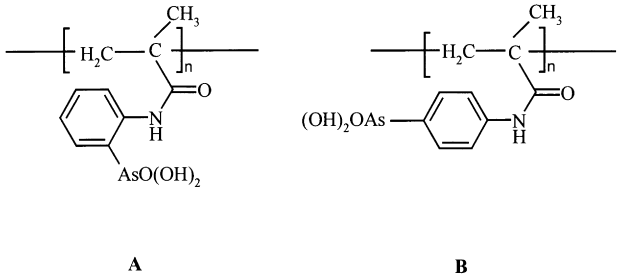

A B

Fig. 1. Structures of the synthesised polymers (A) *o*-MAPHA and (B) *p*-MAPHA.

precipitates. The precipitation is often quantitative and the arsonic acid group acts as a bidentate ligand. It is possible to precipitate a selected metal ion by adjusting the pH.

In this paper we report the synthesis, characterisation and some physico-chemical properties of water-soluble polyelectrolytes in their acid and salt forms. The polymerisation of *o*- and *p*-methacryloylaminophenylarsonic acid (*o*-MAPHA and *p*-MAPHA; Fig. 1) was carried out via free radicals. The reduced viscosity behaviours of the homopolymers were studied as a function of pH and were related to chain expansion and to their flocculation capacity of suspended solids. The efficiencies of turbidity removal for both *o*-MAPHA and *p*-MAPHA are also reported.

Jar-test is an extremely useful technique for determining parameters such as flocculant optimum dosage, sample volume, initial turbidity, stirring speed, floc time and the effect of chemical conditions (ionic strength, pH) in the flocculation process. Jar-test is also used for non-ionic, cationic and anionic polymeric flocculants [9–11].

2. Experimental

2.1. Monomer preparations

The monomers *o*-MAPHA and *p*-MAPHA acids were obtained by condensation reaction of methacryloyl chloride with the corresponding *o*- and *p*-arsanilic acids (*o*- and *p*-aminobenzenearsonic acid; 4- and 2-aminophenylarsonic acid), [2045-00-3] and [98-50-0], according to known procedures [12].

2.2. Polymer preparations

The monomers *o*-MAPHA and *p*-MAPHA acids were polymerised in DMF, using AIBN as the initiator. Argon gas was bubbled inside a glass ampoule containing the monomer, solvent and initiator. The ampoule was sealed with argon gas inside and placed in a constant temperature bath at 70°C for 3 h. Initial concentrations of monomer and initiator were 0.2 and 10^{-3} mol/l, respectively. The polymers were recovered in both cases by precipitation in ethyl ether and were dried at 50°C for 24 h. The polymers *o*-MAPHA and *p*-MAPHA were obtained with a 68.0 and 97.1% yield, respectively. In a similar way, the polymerisation of the monomers in their sodium salt form was carried out using $K_2S_2O_8$ as the initiator in water at 70°C for 3 h.

The polymers in their sodium salt form can also be obtained by the reaction of the poly(*o*-MAPHA and *p*-MAPHA) in their acid form with NaOH in 1:2 weight relation and using 1 ml of water. The polymers were obtained by re-precipitation with acetone followed by drying under vacuum for 12 h at 50°C to get rid of moisture.

2.3. Polymer characterisation

Homopolymer characterisations were carried out by spectroscopic methods. The infrared spectra were measured by using potassium bromide pellets and recorded on a Nicolet Magna model 750 IR spectrophotometer. ^{1}H NMR spectra (DMX 500 Bruker Instruments) were recorded using 5–10 wt% aqueous (D_2O) polymer solutions. Molecular weights of the polymers were determined with a vapour pressure osmometer (UIC model 070) using calibration curves of benzyl/DMF or urea or NaCl/H_2O.

2.4. Viscosity measurements

Viscosities were determined with a modified Ubbelohde viscometer. Polymer solutions were filtered with a Millipore 0.45 μm filter into the viscometer. The concentration used was 0.5 g/dl. Viscosity measurements were carried out at 25 ± 0.02°C, varying the pH in the 2–10 range. Titrations and pH values were recorded by a Metrohm 716 DMS meter.

2.5. Flocculation measurements

Flocculation properties of the synthesised polyelectrolytes were determined by measuring their capacity to separate suspended solids from wastewater as the polymer is added, using a jar-testing device and following the ASTM-D2035 procedure. Wastewater from the UAM-I University treatment plant was used for the flocculation experiments. The main properties of the UAM-I wastewater treatment plant are turbidity, 18–90 nephelometric turbidity units (NTU); pH, 8.2 ± 0.3; chemical oxygen demand (COD), 333 ± 99 mg/l; and volatile suspended solids (VSS), 40 mg/l.

Tests were carried out by placing 1 l samples in glass jars. The pH was then adjusted (2, 4, 6, 8 and 10) using a 2 M sodium hydroxide solution or 2 M sulphuric acid at room temperature. The polymer dosage of 5 mg/l was added and then the solution was briskly stirred at 120 rpm for 1 min followed by slow-speed stirring at 30 rpm for another 20 min according to the ASTM-D2035 standard. Turbidity measurements in NTU were made on samples after 20 min sedimentation time. The tests were also carried out for different polymer dosages (between 1–5 mg/l) at constant pH.

Turbidity measurements were made in a 2100P Portable Turbidimeter (Hach) with an accuracy of ±2%. In all cases results from at least two measurements were reported.

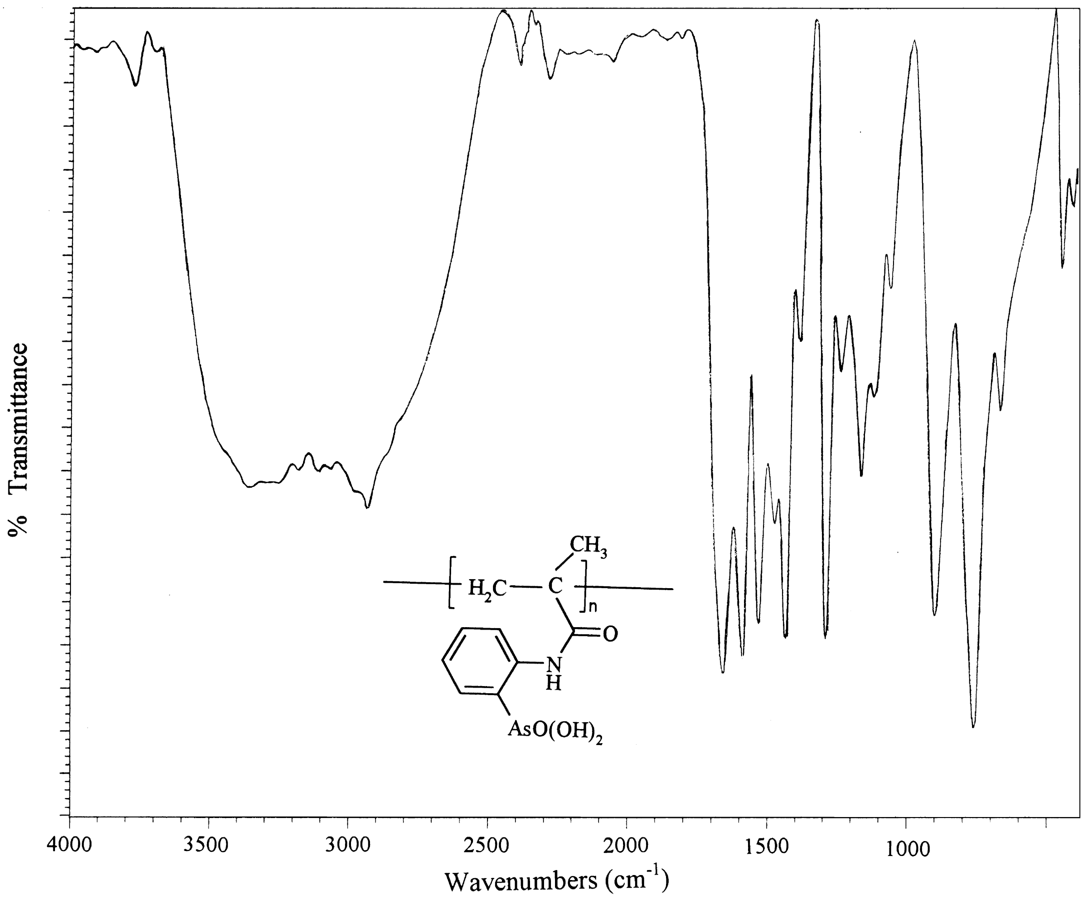

Fig. 2. IR spectrum of polymer *o*-MAPHA in the acid form.

3. Results and discussion

The IR spectrum shows that *o*-MAPHA (Fig. 2) and *p*-MAPHA homopolymers have similar absorption values (values in parentheses are for *p*-MAPHA). The strong and broad band at 2995 (2928) cm^{-1} is assigned to the O–H bond deformation. As=O stretching bands are observed at 1062 (1094) cm^{-1} [13,14]; the C=O stretching band of amide I at 1681 (1661) cm^{-1}; and peaks characteristic of the amide II bands at 1535 (1513) cm^{-1} (–CONHR functional group). The absorption bands at 1163, 1123 (1245, 1183, 1154) cm^{-1} are assigned to the $-AsO(OH)_2$ group [15].

^{1}H NMR spectra of *o*-MAPHA and *p*-MAPHA homopolymers as their sodium salts were recorded. Fig. 3 shows the spectrum corresponding to the Na salt of *o*-MAPHA polymer. The principal evidence of *o*-MAPHA and *p*-MAPHA (values in parentheses are for *p*-MAPHA) homopolymer formation comes from multiplets at 2.61 (2.65) ppm assigned to protons of CH_2 and at 1.80 (1.80) ppm for the CH_3 group of the polymeric chain, as well as the aromatic protons at 8.08, 7.64, 7.54 (7.91, 7.87) ppm.

The number-average molecular weight (M_n) and the second virial coefficient (A_2) obtained from vapour phase osmometry measurements are presented in Table 1. Homopolymers obtained from *o*- and *p*-MAPHA monomers, both in their sodium salt and acid forms, had approximately the same low molecular weight. The values of M_n show that the synthesised products are oligomers of low molecular weight. The *o*-MAPHA polymer has the larger molecular weight.

For compounds similar to the water-soluble polyelectrolytes based on methacryloylaminobenzoic acids, it was found that the solvent used in the polymerisation hindered the formation of high molecular weight products by hydrogen bond interaction. This was due to the fact that an *ortho*-isomer tends to form a planar six-membered cycle whereas the *para*-isomer forms dimers with eight-membered rings [16]. The presence of intra- and inter-molecular hydrogen bonds was determined for methacryloylaminobenzoic acids by IR spectroscopy and viscometry [17].

The formation of low molecular weight products might be attributed to the influence of the solvent on the rate of polymerisation i.e. to the interactions (e.g. hydrogen-bond formation) between the solvent and the newly formed polymer [18].

As it is known, A_2 is a measure of the interaction between

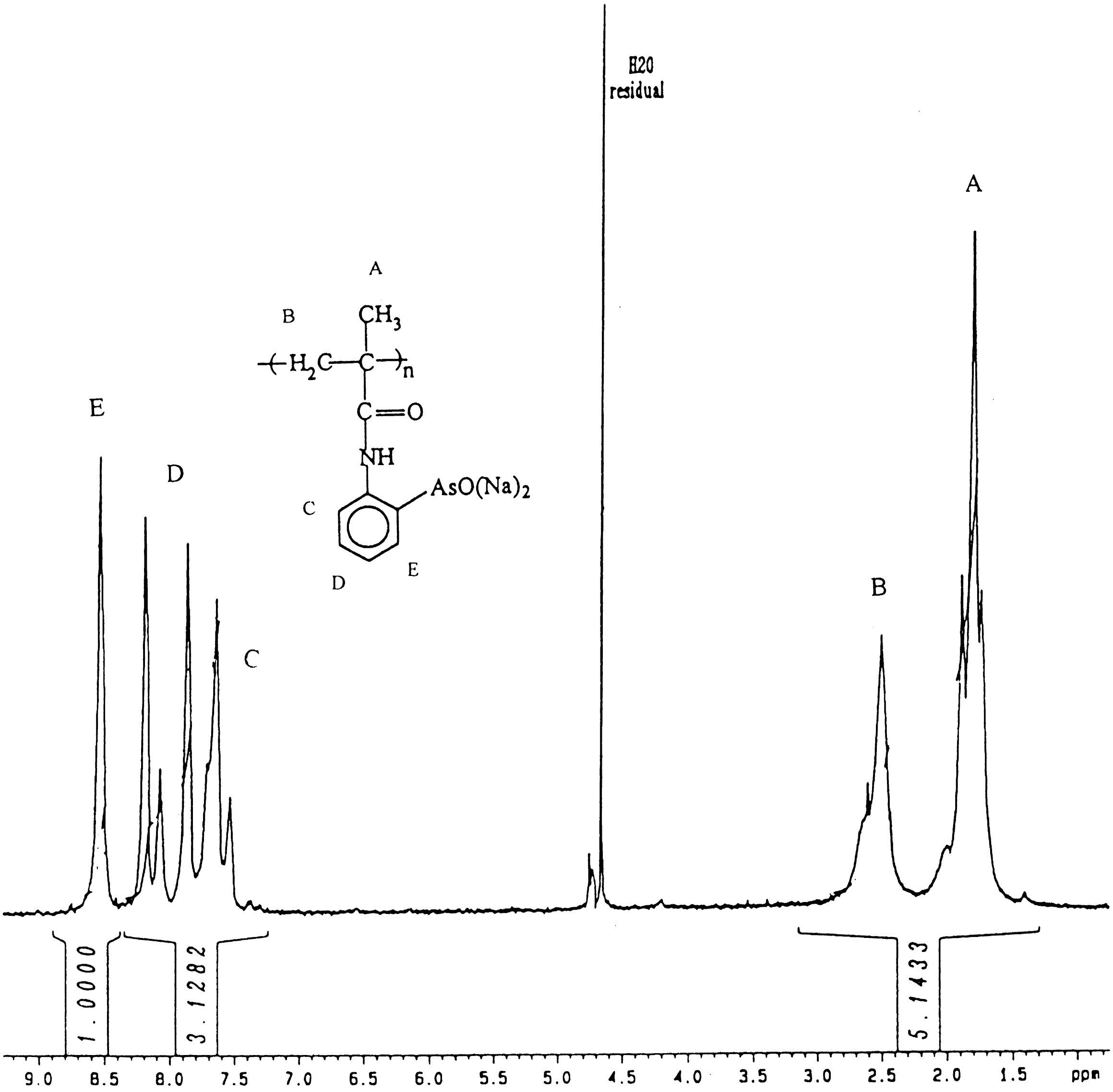

Fig. 3. ^{1}H NMR spectrum of Na salt of *o*-MAPHA polymer.

the solvent and the polymer and is a function of several variables (molecular weight, molecular weight distribution of the polymer and the molecular shape of macro-ions). It is generally accepted that for A_2 values greater than 10^{-2} the solvent is a "good solvent". The results for *o*- and *p*-MAPHA suggest that water is a "good solvent" for these polymers.

Table 1
Number-average molecular weight (M_n) and second virial coefficient (A_2) data for the obtained compounds

Compound	M_n (g/mol)		A_2 (l mol/g^2)
	Calculated	Experimental	
o-MAPHA monomer	285.13	294.68	–
o-MAPHA monomer salt	329.09	330.75	–
o-MAPHA polymer	1711.8	1790.1	0.028
o-MAPHA polymer salt	2054.1	2228.0	0.068
p-MAPHA monomer salt	–	335.5	–
p-MAPHA polymer salt	987.2	998.6	0.057

3.1. Flocculation measurements

Fig. 4 illustrates the removal efficiency (%) as a function of polymer concentration at pH 2 and with an initial turbidity of 29 NTU. Removal efficiency depends on the dosage of the two polymers, because removal of suspended solids increases with the increase in polymer concentration (1–5 mg/l) at pH 2. This result also indicates that both polymers reach turbidity removal efficiencies between 60 and 80% with the *o*-MAPHA showing higher flocculation capacity. The use of flocculant should be limited to 5 mg/l as the maximum concentration in order to reduce or completely eliminate the flocculant from the solution. This is

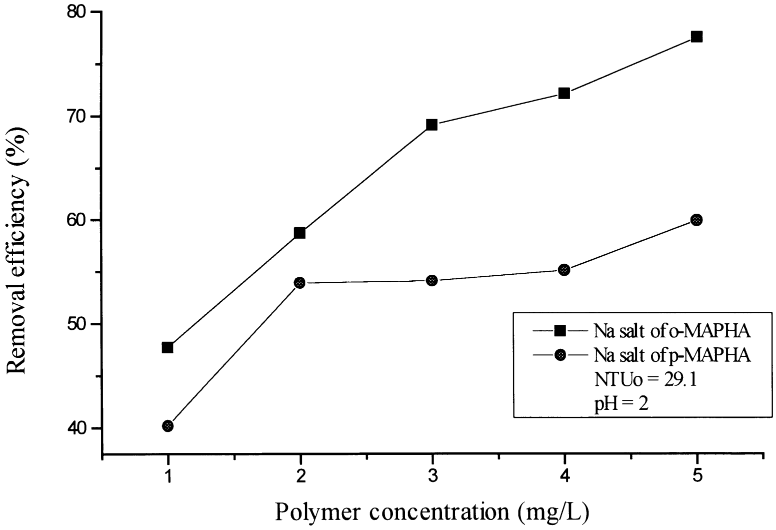

Fig. 4. Removal efficiency (%) as a function of polymer concentration at pH = 2.

because not all the flocculant is precipitated and its presence may cause inconvenient problems in downstream process steps.

It has also been observed that flocculation efficiency depends strongly on solution pH, because a considerable chain expansion might occur in the macromolecules, as detected by reduced viscosity measurements. Fig. 5 shows the solids removal efficiency (%) as a function of pH with a polymer concentration of 5 mg/l. The highest efficiency (about 80%) is observed with *o*-MAPHA at pH 2. Removal efficiency decreases as pH increases for the polymers up to a pH of 4 and then it has a moderate increment. Polymer *p*-MAPHA shows lesser removal efficiency than *o*-MAPHA at pH = 2. Further, both *o*-MAPHA and *p*-MAPHA polymers have the lowest removal efficiency at pH 4 because of coil compactness.

The results in Figs. 4 and 5, for domestic wastewater, show values for removal efficiency at pH 2.0 and polymer dosage of 5 mg/l. Nevertheless, it was found in the literature that the optimal dosage of the polymer flocculant for cleaning wastewater effluent from colloids that cause turbidity should be in the range of 1–2 mg/l [3,23]. If the experimental conditions are changed by increasing the polymer molecular weights, then functional groups will be increased and the performance will most certainly be greatly enhanced.

Fig. 6 shows the removal efficiency for two different initial turbidities NTU levels with the polyelectrolytes

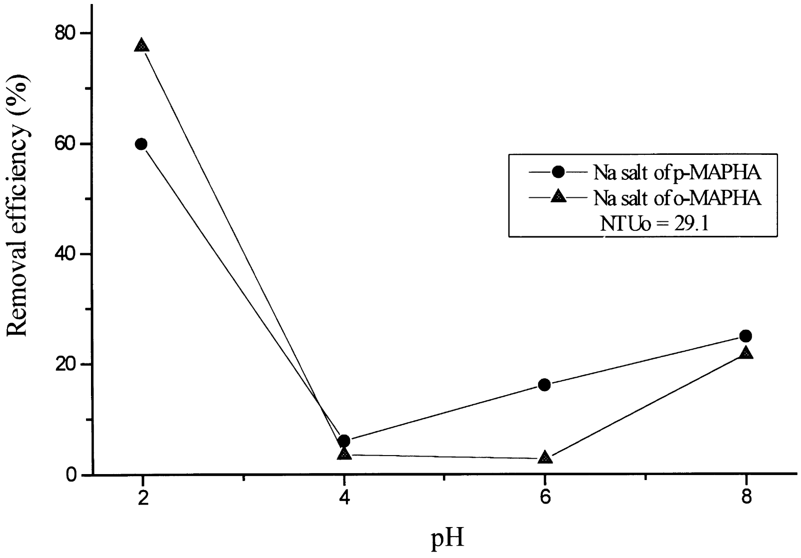

Fig. 5. Removal efficiency (%) as a function of pH for a polymer concentration of 5 mg/l and initial turbidity of 29.1 NTU_0 (initial nephelometric turbidity units).

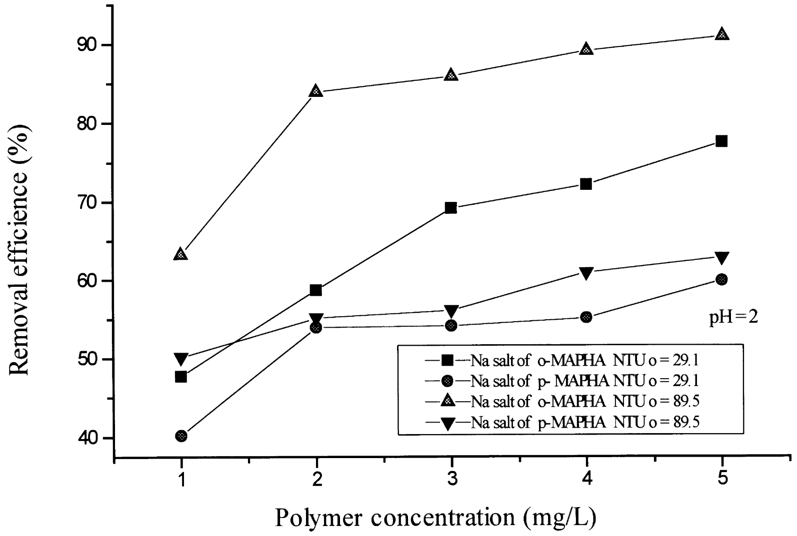

Fig. 6. Comparison between *o*-MAPHA and *p*-MAPHA for total solids removal efficiency versus polymer concentration a different NTU_0 at $pH = 2$.

o-MAPHA and *p*-MAPHA in solution at pH 2. It can also be observed that polymer *o*-MAPHA has a higher capacity for removal of suspended solids (up to 90%) in comparison to *p*-MAPHA for the same dosage of 5 mg/l and at initial turbidity of 89.5 NTU. The different flocculation behaviour of *o*-MAPHA and *p*-MAPHA isomer at the conditions mentioned suggests that different electric charges interactions exist throughout the polymeric chains making the chain expansions different for both polymers. The difference can also be associated with the difference in their molecular weights.

3.2. Viscosity measurements

Viscosity measurements were carried out to confirm conformational changes in the polymers and relate them to the removal efficiency. The pH strongly influences the properties of polyelectrolytes in solution, as pH determines the degree of dissociation of a given ionic group and thus the polyelectrolytes' actual charge density. The effect is very clearly noticeable when one plots η_{spec}/c versus pH. A change in conformation is usually indicated by a more or less abrupt change of the viscosimetric quantity [19].

The effect of the pH versus reduced viscosity of homopolymers was studied. Measurements were made at different pH values (2, 4, 6, 8 and 10) in deionised water as shown in Fig. 7. Also the viscosity increment at $pH = 2$ is observed and can be attributed to chain expansion caused by intramolecular coulombic repulsion of the cations. Similarly, at high pH ($pH > 6$), chain expansion is also attributed to the coulombic repulsions of the negatively charged groups.

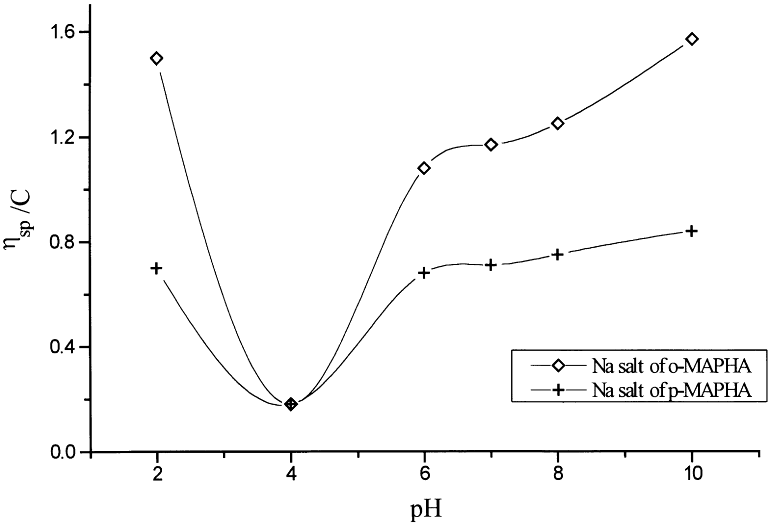

Fig. 7. Reduced viscosity profiles of both homopolymers as a function of pH.

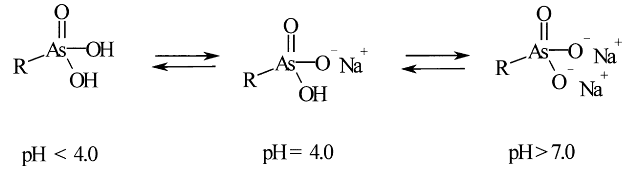

Fig. 8. Two-step dissociation process in arsonic acid group $-AsO(OH)_2$ for *o*-MAPHA and *p*-MAPHA homopolymers.

Charge–charge repulsions of these groups cause an extension of the polymers coil. Hence the reduced viscosity (η_{spec}/c) reaches two maximum values at pH = 2 and 10.

In deionised water both homopolymers exhibit a minimum on the reduced viscosity at pH = 4. As a result of the conformational changes during acid–base titration, homopolymers (in their salt form) undergo a polyanion → polyzwitterion → polycation transition upon lowering of pH. This arises from protonation of the arsonate groups in the homopolymers [20]. Viscosity response is similar to that of naturally occurring proteins and the synthetic copolymers of *N*,*N*-diethylallylamine and acrylic acid [21]. This allows us to propose different dissociation structures at different pH (Fig. 8).

The dissociation constants of the ionogenic groups in the monomers and polyelectrolytes *o*-MAPHA and *p*-MAPHA were measured and are presented in Table 2. One can observe a two-step dissociation process of the arsonic acid group. The pK_as of the polyelectrolytes were less than those of the monomers, as one might expect.

The results of viscosity as well as osmometric measurements indicated that *o*-MAPHA has a higher molecular weight than *p*-MAPHA.

The dissociation of polyelectrolytes in solution leads to a large repulsive force among charged groups, giving rise to a greatly expanded conformation. Gregory [22] reports that charge neutralisation was the main mechanism for flocculation by low molecular weight polyelectrolytes. On the other hand polyelectrolytes are able to flocculate colloidal particles due to adsorption. In most cases, the bonding mechanism between a functional group on the polymers and a site on the colloid surface is quite specific. In addition, molecular weight and degree of branching of the polymers play a mechanistic role in their ability to flocculate [23]. According to the described experimental results, it seems that variations of the chain expansion with pH play an important role in flocculation processes.

Table 2
pK_a values of *o*-MAPHA and *p*-MAPHA homopolymers

Compound	pK_1	pK_2
o-MAPHA monomer	3.28	7.67
p-MAPHA polymer	4.00	9.02
o-MAPHA homopolymer	5.40	8.26
p-MAPHA homopolymer	7.37	9.56

4. Conclusions

The water-soluble low molecular weight products or oligomers *o*-MAPHA and *p*-MAPHA in their acid and salt forms have been prepared by free radical polymerisation and their characterisation was successfully carried out. Such compounds behave as polyelectrolytes due to the presence of the $-AsO(OH)_2$ pendant arsonic group in the polymer chain, as was shown. An important aim of obtaining polymers with these arsonic groups was to test them as flocculants in sewage water treatment. The removal efficiency (%) flocculation studies versus polymer dosage at pH 2 show that *o*-MAPHA polyelectrolyte in the salt form is more effective than *p*-MAPHA as a flocculant for reducing suspended solid levels in the UAM-I University wastewater. However in the same conditions, *p*-MAPHA could remove less suspended solids. Reduced viscosity measurements versus solution pH of the homopolymers can be associated with the polymer chain expansion or polymer conformational changes because the coil expansion is closely related to the pH variations. The flocculation measurements are obviously related to the pH as it has been shown previously. But if one tries to relate the results of the pH variation versus the viscosity with flocculation, one believes that there might be a relation of polymer coil expansion to flocculation. We are convinced that molecular weight increment is an important factor in order to increase flocculation, because the available number of arsonic groups will be augmented in the whole of the macromolecule. We are also convinced that the polymers of *o*-MAPHA and *p*-MAPHA are very good flocculants.

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