Polym. Bull. (2011) 67:441–453
DOI 10.1007/s00289-010-0393-8

ORIGINAL PAPER

Water-soluble copolymers in conjunction with ultrafiltration membranes to remove arsenate ions

Bernabé L. Rivas · María Carmen del Aguirre

Received: 25 July 2010 / Revised: 3 October 2010 / Accepted: 17 October 2010 /

Abstract Water-soluble polymer poly[3-methacryloylamine)propyl)trimethyl ammonium chloride, P(ClMPTA) and the copolymer with 4-vinyl pyridine, poly [(3-methacryloylamine)propyl) trimethylammonium chloride-*co*-4-vinyl pyridine], P(ClMPTA-*co*-4VP) were synthesized by radical polymerization, at different feed mole ratios ClMPTA:4VP 1:1, 1:2, and 2:1. The copolymer compositions were determined by FT-IR and H-NMR spectroscopy and analyzed by TG-DSC. The liquid-phase polymer-based retention (LPR) technique was used to study the water-soluble polymers' arsenic removal properties. The solution's conductivity properties were evaluated at different pH. The copolymers can bind more selectively divalent anionic arsenic species from an aqueous solution (pH 8 $\geq$ pH 6 $>$ pH 4). Assays for the mol ratio copolymer: As(V) 75:1, 37.5:1, 20:1, 10:1, and 5:1 at arsenic concentrations of 10 and 37.5 ppm were carried out. Apparently, the behavior of the copolymers with the solution's pH was similar to pure cationic homopolymer; however, when the retention capacity was expressed as real mass of quaternary ammonium comonomer, the retention values were enhanced for lowest mol ratio 10:1 and 5:1. The retention capacity of exchanger with quaternary ammonium group was improved in presence of a weak base 4-vinyl pyridine comonomer, differently to the behavior showed by those copolymers of ClMPTA with acrylic acid groups as comonomer.

Keywords Water-soluble polymers · Radical polymerization · Membranes · Arsenate separation

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B. L. Rivas (✉) · M. C. del Aguirre
Department of Polymers, Faculty of Chemistry, University of Concepción,
Casilla 160-C, Concepción, Chile
e-mail: brivas@udec.cl

M. C. del Aguirre
Famaf-Science Materials Group, Cordoba National University, Cordoba, Argentina

Introduction

Arsenic is recognized as a micronutrient essential, although its presence, especially As(V), in amounts exceeding the desired level can be detrimental to plant, animal, and human life [1]. Natural processes, such as weathering rocks and volcanism, and iron-ore mine areas, release arsenic into the environment [2]. Human-caused arsenic source [3] includes petroleum refining, thermal power plants, pesticides, ceramics, gold-mines, and fertilizer production. Most research [4–7] has been focused to the control of arsenic contamination of domestic water, where arsenate and arsenite are the primary forms in natural waters. The biological availability as well as the physiological and toxicological effects of arsenic depends on the oxidation state. The As(V) form is less toxic than that As(III). According to the United States Environmental Protection Agency (EPA), the maximum level for drinking water is 10 μg/L [8].

Numerous models have been developed to retain arsenic from water. In hetero-phase form, the ion-exchange and surface complexation model have been proposed. Most of the adsorption data on inorganic oxides has been explained using the surface complexation model [6, 8–10]. On the other hand, the excellent ion-exchange property of organic polymers is also widely recognized [11]. Most recently, the newly discovered hybrid polymeric/inorganic sorbents [12, 13] have shown to improve the retention properties for the different oxidation states of arsenic ensuring selectivity to As(V) and As(III).

However, conventional hetero-phase systems have been successful to remove contaminants from water. Still, environmental decontamination requires finding and implementing potentially useful new materials and methods that have low operating costs and that would be appropriate to the specific conditions of each region in particular. Ultrafiltration and water-soluble polymers are promissory techniques to decontaminate aqueous media [14, 15]. These water-soluble polymers offer low operating costs, without mass transfer problems or diffusion limitations.

Considering our previous study by using polymers containing ammonium groups to remove arsenic(V), the aim of this manuscript is to study through the liquid-phase polymer based retention, LPR, technique the arsenic removal properties of water-soluble copolymers including pyridine groups at the copolymer structure. A study of polymer mol concentration on retention activity is carried out at constant pH where the arsenic species coexist with certain preference of divalent form.

Experimental part

Reagents

[3-Methacryloylamine)propyl)trimethyl ammonium chloride (ClMPTA), (Aldrich) was used as received. 4-vinyl pyridine, (4VP), (Aldrich) was purified by distillation. Ammonium persulfate, (AP, Aldrich) was used as initiator of polymerization (46 mM of $Na_2HAsO_4 \cdot 7H_2O$ solution (Merck)).

Synthesis of homopolymer

Poly[3-methacryloylamine)propyl)trimethyl ammonium chloride, P(ClMPTA) was synthesized by radical polymerization as previously described [16]. In an inert atmosphere, 0.027 mmol of monomer (ClMPTA) and 1.4 mmol of AP were dissolved in 40 mL of water. The reaction was kept at 70 °C under nitrogen for 24 h. The products are soluble in water and lyophilized. The polymerization yield was 97.2%. The product is dissolved in water, purified by ultrafiltration membrane, and fractionated by ultrafiltration membranes with different exclusion limit of molecular weights (10,000, 30,000, 50,000, and 100,000 g mol^{-1}). The different fractions were characterized by FT-IR and ^{1}H-NMR spectroscopy as well as TG-DSC. The ^{1}H-NMR spectra of monomer ClMPTA and homopolymer P(ClMPTA) were comparatively analyzed. In the ^{1}H-NMR spectrum of P(ClMPTA), the absence of the signal at 5.44 and 5.68 δ (ppm) corresponding to H^1 of double bond indicated that the polymerization of the ClMPTA monomer has occurred.

Copolymer preparation

Poly[(3-methacryloylamine)propyl)trimethylammonium chloride-*co*-4-vinyl pyridine], P(ClMPTA-*co*-4VP) was prepared by radical polymerization at different feed mol ratios, 1:1, 1:2, 2:1, respectively. Ammonium persulfate at 1 mol% was used as initiator with water as unique solvent. The reaction was kept at 70 °C for 24 h. The products are soluble in water and lyophilized. The polymerization yield is 99%. Then, the copolymers were purified and fractionated by ultrafiltration membranes as above described. The major fraction yield was 100,000 g mol^{-1}, and this fraction was characterized and used for the LPR experiments.

Liquid-phase polymer-based retention, LPR, procedure

This is a batch-like method where an aqueous solution containing the water-soluble polymer poly[3-methacryloylamine)propyl)trimethyl ammonium chloride, P(ClMPTA) or poly[(3-methacryloylamine)propyl) trimethylammonium chloride-*co*-4-vinyl pyridine] P(ClMPTA-*co*-4VP), and the anion arsenate to be separated are placed in the ultrafiltration cell at a given pH and ionic strength. This is then washed with an aqueous solution contained in the reservoir that may reproduce the same pH and ionic strength values. Conditions may be found at which the ions of interest are retained and other species are removed. The washing method can also be applied to purify a macromolecular compound by eliminating the microsolutes.

By dilution or washing method 0.2 mmol in the range of over 100,00 g mol^{-1} polymer fraction are dissolved in twice-distilled water and the solution containing 0.01 mmol of arsenic is added to the cell solution. The solutions are brought to 20 mL of total volume, and the pH is adjusted by adding 0.1 M NaOH or 0.1 M HNO_3. It is a batch-like method where the washing proceeds only with water at the same pH and ionic strength or proceeds with water at the same pH but variable ionic strength. The washing water in the reservoir is at the same pH value of the cell. Filtration runs are performed under a total pressure of 3.5 bar by using a ultrafiltration membrane with an exclusion rating of 10,000 g mol^{-1}. The total volume is kept constant at 20 mL during the run. The pH is increased by addition of 0.1 M NaOH up to pH 8 or decreased by addition of 1 M HCl up to pH 4. At the first time the by-pass valve act on pass of N_2 gas to the cell, then it is put in liquid form. Simultaneously, in ultrafiltration cell is making a siphon to achieve a constant pass of water. Fractioning of 20 mL are collected by filtration and the metal ion concentration analyzed by AAS.

Measurements

Arsenic concentration is measured in the filtrate by atomic absorption spectrometry by a Perkin Elmer 3100 spectrometer, the quantity retained is determined from the difference with the initial concentration. The Fourier transformed infrared (FTIR) spectra were recorded with a Magna Nicolet 550 and Nexus Nicolet spectrometers. To quantitative analysis, 1 mg of the sample per 100 mg KBr was employed and a total of 145 accumulative scans were applied in the range 1300–1750 cm^{-1}.

The NMR spectra are recorded with a multinuclear Bruker AC 250 spectrometer at 250 MHz, room temperature, and D_2O as solvent. The thermal behavior under N_2 is studied by thermogravimetric analyzer using Polymer Laboratories equipment with a heating rate of 10 °C min^{-1} and sample weight of 2–4 mg.

Measurements of electrolytic conductivity at 25 °C were carried out with a model 4310 conductivity meter. Conductivity assays were performed by measuring the specific conductance (κ, μS/cm). The calibration was made with a standard 0.01 N KCl solution, ($\kappa = 1413$ μS/cm, at 25 °C). As conductivity is dependent of temperature, all samples are immersed in a thermostatic water bath. Samples used for the experiments were: P(ClMPTA) and P(ClMPTA-*co*-4VP) of 100,000 g mol^{-1}, with the solution's concentration of 0.01 M.

Results and discussion

The [1] H-NMR spectra of P(ClMPTA-*co*-4VP) copolymers corroborated the structures (see Fig. 1a, b, c).

The spectrum of P(ClMPTA) showed the signal near to 1 ppm attributed to $–CH_3$ group and the signal at 3.14 ppm corresponding to 9 H^1 of $–CH_3$ of coming from quaternary ammonium group and for the 4VP moiety were showed signals corresponding to two protons at *meta*- and *ortho*-positions of the aromatic ring at 7.44 and 8.26 ppm, respectively. The vinyl protons of main chain, 1.64–2.06 ppm corresponded to the H^1 of $(–CH_2)$ group, and the signal at 2.379 ppm corresponded to H^1 of (–CH) group. The signal at 4.979 ppm corresponds to the protons of D_2O/H_2O. Since the proton type from both homopolymers: 3.14 ppm and 7.44 or 8.26 ppm absorbed in different regions, the copolymer composition could be determined from the spectra by comparing the proton integration ratio areas. However, other methods were also included (see Table 1).

The FT-IR studies were carried out in the range 400–4000 cm^{-1} for homo- and copolymers. They were analyzed for the range 1800–400 cm^{-1}, where the more

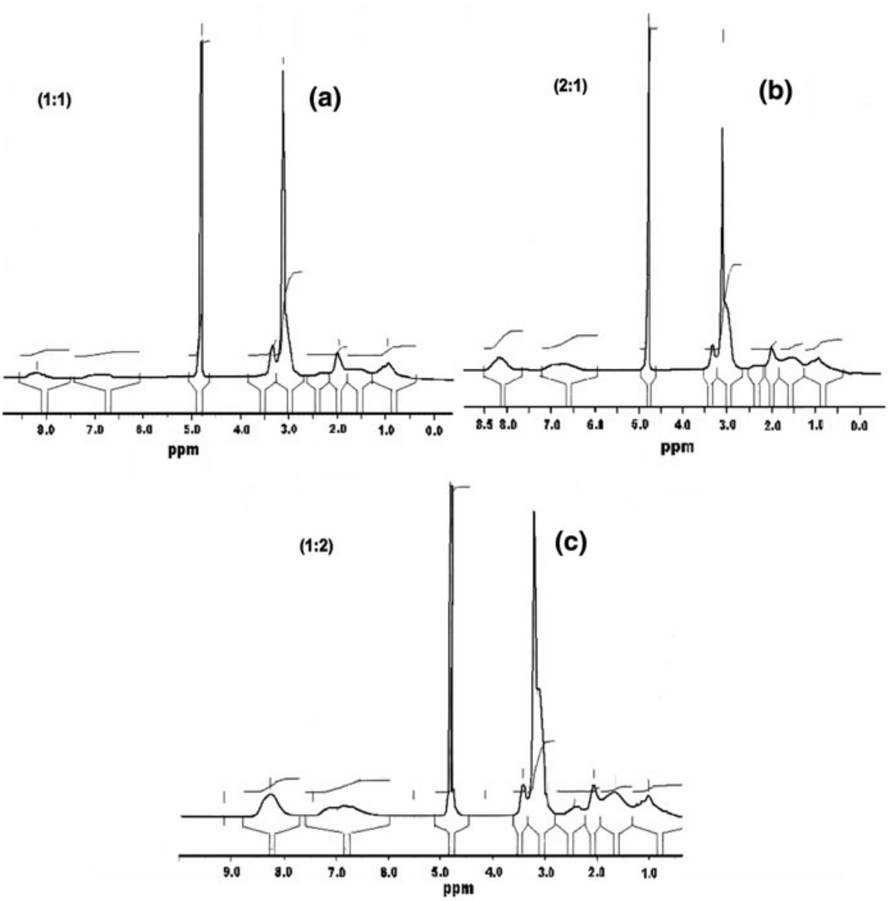

Fig. 1 ^{1}H-NMR spectra, 250 MHz, D_2O of **a, b**, **c** poly[(3-methacryloylamine)propyl) trimethyl ammonium chloride-*co*-4-vinyl pyridine], P(ClMPTA-*co*-4VP), 1:2, 2:1, and 1:1, respectively

Table 1 Mol composition of copolymers P(ClMPTA-*co*-4VP) determined by FT-IR and ^{1}H-NMR spectroscopy

Sample	Feed monomer ratio	FT-IR	^{1}H-NMR	TG (wt%)	
				237–325 °C	325–550 °C
P(ClMPTA)	–	–	–	45	35
P(4VP)	–	–	–	83	
P(ClMPTA-*co*-4VP), 1:1	1:1	1:1.19	1.40:1	46	30
P(ClMPTA-*co*-4VP), 1:2	1:2	1:1.92	1:1.90	54	26
P(ClMPTA-*co*-4VP), 2:1	2:1	2.4:1	2.0:1.0	41	36

Weight loss determined by TG

characteristic peaks are found. The stretching modes of pyridine rings on P(4VP) (in cm^{-1}) can be observed at 1603, 1417, 999, and 619. These absorption bands are characteristics and show different behavior when the pyridine rings are hydrogen bonded [17–19]. Pure P(4VP) [17, 18] has an absorption band at 1597 cm^{-1}, and it shifts to 1603 cm^{-1} by hydrogen bonds. The band at 1415 cm^{-1} should shift approximately 5 cm^{-1} by hydrogen bond formation and for the fully complexed case, this peak is observed to shift at 1421 cm^{-1}. In the case of protonation and coordination bonding, the shifts can be 20 and 40 cm^{-1}, respectively. The spectrum of P(ClMPTA) showed the following most characteristic absorption bands (in cm^{-1}): 1641 ν(C=O), 1486 $\delta(-N^{+}(CH_3)$, 1532 coupling of ν(C–N) and δ(N–H).

The FT-IR spectra for the copolymers show the most important absorption bands (in cm^{-1}) at: 1646, ν(C=O) of amide group, 1486 $\delta(-N^{+}(CH_3))$, 1604, 1419 and 1003, stretching modes of pyridine rings. The peaks at 1486 cm^{-1} of P(ClMPTA) and 1419 cm^{-1} of P(4VP) were used to determine the integration area ratio. Considering these peaks for pure homopolymers, the mol ratio P(ClMPTA)/P(4VP) was calculated for the different copolymers. The results are summarized in Table 1.

The conductivity measurements are considered to be a tool in the physicochemical analysis of polyelectrolyte solution behavior. It is known [20] that the concentration dependency of equivalent conductivity and the chloride ion activity coefficient of the quaternary ammonium salt monomer are not different from those of the strong NaCl electrolyte, confirming that the quaternary ammonium group is a strong electrolyte. The limiting equivalent conductivity for the counter ion chloride, of the polyquaternary ammonium salt is given as $\lambda°_{\text{chloride}} = 76.31$ S cm^{-2} mol^{-1}. The ammonium ion's limiting equivalent conductivity at 25 °C is 73.6 S cm^{-2} mol^{-1}. The equivalent conductivity values of 0.01 M P(ClMPTA) measured at pH 4 and 8 were 67.7 and 82 S cm^{-2} mol^{-1}, respectively; even there was a difference between basic and acid medium, however, the values were not conclusive for the high concentration of 0.01 M of polyelectrolyte. Changes more remarkable could be expected when smallest mol concentration (ca. 10^{-3}–10^{-4} M) of polymer used. The measurements for copolymer solutions at 0.01 M showed average value of 83–89 S cm^{-2} mol, with the mol ratio 1:1 and 2:1 corresponding to the higher values. According to these results, it is expected that the major contribution would be by the action of quaternary ammonium groups, with an easy transport of ions in basic medium, which would be related with conformational changes (cooperative or associative effects, hydrogen bonding, etc.) that suffer the macromolecules at different acid strength of the media (see Table 2).

The thermogravimetric analysis of P(ClMPTA) in nitrogen atmosphere showed a degrading mechanism in several steps. In Fig. 2a, it is observed that it begins to decompose at 264 °C, during which a major weight loss occurs. A characteristic temperature peak occurs at 296 °C and is solved by the first derivative. The last weight loss shows a maximum at 405 °C, which corresponds to ammonium groups [16]. The decomposition of P(4VP) was initiated at the higher temperature of 325 °C with a unique weight loss of 83%. This strong weight loss is attributed to decomposition of the P(4VP) main chain [19]. A maximum temperature peak at 383 °C and a shoulder at 353 °C are shown in Fig. 2b. The thermograms for the copolymers: 2:1, 1:1, 1:2 define the ratio of their monomer moieties. Figure 2c shows the initial decomposition temperature and a profile close to the cationic

Table 2 Conductivity of homo-P(ClMPTA) and copolymers P(ClMPTA) at acid and basic pH and 25 °C

Sample	T (°C)	pH	K_{ob} (μS/cm)	K_{cal} (μS/cm)	$K - \kappa_0$ (μS/cm)	$\Omega = K - \kappa/cp$ (S cm^2/mol)
P(ClMPTA-*co*-4VP), 1:2	25	4	378	563.22	562.7	56.3
P(ClMPTA-*co*-4VP), 1:2	25	8	560	834.40	833.9	83.4
P(ClMPTA-*co*-4VP), 2:1	25	4	560	834.40	833.9	83.4
P(ClMPTA-*co*-4VP), 2:1	25	8	562	837.38	836.9	83.7
P(ClMPTA-*co*-4VP), 1:1	25	4	604	899.96	899.5	89.9
P(ClMPTA-*co*-4VP), 1:1	25	8	819	1220.30	1219.8	121.9
P(ClMPTA)	25	4	433	649.50	649.0	67.7
P(ClMPTA)	25	8	551	820.99	820.5	82.1

$\kappa_0 = 0.5$ μS/cm, distilled water, cp $= 0.01$ M, polymer concentration, $K_{cal} =$ Coeff. K_{ob}, where Coeff $= 1.49$–1.51

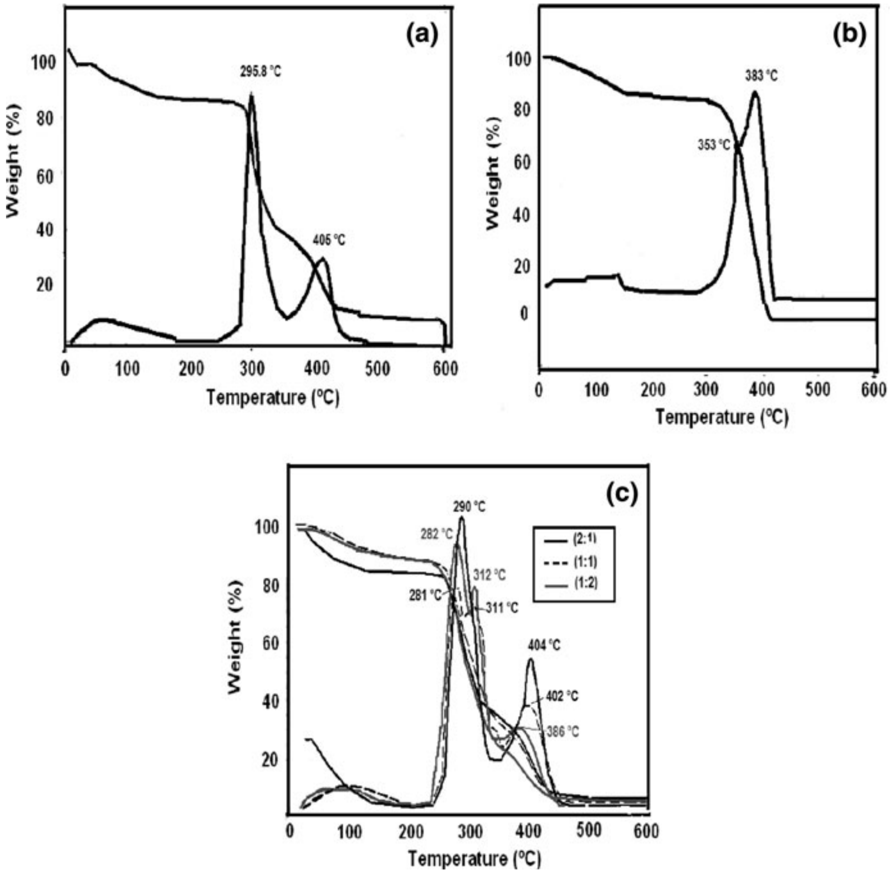

Fig. 2 Thermograms, TG of **a** poly[3-methacryloylamine)propyl)trimethyl amonium chloride, P(ClMPTA), **b** poly(4-vinylpyridine), P(4VP), and **c** poly[(3-methacryloylamine)propyl) trimethyl ammonium chloride-*co*-4-vinyl pyridine], P(ClMPTA-*co*-4VP), 1:2, 2:1, and 1:1

homopolymer. Nevertheless, the first thermal degradation process started at temperature lower than that P(ClMPTA), and the P(4VP) did not produce a stabilizing effect, being in these copolymers the degradation processes enhanced. The main weight loss was found in the first step, where the drop is abrupt and more pronounced for the copolymers in the following order: 1:2 > 1:1 > 2:1. In the first decomposition step, the first derivative showed the characteristic maximum temperature, at 280 °C and 311 °C, for the copolymers 1:1 and 1:2, respectively, and for the copolymer 2:1 a unique peak at 290 °C similarly to P(ClMPTA). In the last step the temperatures were located around that the pure homopolymer; 385 °C for the copolymer 1:2 and 401–404 °C for copolymers 2:1 and 1:1; when the sample is richest in the corresponding comonomer, and a strong weight fall down when the cationic unit content increased in the copolymer sample.

LPR-procedure for arsenate retention

Our previous studies [17, 18] with polyelectrolytes of quaternary ammonium salts, and specifically with P(ClMPTA) [17] showed that As(V) is generally more easily retained at pH at 8 and pH 6 rather than that at pH 4. Thus, we suggested that the anionic exchanger is electroselective to divalent ($HAsO_4^{-2}$) species over monovalent ($H_2AsO_4^{-}$) species. The polymer's binding capacity of polymer was attributed to the anionic exchange between chloride and arsenate anions, and the binding of these with the ammonium quaternary cationic group. This pairing was explained by the water structure-induced ion pairing [21], where the larger, more polarizable ions disrupt the local water structure and it can more easily associate with a given quaternary ammonium ion.

In this work, the copolymers P(ClMPTA-*co*-4VP) prepared from monomer feed mol ratio 1:1, 2:1, and 1:2 were assayed observing the effect of pH on the arsenate retention. Figures 3, 4, and 5 show the retention profile R(%) versus filtration factor,

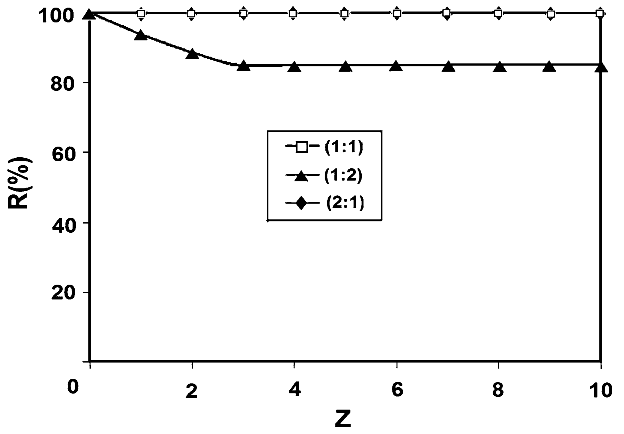

Fig. 3 Retention profile of As(V) at pH 8 for poly[(3-methacryloylamine)propyl)trimethyl ammonium chloride-*co*-4-vinyl pyridine], P(ClMPTA-*co*-4VP), 1:1, 2:1, and 1:1. Polymer amount: 0.2 mmol. Absolute amount As(V) ion: 0.01 mmol

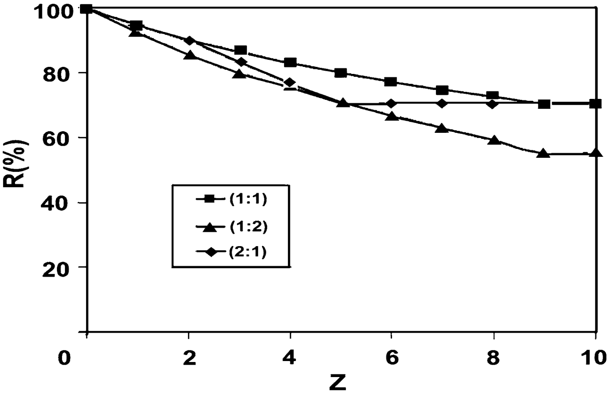

Fig. 4 Retention profile of As(V), at pH 6 for poly[(3-methacryloylamine)propyl)trimethyl ammonium chloride-*co*-4-vinyl pyridine], P(ClMPTA-*co*-4VP), 1:1, 2:1, 1:1. Polymer amount: 0.2 mmol. Absolute amount As(V) ion: 0.01 mmol

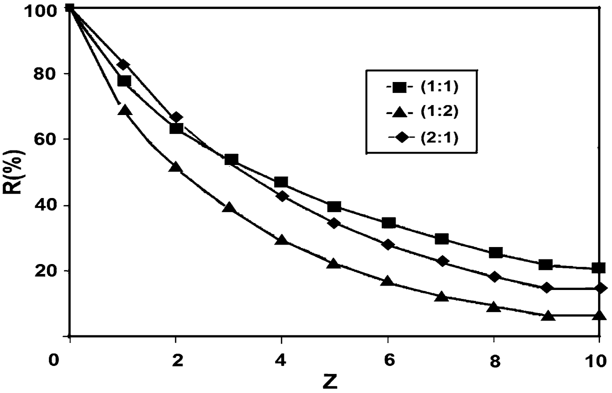

Fig. 5 Retention profile of As(V), at pH 4 for poly[(3-methacryloylamine)propyl)trimethyl ammonium chloride-*co*-4-vinyl pyridine], P(ClMPTA-*co*-4VP), 1:1, 2:1, and 1:1. Polymer amount: 0.2 mmol. Absolute amount As(V) ion: 0.01 mmol

Z at pH 8, 6 and 4, respectively, for three copolymers. In all cases, the mol ratio copolymer:As(V) was 20:1 for 0.2 mmol of copolymer and 0.01 mmol of As(V), in 20 mL of cell volume. The experimental conditions were adjusted to those of the P(ClMPTA) [17] alone, where the retention profile was 100% at pH 8 and 6, and 40% at pH 4. As those cases, the retention ability for copolymers increased with the pH showing the effect of the quaternary ammonium salt polycation to bind selectively divalent arsenate. Selectivity of macromolecular complexes is governed by availability of quaternary ammonium groups. The most indicative is the highest performance of copolymer 1:1, and 2:1 at basic and neutral pH. Comparing the copolymer 1:1, it shows the same efficiency that P(ClMPTA) pure at pH 8 [17], being the 50% the real availability of quaternary ammonium polycation**.** This effect was decreased at pH 4 where the behavior of copolymers 1:1, 2:1, and 1:1 is nearby and the maximum retention capacity decreased at 30%. It can be presumably by the electrostatic contribution and conformational change of polyelectrolytes in solution. It is known [22, 23] that under acidic conditions, weak polybasic vinyl pyridine is almost protonated and is soluble in water due to release of counter ions; in neutral conditions, they are partially ionized and in basic conditions, they are non-protonated. These forms would influence the retention properties at pH 4 being through a coulombic interaction by protonated pyridine group with arsenate anions; however, the lowest retention indicated that exist a cooperative effect between macromolecule components, presumably by the hydrogen bond, that affects the interaction of cationic site with arsenate anions higher than that an electrostatic interaction. It is suggested that macromolecule's conformational changes are more incident that electrostatic properties on retention capacity. It is known that conformation [24] of the poly(vinyl pyridine) coil is balanced by coulomb repulsion and short-range van der Waals attraction. As the degree of protonation decreases or the solution ionic strength increases, extended polymer coils (wormlike) undergo the sharp coil-to-globule phase transition. Studying P2VP solution properties [25] found that the phase transition took place in a very narrow pH range around pH 4. The transition passes through an intermediate state when polymer globules split into necklace-like conformations [26]. These changes were observed also for polyquaternary ammonium salt poly(methacryloyloxyethyl dimethylbenzyl ammonium chloride) [27] in aqueous solution, and adding the 4 mM Na_3PO_4 salt rises a contraction of the coils affected by the electrostatic screening and counter ion condensation effects.

The effect of the polymer concentration P(ClMPTA) has been reported [17]. By increasing the polymer concentration from 0.2 to 2 mmol, retention increased for the set mol ratio polymer:As(V) 20:1. The change of mol ratio polymer:As(V) 20:1, 10:1, and 5:1, at pH 8, with a constant amount of 0.01 mmol of As(V) in 20 mL of volume, or (0.5 mmol/L) is shown in Fig. 6. A decrease of the selectivity to 86% was found for lowest mol ratio.

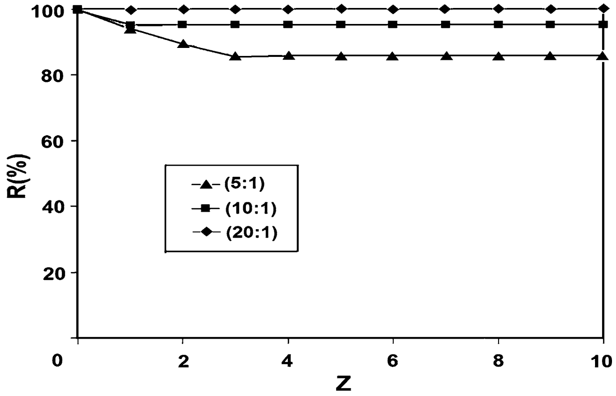

Fig. 6 Retention profile of As(V), at pH 8 for poly[(3-methacryloylamine)propyl)trimethyl ammonium chloride], P(ClMPTA), at mol ratio 20:1, 10:1, and 5:1. Absolute amount As(V) ion: 0.5 mmol/L

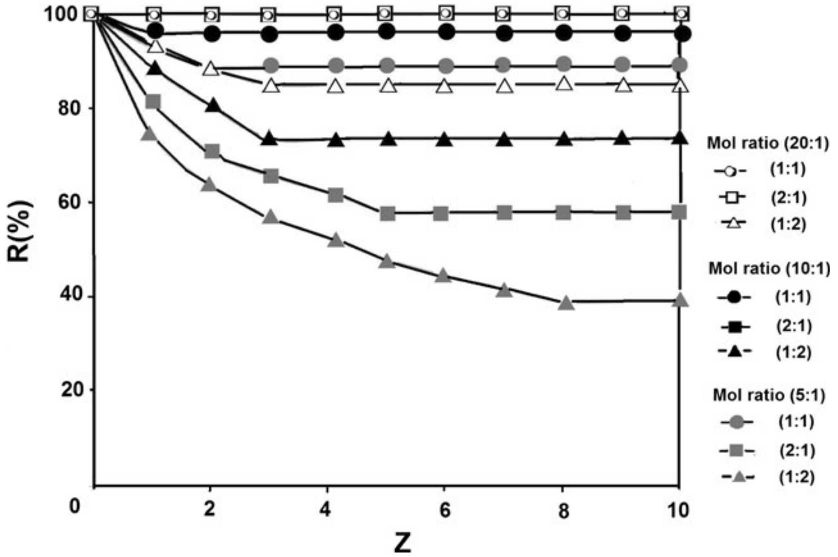

Fig. 7 Retention profile of As(V) at pH 8 for poly[(3-methacryloylamine)propyl)trimethyl ammonium chloride-*co*-4-vinyl pyridine], P(ClMPTA-*co*-4VP), 1:1, 2:1 and 1:2 at mol ratio 20:1, 10:1, and 5:1. Absolute amount As(V) ion 0.5 mmol/L

Figure 7 shows the profile of arsenate retention at pH 8 for copolymers: 1:1, 1:2, 2:1, respectively. Different mol ratio copolymer:As(V) of 20:1, 10:1, 5:1 and at constant concentration of As(V) of 0.01 mmol As(V) in 20 mL of volume, or (0.5 mmol/L) were studied. The selectivity of copolymer 1:1 is relevant, even when the mol ratio is 5:1, the retention was above 90%. Comparing the retention capacities, the copolymers have a higher effect than that the homopolymer quaternary ammonium salt**,** because 1:1, 2:1, and 1:2 shows a 50, 66, and 33% of quaternary ammonium polycation, respectively. But if it is considered the retained content as As wt% versus comonomer mass in each structure for each feed ratio, the results in Table 3 show the differences in the efficiency when it is expressed as wt% As retained/g comonomer P(ClMPTA) or wt% As retained/mg $N^+(CH_3)_3$ for copolymers. A different behavior was showed when the P(ClMPTA) was copolymerized with acrylic acid, AA at the same feed mol ratio 1:1; 1:2; and 2:1 and used in similar pH conditions [17]. The negligible retention at the feed mol ratio 1:1 independently of pH was explained by an interaction of the COO^- group of the P(AA) with the $-N^+(R_3)$ groups of P(ClMPTA) by charge transfer that should have blocked both functional groups. In the present case from the transition at acid pH, where the whole polyelectrolyte complex undergoes a conformation change before adopting a new stable state, depending on the charge density, contributions of non-electrostatic interactions (hydrogen binding), it is probable the arrangement of outer-chain containing the $-N^+(CH_3)_3$ group to receive the arsenate anions, because the comonomer containing this group has the major affinity by water. Poly(vinyl pyridine) has poor affinity by water. The complexes conformation being (2D)

Table 3 Retention of arsenic(V) in function of net mass of P(ClMPTA) and $N^+(CH_3)_3$

Polymer	Mol ratio feed[a]	As (wt%)	Mass P(ClMPTA) (g)	As retained/ mass comonomer (wt%/g) × 10^3	As retained/ mass $N^+(CH_3)_3$ (wt%/mg)
P(ClMPTA)	5:1	86	0.01104	7.79	29.20
P(ClMPTA-*co*-4VP), 1:1		88	0.00407	21.61	80.86
P(ClMPTA-*co*-4VP), 2:1		58	0.00601	9.65	36.10
P(ClMPTA-*co*-4VP), 1:2		39	0.00237	16.52	61.57
P(ClMPTA)	10:1	95	0.02207	4.30	16.10
P(ClMPTA-*co*-4VP), 1:1		96	0.00814	11.81	44.10
P(ClMPTA-*co*-4VP), 2:1		100	0.01202	8.32	31.12
P(ClMPTA-*co*-4VP), 1:2		74	0.00474	15.53	58.41
P(ClMPTA)	20:1	100	0.04415	2.26	8.47
P(ClMPTA-*co*-4VP), 1:1		100	0.01628	6.14	22.98
P(ClMPTA-*co*-4VP), 2:1		100	0.02416	4.14	15.50
P(ClMPTA-*co*-4VP), 1:2		85	0.00947	8.97	33.59

[a] 0.05 mmol polymer, 0.01 mmol As(V); 0.1 mmol polymer, 0.01 mmol As(V); 0.2 mmol polymer, 0.01 mmol As(V)

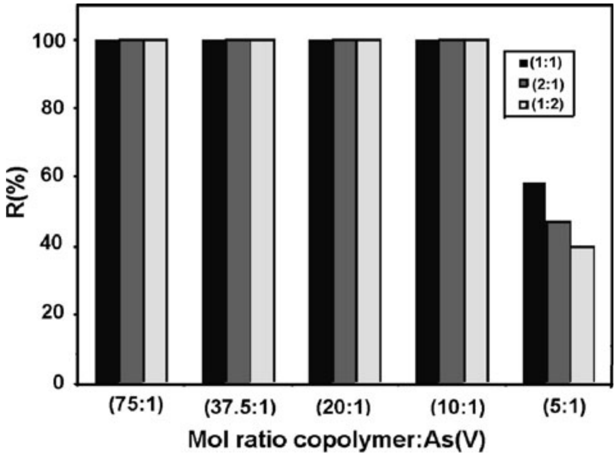

Fig. 8 Retention values of 0.13 mmol/L As(V), by different mol ratio copolymers: As(V) 75:1, 37.5:1, 20:1, 10:1, 5:1 at pH 8 and Z = 10

uncoiling or (3D) globular or necklace will show the part less hydrophobic of macromolecules available to arsenate anions.

For the range of polymer concentrations, a decrease in arsenic concentration to 10 ppm (0.13 mmol/L) is shown in Fig. 8. At filtration factor $Z = 10$, the maximum retention at basic pH is reached with mol ratios: 75:1, 37.5:1, 20:1, and 10:1 for all the copolymers.

Conclusions

The ability retention for As(V) in pH range of 4–8 for copolymers P(ClMPTA-*co*-4VP) 1:1, 1.2, and 2:1 showed a similar profile that pure cationic polymer, being a higher selectivity at basic and neutral pH. However, the effective retention capacity of polyelectrolyte with quaternary ammonium group was enhanced in presence of weakly basic pyridine groups, at difference other experiences with acrylic acid groups as co-monomer and if it is considered that the net mass of P(ClMPTA) in the copolymers 1:1, 1:2, and 2:1, was lower than pure P(ClMPTA), but the profile of retention R(%) was higher or similar to the homopolymer, using the mol ratio polymer:As(V) 20:1, 10:1, and 5:1. It is probable that conformational changes suffered by macromolecules, modify the media strength, producing higher arsenic retention ability.

Acknowledgements The authors thank to FONDECYT (Grant No 1070542), PIA (Grant ACT 130), and “Centro de Investigación de Polímeros Avanzados”, CIPA.

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