

Water-Soluble Copolymers from Functionalized Monomers (sodium *o*- and *p*-methacryloylaminophenylarsonate): Synthesis and Characterization

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Received 24 August 2009; accepted 14 March 2010

DOI 10.1002/app.32448

Published online 30 June 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Copolymers of sodium *o*-methacryloylaminophenylarsonate (*o*-MAPHA-Na) **1** and *p*-methacryloylaminophenylarsonate (*p*-MAPHA-Na) **2** with sodium acrylate (AA-Na) **3**, sodium methacrylate (AM-Na) **4** and acrylamide (AAD) **5** were prepared by free radical polymerization in aqueous media at 70°C using potassium persulfate (K₂S₂O₈) as the initiator. The total monomer concentration was carried out at 0.5M and the feed ratio (**M**₁ : **M**₂) was varied from 10 : 90 to 90 : 10 mol%. The kinetic study was carried out by dilatometric method. The copolymer compositions were calculated by arsenic content in the copolymers. The As content (ppm) was determined by atomic absorption spectrometry (AAS). The

reactivity ratios (r_1 , r_2) were estimated by the Kelen-Tüdös linearization method as well as error-in-variables method using the computer program RREVM[®]. In all cases, $r_1 < 1$ and $r_2 > 1$, indicating a tendency to form random copolymers. The values suggest that the copolymers contain a larger proportion of comonomer (i.e., AA-Na, AM-Na, or AAD). Weight-average molar masses (\overline{M}_w) of copolymers were determined by multi-angle light scattering. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2849–2858, 2010

Key words: copolymerization; reactivity ratios; water-soluble polymers; polyelectrolytes; sodium *o*- and *p*-methacryloylaminophenylarsonate

INTRODUCTION

High molar mass materials may be modified by the introduction of functional groups, and thus, the synthesis and use of functionalized water-soluble polymeric materials continues to have great research interest. A functionalized polymer may be synthesized by two approaches:¹ (a) by modification of a readily available polymer through attachment of the required functional group or (b) by formation of a polymer or copolymer from a monomer bearing the desired functional group.

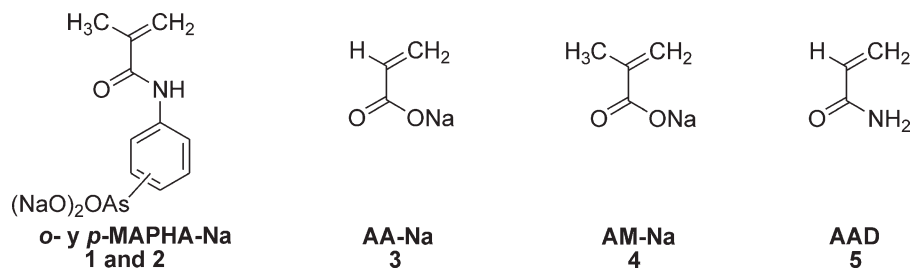
McCormick et al.^{2–7} have extensively investigated functionalized copolymers to prepare copolymers showing tolerance toward added electrolytes. Such polymers have applications for viscosity modification, petroleum recovery, formulation of coatings, and drag reduction. They reported the synthesis and structural study of copolymers using monomers with sulfonate (SO₃⁻) and carboxylate (COO⁻) functional groups. The composition of the copolymers

was conducted by determination of reactivity ratios using several methods like Fineman-Ross,⁸ Kelen-Tüdös,⁹ and nonlinear least-squares.¹⁰ The values of the reactivity ratios, r_1 and r_2 , of synthesized copolymers showed alternating and random tendencies. For example, for poly(*N*-vinylformamide-*co*-2-(acrylamido)-2-methylpropanesulfonate) [poly(NVF-*co*-NaAMPS)], $r_1 = 0.25$ and $r_2 = 0.24$, while for poly(*N*-vinylformamide-*co*-3-acrylamido-3-methylbutanoate) [poly(NVF-*co*-NaAMBA)], $r_1 = 0.25$ and $r_2 = 0.29$. These values indicate an alternating incorporation of monomers into the final copolymers. The copolymers were prepared by free radical polymerization at 45°C in aqueous solution using 2,2'-azobis(*N,N*-dimethyleisobutyramidine) dihydrochloride as the initiator.²

Functionalized copolymers may also be applied to medicinal uses and to biological systems. Copolymers of hydrogels and copolymers based on *N*-vinyl-2-pyrrolidone (NVP) have been synthesized for biological applications.^{11–15} The reactivity ratios have been used to predict the copolymer composition and properties such as swelling, hydrophilic/hydrophobic balance, polarity, and solubility of this kind of copolymer. Bauduin et al.¹² copolymerized a methacrylate containing a derivate of acetylsalicylic acid (ASA) with NVP. The reactivity ratios were calculated by several methods, with the Tidwell-Mortimer

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Contract grant sponsor: CONACYT; contract grant number: CONACYT 44237-Y, 46366.



Scheme 1 Structures of monomers.

procedure giving the best results, yielding reactivity ratios of $r_1 = 0.85$ and $r_2 = 0.340$. These values indicate an alternating incorporation of monomers into the final copolymers. The copolymers were prepared by free radical polymerization at 80°C in acetonitrile using 2,2'-azobis(2-methylpropionitrile; AIBN) as initiator. Nurkeeva et al.¹³ synthesized copolymers and hydrogels by radical polymerization of [2-(methacryloxy)ethyl]trimethylammonium chloride (MADQUAT) and 2-hydroxyethylacrylate (HEA). Linear copolymers were obtained in a water-ethanol (30 : 70) mixture in the presence of AIBN as an initiator at 60°C . The determined reactivity ratios of $r_1 = 0.65$ and $r_2 = 1.35$ confirmed a random sequence in the copolymer.

Our laboratory has been developing functional polymers with versatile characteristics. We have focused our attention on water-soluble polyelectrolytes containing a precipitating group, namely $-\text{AsO}(\text{OH})_2$, which allows the synthesis of soluble polymeric compounds with highly selective ligands [poly(*o*- and *p*-methacryloylaminophenylarsonic acids) (poly(*o*- and *p*-MAPHA)) and their sodium salts forms],^{16,17} in order to apply them to removal of trace of metal ions from solution or as flocculants.¹⁸

The $-\text{AsO}(\text{OH})_2$ group is an important functionality of organic analytical reagents that have been used for separations of ionic metals such as Al, Be, In, Th, and Zr.¹⁹ Benzenearsonic acids and analogs react with several metal ions at different pH values to form precipitates and the process is often quantitative when the arsonate group acts as a bidentate ligand.^{20–24} Recently reported compounds such as monomers *o*- and *p*-methacryloylaminophenylarsonic acids (*o*- and *p*-MAPHA 19 and 20, which contain the $-\text{AsO}(\text{OH})_2$ group, exhibit good nonlinear optical (NLO) properties.²⁵

In contrast, the $-\text{COO}^-$ and $-\text{CONH}_2$ groups are able to form coordination bonds with metal ions.²⁶ The coordination of $-\text{COO}^-$ group depends of the medium pH.^{27,28} At pH = 7, a monodentate configuration occurs and at higher pH (11–14), an asymmetric bidentate bridging structure is obtained.

Our interest is the comparison of polymers obtained from copolymerization of functionalized monomers such as 1 and 2 with comonomers 3, 4,

and 5 in aqueous media. The copolymer produced may have striking features, which derive from the properties of the arsonate group ($-\text{AsO}(\text{ONa})_2$) with carboxylate ($-\text{COO}^-$) and amide ($-\text{CONH}_2$) groups attached within a polymeric matrix. The structures of such monomers are shown in Scheme 1.

In the present article, we report the synthesis and characterization of copolymers of 1 and 2 with 3, 4 and 5 at different feed ratios ($M_1 : M_2$). The copolymer compositions were calculated by the arsenic content (ppm) of the copolymers, which was measured by atomic absorption spectrometry (AAS). The reactivity ratios were estimated by the Kelen-Tüdös and the error-in-variables methods in order to predict the structure of the resulting copolymers.

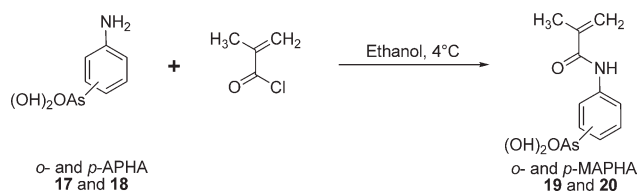
EXPERIMENTAL

Materials

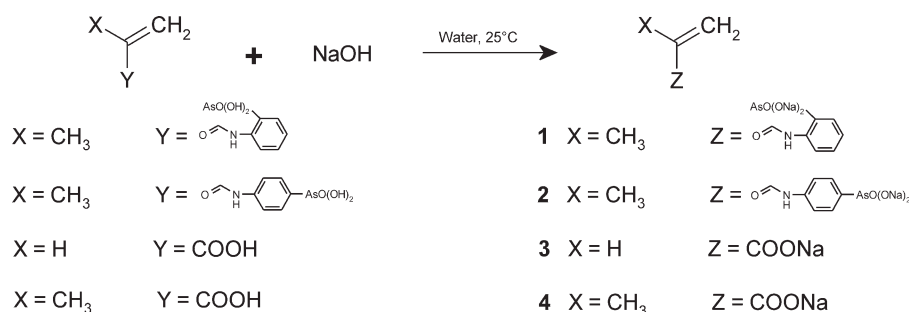
Acrylic acid (AA 15) and methacrylic acid (AM 16), supplied by Sigma-Aldrich (México) were distilled under vacuum distillation. Acrylamide (Aldrich) was recrystallized in warm chloroform. Methacryloyl chloride (Aldrich) was distilled by simple distillation and used immediately. The initiator potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$; Aldrich) was recrystallized from warm water. *o*- and *p*-Aminobenzenearsonic acids (*o*- and *p*-APHA 17 and 18; Aldrich), and sodium hydroxide (NaOH; Fermont, México) were used as received.

Monomer synthesis

The *o*- and *p*-MAPHA monomers 19 and 20 were obtained by condensation reaction of methacryloyl chloride with the corresponding *o*- and *p*-APHA 17



Scheme 2 Condensation reaction to obtain the monomers 19 and 20.



Scheme 3 Neutralization reaction to obtain the monomers **1**, **2**, **3**, and **4**.

and **18**, according to the reported procedure (Scheme 2).¹⁸ Monomers in salt form (**1**, **2**, **3**, and **4**) were synthesized by neutralization reaction with NaOH (Scheme 3).¹⁸

Synthesis of **19** and **20**

To an ethanolic solution (150 mL) of **17** and **18** (0.0658 mol), freshly distilled methacryloyl chloride (0.07896 mol) was added dropwise during 105 min. The reaction mixture was magnetically stirred for 6 h at 4°C, and then water (4°C) was added to precipitate **19** and **20**. The resulting mixture was filtered and a white powder was obtained. Monomers **19** and **20** were recrystallized from water and vacuum dried at 95°C (yield 40% and 77%, respectively).

Synthesis of **1** and **2**

Monomers **19** and **20** (0.014070 mol) were mixed with NaOH (0.02814 mol) in a minimum volume of water. The homogeneous solutions were precipitated adding them dropwise to acetone. The mixtures were filtered to obtain a white powder, which were vacuum dried at 95°C (**1** yield = 94% and **2** yield = 96%).

Synthesis of **3** and **4**

15 and **16** (0.05875 mol) were dissolved with NaOH (0.05875 moles) in a minimum volume of water. Each homogenous solution was precipitated by adding it dropwise to acetone. The mixtures were filtered to obtain a white powder, which were vacuum dried at 95°C (**3** yield = 90% and **4** yield = 77%).

The formation of monomers **1**, **2**, **3**, and **4** were confirmed by IR and ¹H-NMR spectroscopic techniques. Typical monomers absorption bands of IR are listed in Table I and characteristic monomers peaks assignments of ¹H-NMR are listed in Table II.

Copolymer synthesis

The copolymers poly(*o*-MAPHA-Na-*co*-AA-Na) **6**, poly(*o*-MAPHA-Na-*co*-AM-Na) **7**, poly(*o*-MAPHA-Na-*co*-AAD) **8**, poly(*p*-MAPHA-Na-*co*-AA-Na) **9**, poly(*p*-MAPHA-Na-*co*-AM-Na) **10**, and poly(*p*-MAPHA-Na-*co*-AAD) **11** were synthesized at different feed molar ratios: 10 : 90 **a**, 25 : 75 **b**, 50 : 50 **c**, 75 : 25 **d** and 90 : 10 **e**. All copolymerizations can be represented by a general copolymerization reaction (Scheme 4).

The kinetic polymerizations were carried out in a glass dilatometer, consisting of a 5-mL bulb and a capillary tube of 2.0-mm internal diameter and 10-cm length.

TABLE I
Typical Absorption Bands in IR of Monomers

Group	Monomers				
	1	2	3	4	5
	cm ⁻¹				
ν N-H	3521	3272	–	–	3343 and 3185
ν C=O	1675	1672	–	–	1672
ν C=C	1607	1626	1636	1645	1645
ν C=C _{arom}	1583	1591	–	–	–
δ N-H	1545	1521	–	–	–
δ N-H ₂	–	–	–	–	1612
ν As=O	1062	1096	–	–	–
δ CH _{gem-out}	850	868	898 and 898	920	987 and 960
ν COO _{sym} ⁻	–	–	–	1559	–
ν COO _{sym} ⁻	–	–	1421	1418	–

TABLE II
Characteristic Chemical Shifts of Protons in Monomers

Protons	Monomers				
	1	2	3	4	5
	ppm (number of integrated protons, multiplicity)				
—CH ₃	2.05 (3H, s)	2.047 (3H, s)		1.853 (3H, s)	
=CH ₂	5.61 (1H, s)	5.626 (1H, s)	5.633 (1H, dd)	5.321 (1H, s)	5.664 (1H, m)
	5.98 (1H)	5.869 (1H, s)	5.991 (1H, dd)	5.631 (1H, s)	6.043 (1H, m)
—CH			6.113 (1H, q)		6.129 (1H, m)
—C ₆ H ₄ AsO(ONa) ₂	7.291 (1H, t)	7.652 (2H, d)			
	7.542 (1H, t)	7.814 (2H, d)			
	7.717 (1H, d)				
	8.155 (1H, d)				

The general procedure to obtain these copolymers is as follows: an aqueous solution of the two monomers (final concentration was 0.5M) was prepared in a 5 mL flask. The initiator was prepared in water (2.7 mg/mL) and 1 mL was placed in the dilatometer. For all polymerizations, the initiator concentration was $2 \times 10^{-3}M$. Both solutions were bubbled with ultrahigh-purity argon for 20 min and sealed with a rubber septum. The solution of the monomers (4 mL) was transferred to a dilatometer via syringe, and the dilatometer was placed in a water bath at 70°C (± 0.02). The conversion was followed by volume contraction during polymerization, and the overall and monomers conversions (%) were determined. The copolymerization reactions proceeded to about 20% conversion and then they were stopped by cooling the dilatometers in an ice-water bath. The copolymers were precipitated in acetone. Copolymers 6–8 were purified by repeated dissolution in methanol followed by precipitation with isopropyl alcohol, while copolymers 9–11 were purified by repeated dissolution in methanol followed by precipitation with chloroform. The obtained copolymers were placed in a vacuum oven at 100°C for 36 h.

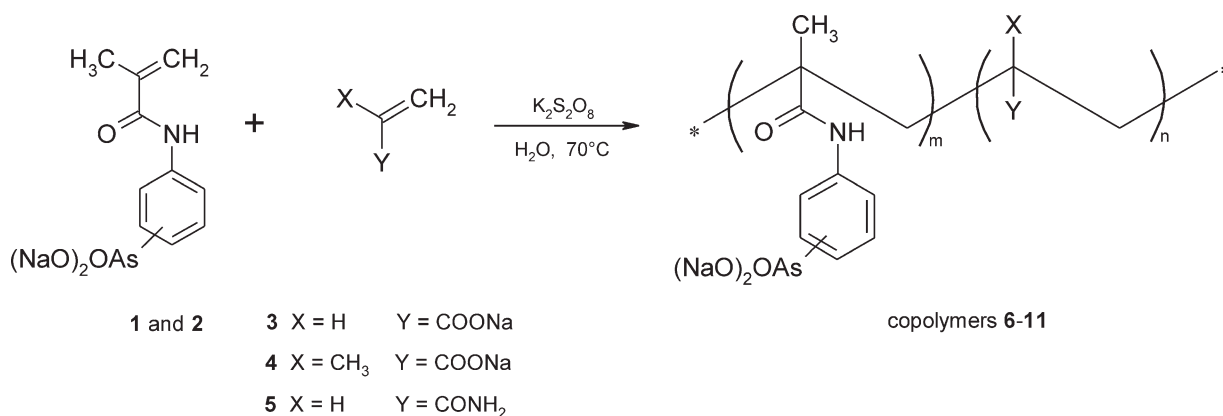
The structures of copolymers 6–11 were characterized by IR and ¹H-NMR. Typical IR absorptions

bands and the characteristic peaks assignments from ¹H-NMR of copolymers 6–11 are listed in Tables III and IV, respectively.

General characterization methods

Monomers and copolymers were characterized by proton nuclear magnetic resonance spectroscopy (¹H-NMR) and infrared spectroscopy (FTIR). ¹H-NMR was carried out with a Varian unity 300 MHz spectrometer using D₂O as solvent and tetramethylsilane as internal standard. FTIR spectra were determined in a Bruker Vertex 70 spectrometer using the diffuse reflectance accessory.

The copolymer compositions were calculated by the arsenic content in the copolymers. The As content (ppm) was determined with a Perkin Elmer Analyst 200 spectrometer equipped with an electrodeless discharge lamp (400 mA) at 193.7 nm, with slit width of 2.7/2.3 nm. The atomization of the samples was carried out at 2300°C. Flow rates of acetylene and air were 2.5 and 10 L/min, respectively. To validate the method and to obtain the experimental error associated with copolymer composition measurements, the values of As content of 1, 2, 17–20, poly(*o*-MAPHA-Na) and poly(*p*-MAPHA-Na) were determined. The experimental error was 3%.



Scheme 4 General copolymerization reaction.

TABLE III
Characteristic Absorption Bands in Infrared Spectroscopy of Copolymers

Group	Copolymers					
	6	7	8	9	10	11
	cm ⁻¹					
v N—H	3126–3190	3256–3302	3243–3253	3195–3273	3173–3286	3179–3295
v N—H ₂	–	–	3520	–	–	3515–3525
v C=O	1667–1686	1665–1684	1675–1681	1668–1674	1664–1676	1669–1680
v C=C _{arom}	1579–1582	1578–1580	1581–1583	1586–1587	1586–1587	1588–1592
δ N—H	1538–1549	1538–1547	1581–1583	1513–1564	1513–1543	1588–1592
δ N—H ₂	–	–	1301–1320	–	–	1237–1250
v As=O	1058–1065	1062–1098	1061–1065	1095–1097	1095–1097	1095–1110
v COO ⁻ _{asym}	1549–1553	1538–1547	–	1518–1564	1513–1543	–
v COO ⁻ _{sym}	1409–1416	1440–1436	–	1447–1448	1418–1420	–

Copolymer densities are necessary to calculate conversions % achieved by dilatometry. The copolymers density measurements were obtained at room temperature using a Brand pycnometer of 5 mL capacity. The solvent used was cyclohexane (Fermont, $\rho = 0.779$ g/mL). To validate the method and to obtain the experimental error associated with the conversion measurements, the density of acrylamide (Aldrich, recrystallized in warm chloroform, $\rho = 1.13$ g/mL) was determined, giving 1.0996 g/mL. The experimental error was 2.69%.

Copolymers also were characterized by absolute polymer molar mass. Absolute polymer molar masses (weight-average molar mass \bar{M}_w) were measured with a multi-angle light scattering 8-angle DAWN HELEOS Wyatt detector (Wyatt Technology) and operating at 658 nm wavelength. The software used was ASTRA 5.3.2.15 (Wyatt Technology), for data acquisition and evaluation. The differential refractive index increments (dn/dc) of copolymers were determined using a refractive index detector (Optilab rEX, Wyatt Technology) at 690 nm with 0.5M NaCl in water.

RESULTS AND DISCUSSION

Spectroscopic analysis

The molecular structures of the copolymers 6-11 were characterized by IR and ¹H-NMR analysis.

From IR spectra, formation of copolymers was confirmed by the absence of stretching bands C=C (v C=C) at 1607, 1626, 1636, 1645, and 1645 cm⁻¹, and the bending bands C—H (δC—H) at 850, 868, 898, and 898, 920, and 987 and 960 cm⁻¹, for the monomers 1, 2, 3, 4, and 5, respectively. On the other hand, the appearance of bands vC=O (1664–1684 cm⁻¹), v COO⁻_{asym} (1513–1564 cm⁻¹), v COO⁻_{sym} (1409–1320 cm⁻¹), vNH₂ (3515–3520 cm⁻¹) and δNH₂ (1237–1320 cm⁻¹) indicated the presence of 1, 2, 3, 4, and 5 in copolymers 6-11. From ¹H-NMR spectra, copolymer formation also was followed by disappearance of geminal protons signals (5.321–6.129 ppm; Table II) and the corresponding appearance of methylene protons at 1.4–2.6 ppm (Table IV).

Copolymer conversion

The overall conversion was calculated from the following expression:²⁹

$$\text{Conversion \%} = \frac{\Delta V}{VK} \times 100,$$

where V and ΔV are the initial volume of the reaction mixture in the dilatometer and the change of its volume with time, respectively; and K is the contraction factor of copolymerization,

TABLE IV
Characteristic Chemical Shifts of Protons of Copolymers

Protons	Copolymers					
	6	7	8	9	10	11
	ppm					
—CH ₃ of 1 or 2	1.6–0.3	1.65–0.95	1.5–0.9	1.6–0.2	1.5–0.9	1.6–0.4
—CH ₃ of 4	–	1.10–0.7	–	–	1.1–0.3	–
—CH ₂ of backbone	2.6–1.5	2.15–1.50	2.5–2.0	2.8–1.4	2.5–1.4	2.6–1.6
(—CH) of 3 or 5	1.7–1.1	–	2.0–1.4	1.7–0.9	–	2.0–1.2
—C ₆ H ₄ AsO(ONa) ₂ of 1 or 2	8.3–6.5	8.4–6.8	8.3–7.1	8.4–6.6	7.8–6.9	8.0–6.8

TABLE V
Overall (t) and Monomers (1, 2, 3, 4, 5) Conversions (%) of Copolymers

Feed ratio	6			7			8			9			10			11		
	t	1	3	t	1	4	t	1	5	t	2	3	t	2	4	t	2	5
a	11.67	8.68	12.00	19.74	9.34	20.89	14.35	3.93	15.51	10.77	9.00	10.97	17.05	9.17	17.92	16.26	11.49	16.79
b	7.17	4.68	8.00	16.61	8.96	19.15	10.77	4.41	12.89	10.77	8.01	11.69	10.77	7.74	11.78	10.77	6.31	12.26
c	4.49	2.59	6.39	13.02	9.05	16.99	8.07	4.23	11.91	4.49	3.32	5.66	4.49	3.02	5.96	5.38	3.88	6.87
d	1.79	1.20	3.55	10.13	7.90	16.82	1.79	1.12	3.79	2.69	1.72	5.60	2.69	2.04	4.64	4.91	3.69	8.5
e	–	–	–	6.08	4.95	16.23	–	–	–	0.90	0.51	4.39	1.79	1.42	5.13	2.51	1.96	7.46

$$K = K_1\omega + K_2(100 - \omega),$$

where K_1 and K_2 are the contraction factors for monomer (1 or 2) and comonomer (3, 4, or 5), respectively; ω is the content of monomer (1, 2) in the initial monomer mixture.

The factors K_1 and K_2 were determined using the equation:

$$K_1, K_2 = \frac{(\rho_p - \rho_m)}{\rho_p},$$

where ρ_p and ρ_m are the densities of the copolymer and monomer, respectively, as calculated by pycnometry.

The overall conversion was also calculated using the correction factor K' .²⁹

$$K' = K[1 + \alpha_m](T_1 - T_2),$$

where α_m is the cubic expansion coefficient of the monomer solution, and T_1 and T_2 are the respective temperatures at which the experiment was performed and at which the dilatometer was filled. The values of α_m were calculated as follows:

$$\alpha_m = \left(\frac{1}{V}\right) \left(\frac{dV}{dT}\right),$$

where dV is the change in volume of reaction mixture; V , initial volume; and dT , temperature range corresponding to the volume change dV .

The conversion values were very similar to those obtained with K .

The monomer conversions reported were calculated from the overall conversions and the copolymer composition.³⁰ The overall and monomers conversions are shown in Table V.

Copolymer composition

Compositions of copolymers 6-11 (m_1 and m_2) at different molar feed ratios (M_1 and M_2) were determined by AAS; monomers 1 and 2 contained arsenic while comonomers 3, 4, and 5 do not. Thus, the arsenic content in the copolymers can be used to estimate the copolymer composition.

The content of arsenic in each sample of copolymer was calculated from experimentally obtained average ppm (Table VI), and the weight percentage of arsenic in copolymer (As%) is given by

$$\text{As \% in copolymer} = \frac{\text{As in sample}}{\text{weight of sample}} \times 100$$

The weight percentage ($x_1\%$) of monomer in copolymer was calculated as follows:

$$x_1 \% = \frac{\text{As \% in copolymer}}{\text{As \% in monomer}} \times 100$$

The molar percentage (mol %) of monomer in copolymer was obtained by the equation:

$$m_1 \% = \frac{(x_1/M_{W1})}{((x_1/M_{W1}) + (x_2/M_{W2}))}$$

TABLE VI
Arsenic Content in the Copolymers

Feed ratio	6		7		8		9		10		11	
	As		As		As		As		As		As	
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%
a	31.690	5.00	26.000	2.99	2.63	11.55	30.635	8.32	29.178	3.36	38.429	5.93
b	38.690	9.24	31.800	7.33	7.86	34.53	55.039	11.28	40.233	9.14	36.711	10.08
c	38.140	13.34	33.491	14.08	14.39	62.21	36.740	15.31	41.315	13.96	36.565	16.47
d	36.010	14.76	37.400	18.46	18.32	80.48	34.380	17.38	38.293	18.23	38.437	19.51
e	–	–	38.020	20.33	–	–	35.790	17.88	38.603	20.11	41.052	20.86

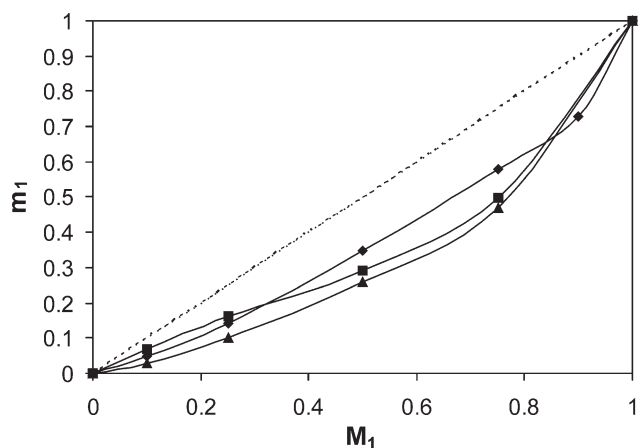


Figure 1 Mol percent of monomer 1 in copolymers 6–8 (m_1) as a function of 1 feed ratio (M_1). Copolymer 6 (■), copolymer 7 (◆) and copolymer 8 (▲). The dashed line represents ideal incorporation (---).

where M_{W1} , molar mass of monomer; M_{W2} , molar mass of comonomer.

Figures 1 and 2 show the copolymer composition plots (m_1) of 1 and 2 versus the molar feed ratio (M_1) of monomers 1 and 2 for copolymers 6–11. According to the plots, the synthesized copolymers are richer in the comonomers than in monomers, suggesting that the comonomers are the more reactive species. This behavior is typical of copolymerizations which present a tendency to add both monomers in a random way.³¹

Reactivity ratios

The estimation of reactivity ratios r_1 and r_2 were calculated by the Kelen-Tüdös (KT)⁹ linearization method, as well as by the error-in-variables model (EVM)^{31–33} using the computer program Reactivity Ratio Calculator Version 2.3 (RREVM[®])^{34,35} nonlinear method. The KT method is a linearization of the Mayo-Lewis equation and can be used to obtain at least good initial r_1 and r_2 estimates. On the other hand, the EVM method (based on nonlinear least-squares) is the most appropriate statistical method because it takes into account the error in both the independent and dependent variables (i.e., the monomer feed and copolymer compositions, respectively). Determination of reactivity ratios with EVM was made using the computer program RREVM[®] based on a nonlinear minimization algorithm starting from values of r_1 and r_2 obtained by the KT method. The obtained r_1 and r_2 values with EVM were generated using errors of 0.07% for monomer feed composition and 3% for the copolymer composition.

The 95% confidence region (also calculated with the computer program RREVM[®]) is an indicator of the experimental error and the accuracy of the ex-

perimental conditions used to generate the composition data. We have used the reactivity ratios values determined with EVM to give the 95% confidence region defined by the area of the elliptical diagrams in Figure 3. The dimensions of elliptical diagrams in all cases confirmed a good approximation of reactivity ratios, as indicated by the relatively small dimensions of the ellipses.

Table VII shows the reactivity ratios obtained by the KT and EVM methods, as well as the α parameter values for the KT method. The reactivity ratios calculated with the KT method were found to be comparable with those found with the EVM method. In all copolymerizations, $r_1 < 1$ and $r_2 > 1$. Because of $r_1 < 1$, propagating chain radicals ending in monomers 1 and 2 preferentially added comonomers 3, 4, or 5, affording copolymers richer in comonomers units. Such behavior is known as “moderate Bernoullian behavior” and occurs when r_1 and r_2 values are close in magnitude (e.g., 0.5 and 2).¹ The formed copolymers have the two monomer units distributed randomly and are referred as a random copolymers.

According to the structures of the radicals and the comonomers, radicals 1 and 2 add preferentially to comonomers 3 and 4, probably due to factors such as steric hindrance and electrostatic repulsion. It could be that the addition of radicals 1 and 2 to their respective monomers is more hindered than the addition to comonomers 3 and 4. Electrostatic repulsions among radicals 1 and 2 and comonomers 3 and 4 may be lower than the electrostatic repulsions among their respective monomers.

In contrast, comonomer 5 does not have a formal charge, perhaps accounting for the preferred addition of the radicals 1 and 2. In fact, McCormick and coworkers^{2,7,36–38} found the same behavior when acrylamide was copolymerized with the

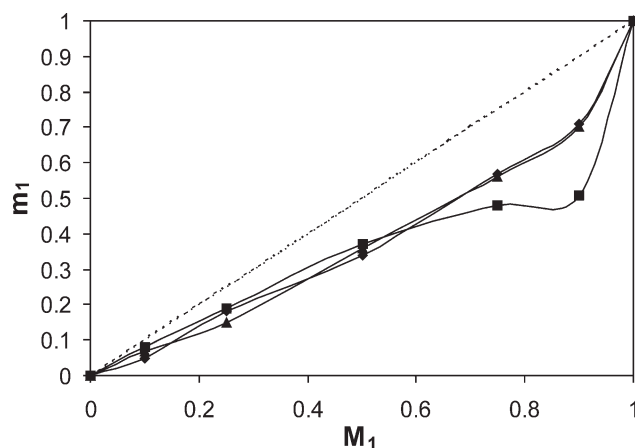


Figure 2 Mol percent of monomer 2 in copolymers 9–11 (m_2) as a function of 2 feed ratio (M_2). Copolymer 9 (■), copolymer 10 (◆) and copolymer 11 (▲). The dashed line represents ideal incorporation (---).

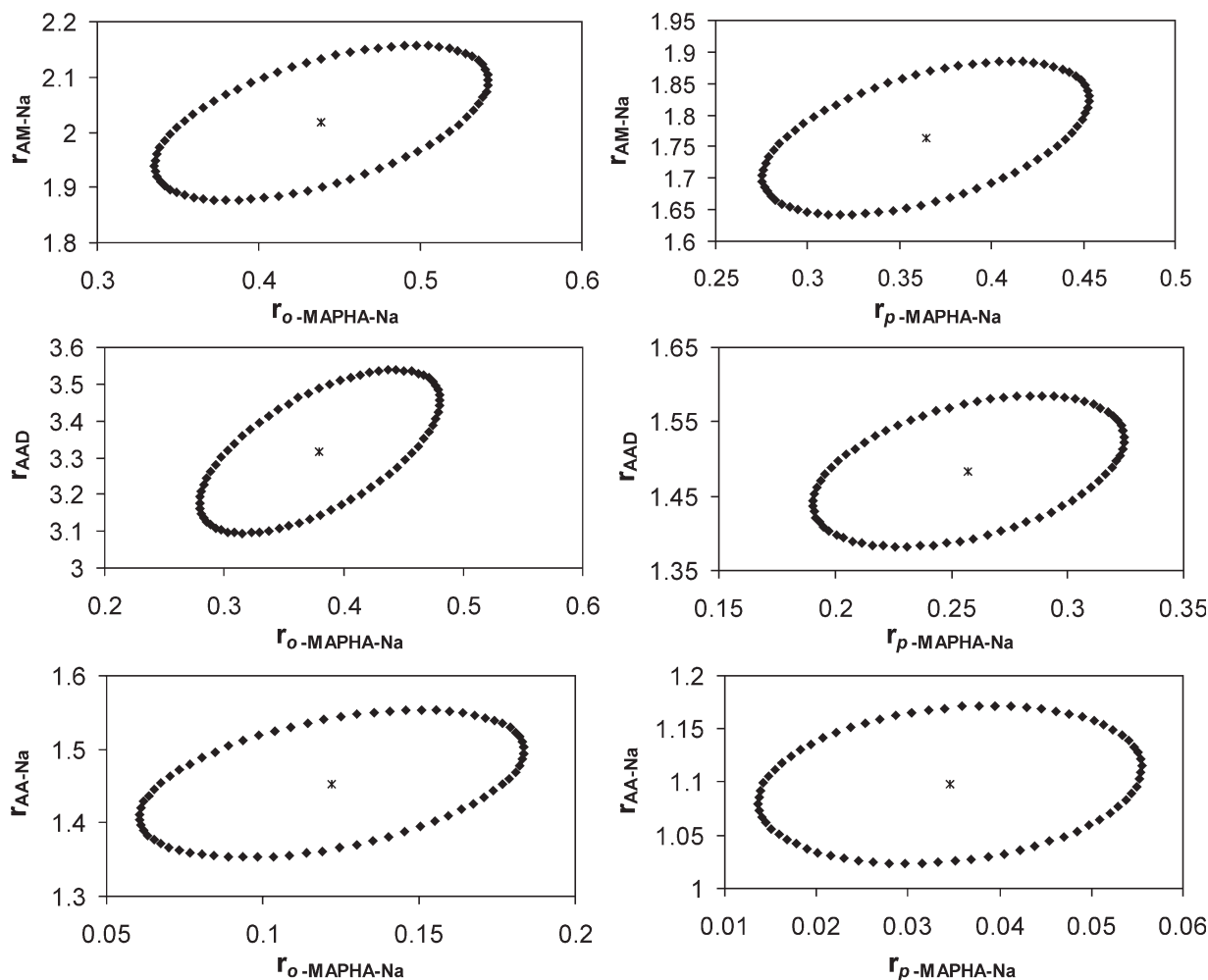


Figure 3 The 95% confidence region for reactivity ratios determined by EVM for copolymers.

anionic monomers sodium-3-acrylamido-3-methylbutanoate (NaAMBA),⁷ sodium-2-acrylamido-2-methylpropanesulfonate (NaAMPS),^{36,37} and sodium acrylate (NaA).³⁸ In accordance with their results, acrylamide is preferentially added at all compositions, this behavior being more prevalent for carboxylate-containing comonomers, and may be suggestive of

some type of hydrogen-bonding interaction with acrylamide.

Light scattering studies

Molar masses and second virial coefficients (A_2) were determined for copolymers in this study at

TABLE VII
Reactivity Ratios for Copolymers

Copolymer	Method	α (for KT)	r_1	r_2	$r_1 r_2$
6	KT	1.21	0.0956	1.4248	0.1362
	EVM		0.1221	1.4532	0.1774
7	KT	2.65	0.3382	1.9043	0.6440
	EVM		0.4388	2.0170	0.8851
8	KT	2.01	0.3899	3.3665	1.3126
	EVM		0.3800	3.3165	1.2603
9	KT	3.32	0.0535	1.0657	0.0570
	EVM		0.0361	1.0985	0.0397
10	KT	2.79	0.2806	1.6718	0.4691
	EVM		0.3642	1.7633	0.6422
11	KT	2.39	0.2397	1.4636	0.3508
	EVM		0.2608	1.4861	0.3876

TABLE VIII
Physicochemical Parameters of Copolymers 7 and 10^a

Copolymer	$m_1 : m_2$	dn/dc (mL/g)	$M_w \times 10^{-5}$ (g/mol)	$A_2 \times 10^4$ (mL mol/g ²)
7a	5 : 95	0.1404 ± 0.0009	1.450 ± 0.039	3.784 ± 0.410
7b	14 : 86	0.1536 ± 0.0023	1.814 ± 0.032	3.516 ± 0.116
7c	35 : 65	0.1548 ± 0.0014	3.746 ± 0.045	1.613 ± 0.084
7d	58 : 42	0.1600 ± 0.0041	4.792 ± 0.073	1.358 ± 0.079
7e	73 : 27	0.1620 ± 0.0020	4.370 ± 0.053	1.349 ± 0.071
10a	5 : 95	0.1333 ± 0.0058	1.372 ± 0.033	2.499 ± 0.196
10b	18 : 82	0.1544 ± 0.0023	1.916 ± 0.034	2.984 ± 0.122
10c	34 : 66	0.1696 ± 0.0002	1.966 ± 0.157	2.065 ± 1.019

^a Poly(*o*-MAPHA-Na): dn/dc = 0.17 ± 0.0002 mL/g, M_w = 0.9934 ± 0.054 × 10⁵ g/mol, A_2 = 1.791 ± 0.113 mL/mol⁻¹/g⁻².

25°C and 0.5M NaCl. In general, the molar mass for copolymers 6–11 ranged from (1.806 ± 0.064) × 10⁴ to (7.706 ± 0.536) × 10⁵, with the molar mass increasing as M_1 of 1 and 2 in the copolymer increased. Table VIII shows some representative values. The values of A_2 are close to zero, meaning that the strength of the interaction between the molecules and the solvent is equivalent to the molecule-molecule interaction strength. Under these conditions, the solvent is a theta solvent and the chains of the polymer approach an ideal configuration.

CONCLUSIONS

Copolymers of *o*- and *p*-MAPHA-Na with AA-Na, AM-Na, and AAD were prepared by free radical polymerization in aqueous solution. The copolymer compositions were calculated from the arsenic content of the copolymers, as determined from AAS measurements.

The reactivity ratios were calculated by the KT linearization method, as well as the EVM using the computer program RREVM[®]. The reactivity ratios calculated with the KT method correlated well with those obtained by the EVM method. The 95% confidence region (also calculated with computer program RREVM[®]), represented by the elliptical diagrams, confirmed a good approximation of the reactivity ratios, as indicated by the relatively small dimensions of the ellipses.

In all cases, $r_1 < 1$ and $r_2 > 1$, therefore, in this system, there is a tendency to form random copolymers richer in comonomer (i.e., AA-Na, AM-Na, or AAD). According to the radicals and comonomers structures, *o*- and *p*-MAPHA-Na radicals add preferentially to AA-Na and AM-Na, probably due to steric hindrance and electrostatic repulsion. Perhaps the addition of *o*- and *p*-MAPHA-Na radicals to their respective monomers is more hindered than the addition to AA-Na and AM-Na. With respect to electrostatic repulsions among *o*- and *p*-MAPHA-Na radicals and AA-Na and AM-Na, these forces are

probably less than electrostatic repulsions among their respective monomers. On the other hand, AAD does not have a formal charge and this factor could be the cause for the preferred addition of the *o*- and *p*-MAPHA-Na radicals.

The authors acknowledge the PhD scholarship to BAY-M.

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