

## Water soluble copolymers using functionalized monomers (sodium *o*- and *p*-methacryloylaminophenylarsonate). Synthesis and Characterization.

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### 1. 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 (MA-Na) **4** and acrylamide (AAD) **5** were prepared by free radical polymerization in aqueous media at 70°C using potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) as initiator. The total monomer concentration was carried out at 0.5M and the feed ratio (M<sub>1</sub>:M<sub>2</sub>) was varied from 10:90 to 90:10 mol%. The copolymer compositions were determined from atomic absorption spectroscopy and <sup>1</sup>HNMR. The reactivity ratios (*r*<sub>1</sub> and *r*<sub>2</sub>) calculated by Fineman-Ross method for poly(*o*-MAPHA-Na-co-AA-Na) **6** were *r*<sub>1</sub> = 4.53 and *r*<sub>2</sub> = 75.67; for poly(*o*-MAPHA-Na-co-AM-Na) **7**, *r*<sub>1</sub> = 4.52 and *r*<sub>2</sub> = 2.43; for poly(*o*-MAPHA-Na-co-AAD) **8**, *r*<sub>1</sub> = -1.25 and *r*<sub>2</sub> = 0.36; for poly(*p*-MAPHA-Na-co-AA-Na) **9**, *r*<sub>1</sub> = 1.06 and *r*<sub>2</sub> = -0.03; for poly(*p*-MAPHA-Na-co-AM-Na) **10**, *r*<sub>1</sub> = 9.52 and *r*<sub>2</sub> = 1.59; and for poly(*p*-MAPHA-Na-co-AAD) **11**, *r*<sub>1</sub> = 5.93 and *r*<sub>2</sub> = 3.04. The values suggest block copolymers formation. However, copolymers obtained could have large blocks of *o*- or *p*-MAPHA-Na and short blocks of comonomer. Copolymers weight-average molecular weight ( $\overline{M}_w$ ) of copolymers was between 6.3x10<sup>4</sup> - 7.7x10<sup>5</sup> g/ mol and were determined by low-angle laser light scattering.

### 2. Introduction.

The synthesis and use of functionalized water soluble polymeric materials have continuous research interest due to the possibility of introducing the properties of a functional group to high molecular weight materials. McCormick et al. [1-3] have conducted an extensive research on functional copolymers in order to prepare copolymers showing tolerance to added electrolytes. Such polymers have applications in viscosity modification, petroleum recovery, formulation of coatings and drag reduction. They reported the synthesis and structural study of copolymers using monomers with functional groups sulfonate (SO<sub>3</sub><sup>-</sup>) and carboxylate (COO<sup>-</sup>). The composition of the copolymers studied was conducted by determination of reactivity ratios using several methods like Fineman-Ross [4], Kelen-Tudos [5] and nonlinear least-squares [6]. *r*<sub>1</sub> and *r*<sub>2</sub> values of copolymers synthesized showed alternating and random

tendencies. Other important applications of functionalized copolymers are the use in medicine and biological systems. Hydrogels copolymers [7-8] and copolymers based on N-vinyl-2-pyrrolidone (NVP) [9-10] have been synthesized for this biological applications. The reactivity ratios are used to predict the copolymer composition and properties such as swelling, hydrophilic/hydrophobic balance, polarity and solubility of this kind of copolymers.

Our interest is the comparison of polymers obtained from copolymerization of functionalized monomers such as *o*-MAPHA-Na **1** and *p*-MAPHA-Na **2** with comonomers AA-Na **3**, AM-Na **4** and AAD **5** in aqueous media, because the copolymer produced may have striking features, which come from of the properties of arsonate group  $-\text{AsO}(\text{ONa})_2$  (chelating group [11]) with carboxilate ( $\text{COO}^-$ ) and amido ( $\text{CONH}_2$ ) (these groups are able to form coordination bonds with metal ions [12]).

In present work we report the synthesis and characterization of copolymers from **1** and **2** with **3**, **4** and **5** with at different feed ratio ( $M_1:M_2$ ). The copolymer compositions were determined from atomic absorption spectroscopy and  $^1\text{H}$ NMR. The reactivity ratios were determined by Fineman-Ross method in order to predict the structure of resulting copolymers and the absolute molecular weight.

### 3. Experimental section.

**3.1. Monomer Synthesis:** The *o*- and *p*-MAPHA monomers were obtained by condensation reaction of methacryloyl chloride with the corresponding *o*- and *p*-APHA, according to the reported procedure (yield 40% and 77% respectively) [13]. *o*- and *p*-MAPHA-Na, AA-Na and AM-Na were synthesized by neutralization reaction with NaOH (yield: 94%, 96%, 90% and 77%, respectively) [13].

**3.2. 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**, 75:25 **b**, 50:50 **c**, 25:75 **d** and 10:90 **e**.

General procedure to obtain these copolymers is the next: A solution at 0.5M of two monomers in water was placed in a 5mL flask. A solution of initiator was prepared in water and placed in the dilatometer. For all polymerization initiator concentration of was  $2 \times 10^{-3}$  mol/L. Both solutions were bubbled with ultrahigh-purity argon for 20 min and sealed with a rubber septum. Solution of monomers was added to a dilatometer using a syringe. The dilatometer was placed in a water bath at  $70^\circ\text{C}$  ( $\pm 0.02$ ) for 7h. The monomer conversion was

followed by volume contraction during polymerization. The polymerization was stopped by cooling the dilatometer in ice-water bath. The polymer was precipitated in acetone and washed first in ethanol or methanol and then in N,N-dimethylformamide at 138°C. The copolymers obtained were placed in a vacuum oven at 90°C for 36h. The structures of copolymers **6–11** were characterized by IR, and  $^1\text{H}$  NMR.

#### 4. Results and Discussion.

Composition of copolymers **6–11** at different feed ratios was determined by  $^1\text{H}$  NMR spectroscopy. In figure 1, copolymer composition plots of the mol% of **1** and **2** in the copolymer versus the mol% of **1** and **2** in the feed for copolymers **6–11** are shown. The short dashed lines which pass through the origin represent ideal incorporation while the curves through the data points were obtained by a spline smoothing fit. Copolymers synthesized exhibit a significant deviation from the dashed line and they have an azeotropic point. The azeotropic points are approximately 13 mol%, 40 mol%, 10 mol% and 25 mol % for the copolymers **6**, **7**, **10**, and **11** respectively. Above this point, more **1** or **2** is incorporated into copolymers than is present in the feed while below this point, less **1** or **2** is incorporated. This behavior suggests there is a tendency to form block copolymers, which is rarely encountered. Copolymers obtained will have large blocks of **1** or **2** and short blocks of comonomer. It seems *o*- or *p*-MAPHA-Na tend to form homopolymers. In copolymers **8** and **9**, monomers **1** and **2** are preferentially added at all compositions.

To further investigate the tendency to form blocks of these copolymers, reactivity ratios were determined. Fineman-Ross method was employed to calculate  $r_1$  and  $r_2$  values, and the results obtained are listed in table 1. The propensity to form block copolymers is the result of several factors like, electronic effects, coulombic repulsions and radical stability. Monomers used are electron accepting due to they have strong electron-withdrawing groups, in addition, all of them are anionically charged (excepted **5**).

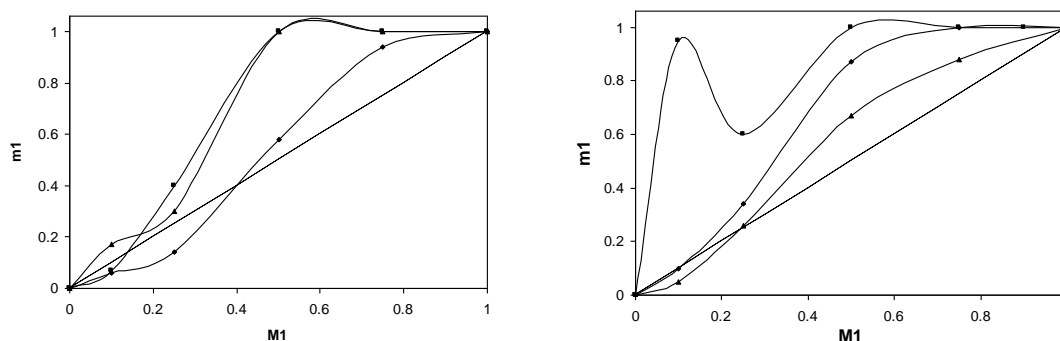


Figure 1. (a) Mol % of **1** in copolymer **6** (■), copolymer **7** (▲) and copolymer **8** (◆). (b) (a) Mol % of **2** in copolymer **9** (■), copolymer **10** (▲) and copolymer **11** (◆). The short dashed line represents ideal random incorporation.

Table 1. Reactivity ratios for copolymers obtained.

Copolymer	Fineman-Ross		$r_1 r_2$
<b>7</b>	$r_1 = 4.52$	$r_2 = 2.43$	10.9836
<b>10</b>	$r_1 = 9.52$	$r_2 = 1.59$	15.1368
<b>8</b>	$r_1 = -1.25$	$r_2 = 0.36$	-0.4450
<b>11</b>	$r_1 = 5.93$	$r_2 = 3.04$	18.0272
<b>6</b>	$r_1 = 453$	$r_2 = 75.67$	34278.51
<b>9</b>	$r_1 = 1.06$	$r_2 = -0.03$	-0.0346

## 5. Conclusions.

Monomers *o*- and *p*- MAPHA-Na only copolymerize with AA-Na, AAD, and AM-Na at low feed molar ratio forming block copolymers. Block copolymers obtained are richer in *o*- and *p*- MAPHA-Na.

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## 7. References.

1. Kathmann E.E., White L.A., McCormick C.L. *Macromolecules* 1996, **29**, 5268
2. McCormick C.L. and Salazar L.C. *Macromolecules* 1992, **25**, 1896
3. McCorkick C.L., Blackmon K.P. *J. Polym. Sci. Part A Polym. Chem.* 1986, **24**, 2635
4. Fineman M., Ross S. *J. Polym. Sci.* 1950, **5**, 259
5. Kelen T., Tudos F. *J. Macromol. Sci. Chem.* 1975, **A9**,1
6. Tidwell P.W., Mortimer G.A. *J. Polym. Sci. Part A.* 1965, **3**, 369
7. Atta A.M., Abdel-Azim A.A. *Polym. Adv. Technol.* 1999, **10**, 187
8. Nurkeeva A.S., Mun G.A., Sergaziyev A.D., Fefelova N.A., Sarsenbaeva A.S., Khutoryanskiy V.V. *J. Polym. Sci. Part B Polym. Phys.* 2006, **44**, 845
9. Bauduin G., Boutevin B., Belbachir M., Meghabar R. *Macromolecules* 1995, **28**, 1750
10. Alencar de Queiroz A.A., Gallardo A., San Román J. *Biomaterials* 2000, **21**, 1631
11. Cheng K.L., Ueno K., Imamura T. *Handbook of Organic Analytical Reagents*, CRC Press, Boca Raton, F.L. 1982
12. Rivas B.L., Pereira E.D., Moreno-Villoslada I. *Prog. Polym. Sci.* 2003, **28**, 173

13. Percino J. *PhD Thesis Dissertation*, University of Alma-Ata, Kazhaksthan, 1991