

Free Radical Polymerization Kinetics of Monomers Functionalized with $-\text{AsO}(\text{OH})_2$ in Aqueous Media

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ABSTRACT: The free radical polymerization kinetics of the isomer sodium salts of *o*- and *p*-methacryloylaminophenylarsonate in aqueous solution have been studied using a dilatometric method. The polymerizations, initiated with potassium persulfate, were carried out at a constant monomer initial concentration of 0.50 mol/L and the initiator initial concentration was fixed at one of the following: 1.00, 2.00, 5.00, 8.00, or 10.00 ($\times 10^{-3}$ mol/L). Another set of polymerizations were carried out at a constant initiator initial concentration of 2×10^{-3} mol/L and the monomer initial concentration was fixed at one of the following: 0.20, 0.30, 0.50, 0.70, or 1.00 (mol/L). The polymerization reactions were conducted isothermally at 70°C. The order with respect to initiator was consistent with the classical kinetic rate equation, while the order with respect to monomer was

greater than unity. The effects of temperature on the polymerization rate were also investigated and the activation energy gave values of 20.66, 22.68, and 23.22 kcal mol⁻¹ K⁻¹ over a temperature range of 50–70°C. For the case of *o*-methacryloylaminophenylarsonic acid monomer, its kinetic study was carried out in DMF as solvent and AIBN initiator. *p*-Methacryloylaminophenylarsonic acid was too insoluble in DMF to be studied. The polymers obtained were characterized by H-NMR, IR, and viscosity. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1662–1669, 2004

Key words: polymerization kinetics; dilatometry; water-soluble polymers; polyelectrolytes; sodium salts of *o*- and *p*-methacryloylaminophenylarsonate monomers

INTRODUCTION

Water-soluble polymers are of great importance in nature and of great interest from the scientific point of view. They are used as flocculators for sewage purification, for concentration and extraction of metals, reduction of hydrodynamic resistance, as structure formers for soils and so on.^{1,2} The interesting properties that are characteristic of polyelectrolytes are due to charged groups attached (generally, covalently) to the chain.³ Our interest was in obtaining new polyelectrolytes with the functional group $-\text{AsO}(\text{OH})_2$ (arsonic acid). The arsonic group is contained in different compounds of low molecular weight and therefore has been used for different analytical applications.⁴ For example, the compounds Arsenazo I [2-(4,5-dihydroxy-2,7-disulfo-3-naphthylazo)-phenylarsonic acid],^{5–8} Arsenazo III [2,7-bis(2-arsonophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonic acid],^{9–13} *o*-arsanilic acid, and phenylarsonic acid derivatives^{14–16} react with a wide variety of metal ions to form colored soluble chelates at different pH. The reactions are of practical importance because of their high selectivity.

Free radical polymerization of monomers with methacryloyl moieties is a convenient way to obtain linear homopolymers with arsonic acid groups ($-\text{AsO}(\text{OH})_2$) attached.^{17,18} The polymers produced may have noteworthy features, which come from those properties of the $-\text{AsO}(\text{OH})_2$ group and those properties of the polymeric matrix. Such polymers show a polyelectrolyte effect due to the presence of arsonic acid groups. Recently the flocculation capacity of suspended solids, as well as the turbidity removal efficiencies, have been determined¹⁹ for *o*- and *p*-methacryloylaminophenylarsonic acid (*o*-MAPHA and *p*-MAPHA) monomers.

Our interest in the polymerization kinetic studies of ionogenic monomers such as *o*-MAPHA and *p*-MAPHA appears because the polymerization reaction of monomers containing ionomer groups sometimes has a different behavior compared to a classical system.^{20–22} The results of a kinetic prior study^{22,23} of free radical polymerizations of the *o*-, *m*-, *p*-methacryloylaminobenzoic acid in ethanol, DMF, showed that the reaction rate decreased in the order *o*-MAB > *m*-MAB > *p*-MAB and the reaction order was found to be greater than 1. Also the reaction order in relation to the initiator was 0.50, as is the case of a classical system. In the polymerization kinetics²⁴ of the sodium salts of *p*- and *o*-methacryloylaminobenzenesulphonic acid in water and in water–acetic acid solutions, the

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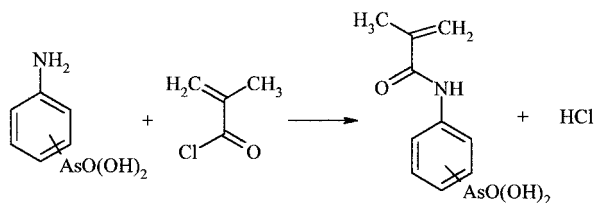


Figure 1 Condensation reaction to obtain the *o*-MAPHA and *p*-MAPHA.

authors reported that the initial rate of the reaction in an aqueous media increases abruptly and nonlinearly as the initial concentration of the monomer is increased. The orders found for the reaction with respect to the monomer decrease going from water to a water-acetic medium were from 1.84 to 1.33. Also a similar behavior is reported^{25,26} in the polymerizations of *N,N*-dialkylammonium chloride, *N,N*-diallylammonium chloride, and the sodium salts of *p*-styrene sulfonic acids, i.e., the increment in the reaction order with respect to the monomer increases as the initial concentration is increased.

Here, we report a study of the radical polymerization of two monomers: sodium *o*- and *p*-methacryloylaminophenylarsonate (*o*- and *p* MAPHA-Na) in aqueous media at 70°C using potassium persulfate as initiator, in which we have monitored the reaction through a well-established dilatometric method. Besides, the polymerization kinetics for the *o*-methacryloylaminophenylarsonic acid isomer in organic solvent DMF and AIBN were studied, which allowed us to compare the solvent effect on the polymerization rate. The polymerization rates (R_p) and reaction order with respect to *o*- and *p*-MAPHA was studied as a function of the monomer concentrations and initiator concentrations. The polymers obtained were characterized by H-NMR, infrared (IR), and viscosity.

Experimental

Materials and instruments

The initiators potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$, EM Science) and 2,2'-azobisisobutyronitrile (AIBN, Alfa Aesar) were used as supplied.

Melting points (mp) were measured with a SEV (0–300°C) apparatus and are uncorrected. Infrared spectra were recorded from KBr compressed tablets in a Nicolet Magna IR spectrophotometer Model 750. The H-NMR spectra were obtained on a Jeol Eclipse 400 MHz NMR spectrometer.

Monomer syntheses

The *o*- and *p*-MAPHA monomers and their sodium salt forms *o*- and *p*-MAPHA-Na (Figs. 1 and 2) were

synthesized and purified according to the method described in the literature.¹⁸

Preparation of the *o*-methacryloylaminophenylarsonic acid monomer

To an ethanolic solution (30 mL) of the *o*-aminophenylarsonic acid (46.1 mmol), freshly distilled methacryloyl chloride (55.3 mmol) was added dropwise. The reaction mixture was magnetically stirred for 2 h at 4°C. The *o*-MAPHA monomer precipitated with water at room temperature and after simple filtering and air-drying was obtained as a white powder (yield = 90%, mp = 145°C).

Preparation of the *p*-methacryloylaminophenylarsonic acid monomer

Treatment as above upon the same quantities of reagents gave the *p*-MAPHA monomer as a white powder also (yield = 93%, mp > 300°C).

Preparation of the *o*- and *p*-MAPHA monomers in their salt form

The salts were obtained by mixing the *o*- and *p*-MAPHA monomers (3.5 mmol) with NaOH (7.01 mmol) in 1 mL of water. The homogeneous solutions were treated with acetone to obtain white precipitates after air drying (mp > 300°C both).

Dilatometry

Dilatometry studies were carried out in a glass dilatometer (volume 5.00 mL) equipped with a capillary (length 13 cm) according to the literature.^{27,28} Monomer solutions were prepared in water or DMF that had concentrations of 0.20–1.00 mol/L. The initiators AIBN or $\text{K}_2\text{S}_2\text{O}_8$ were added and the dilatometer was filled. Oxygen was removed by bubbling the solutions with high purity argon gas and then sealed. The dilatometer was dipped in a water bath kept at constant temperature (± 0.02) with a DynaSense (Scientific Instruments, Inc.). The polymerization kinetics were carried out at monomer initial concentration that was kept constant at 0.50 mol/L with initiator initial

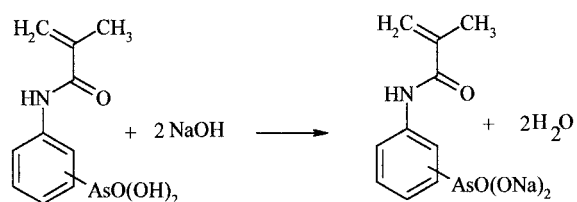


Figure 2 Reaction to obtain the sodium salts of *o*- and *p*-MAPHA-Na.

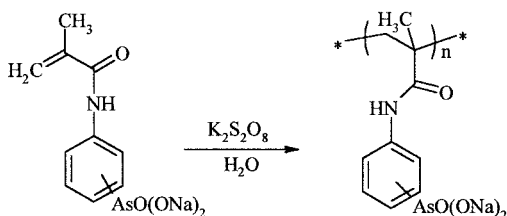


Figure 3 Polymerization reaction to obtain the poly(*o*- and *p*-MAPHA—Na).

concentrations of 1.00, 2.00, 5.00, 8.00, or 10.00 ($\times 10^{-3}$ mol/L). The initiator initial concentration was kept constant at 2×10^{-3} mol/L, while the monomer initial concentration was fixed at one of the following: 0.20, 0.30, 0.50, 0.70 and 1.00 mol/L. The monomer conversion was followed by volume contraction during polymerization.

Characterization

The products from the polymerization (Figs. 3 and 4) were characterized by IR and H-NMR and the results indicated that the polymerization was carried out.^{18,19} The principal evidence from IR for each monomer polymerization was the disappearance of the signal at 1,624 and 1,625 cm^{-1} due to stretching vibration of the C=C of the $\text{CH}_2=\text{C}(\text{CH}_3)-$ group, which was observed in the monomers *o*-MAPHA, *p*-MAPHA—Na, and *o*-MAPHA—Na spectra before polymerization, as well as a band at 905 and 885 cm^{-1} assigned to δ C—H for the geminal protons in the $\text{CH}_2=\text{C}(\text{CH}_3)-$ group. The H-NMR spectrum of each compound shows that the two singlets due to geminal protons $\text{CH}_2=\text{C}(\text{CH}_3)-$ between 5.6192 and 6.0330 ppm. have disappeared.

Viscometric measurements

Measurements were conducted with a temperature-controlled bath using an Ubbelohde glass capillary viscometer. The relative viscosities of sample solutions with a different concentration at 25°C using DMF and a solution of 0.1N NaOH as solvent with subsequent dilutions from 0.20–0.70 $\text{g}(\text{dL})^{-1}$ were determined.

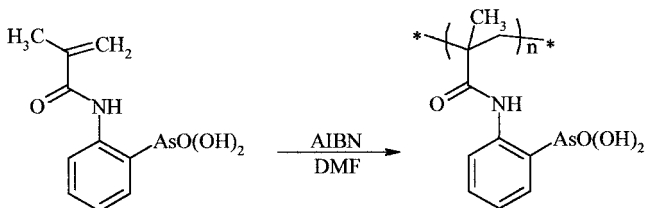


Figure 4 Polymerization reaction to obtain the poly(*o*-MAPHA).

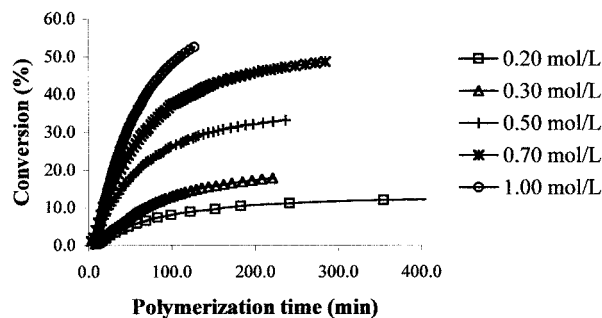


Figure 5 Effect of *o*-MAPHA monomer concentration on the conversion rate [M_0] = 0.20–1.00 mol/L, $[I] = 2 \times 10^{-3}$ mol/L, $T = 70^\circ\text{C}$, in DMF.

Reduced (η_{sp}/c) viscosities were calculated and extrapolated to zero concentration to give the intrinsic viscosities.

RESULTS AND DISCUSSION

The *o*- and *p*-MAPHA monomers and their sodium salts (*o*-MAPHA—Na, *p*-MAPHA—Na) do not polymerize without an initiator.

The polymerization of the monomers *o*-MAPHA, *o*-MAPHA—Na, and *p*-MAPHA—Na was studied over a concentration range of 0.20–1.00 mol/L, using an initiator concentration kept at a constant value of 2.00×10^{-3} mol/L and a reaction temperature kept constant at 70°C. Figures 5, 6 and 7 show the conversion versus polymerization time at different monomer concentrations. All the curves showed the same trend with an increase in conversion as the polymerization proceeded, i.e., the conversion also increased with increasing monomer concentration.

The ideal model of free radical polymerization is simple in that the initiator decomposes, giving free radical fragments (primary radicals), the monomer adds on the radical, and termination occurs by mutual deactivation between two macroradicals. Steady-state

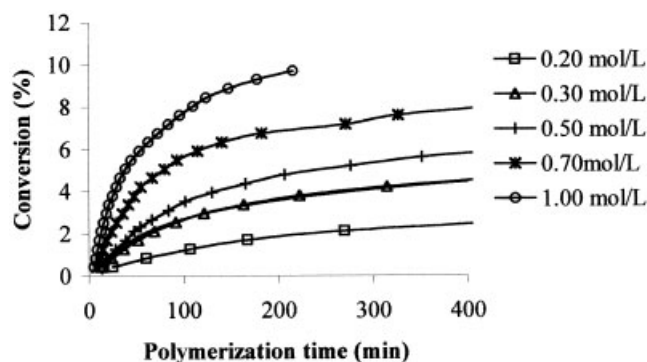


Figure 6 Effect of *o*-MAPHA—Na monomer concentration on the conversion rate [M_0] = 0.20–1.00 mol/L, $[I] = 2 \times 10^{-3}$ mol/L, $T = 70^\circ\text{C}$, in aqueous media.

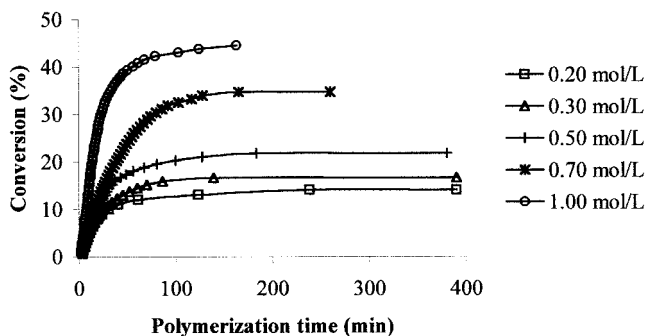


Figure 7 Effect of *p*-MAPHA-Na monomer concentration on the conversion rate $[M_0] = 0.20\text{--}1.00$ mol/L, $[I] = 2 \times 10^{-3}$ mol/L, $T = 70^\circ\text{C}$, in aqueous media

free radical concentrations are maintained in the course of this ideal reaction. Often one needs to compare experimental observations from a specific initiator–monomer–solvent system with ideal behavior and explain any deviations from such reference kinetic models. A simple approach to achieve this would be to use eq. 1

$$R_p = \frac{k_p}{k_t^{1/2}} \times \{2f \times k_d\}^{1/2} [M_0][I_0]^{1/2} \quad (1)$$

where k_d , k_p , and k_t are the initiator decomposition, propagation, and termination rate constant, respectively; f is the initiator efficiency factor (a constant for the initiator–monomer–solvent system), $[M_0]$ and $[I_0]$ are the initial monomer and initiator concentration, respectively; a factor of 2 arises from the decomposition of a mol initiator. The term $k_p/k_t^{1/2}$ is a characteristic ratio that is a measure of a given propensity for kinetic growth. Because K is constant, keeping any one of the second or third terms in the eq. 2 constant at a giving time, the $\ln R_p$ versus $\ln[M_0]$ plots at constant $[I_0]$ and $\ln R_p$ versus $\ln[I_0]$ at constant $[M_0]$, plots were made. They are shown in Figures 8, 9, and 10.

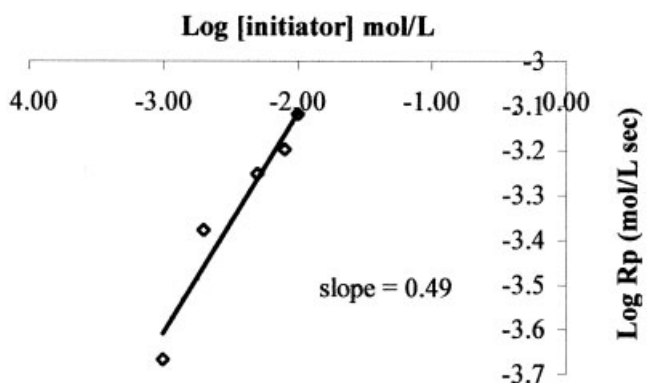


Figure 8 Variation of $\log R_p$ with $\log [AIBN]$ and fixed $[o\text{-MAPHA}] = 0.50$ mol/L at 70°C in DMF.

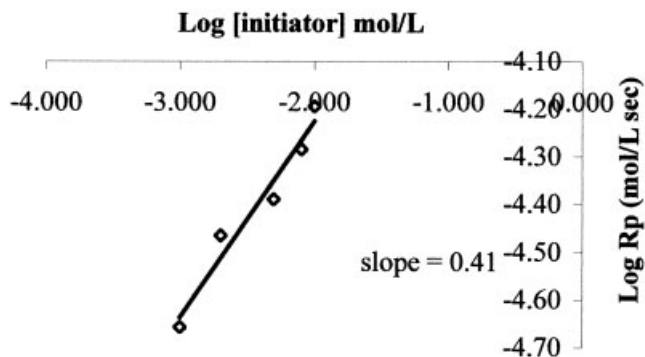


Figure 9 Variation of $\log R_p$ with $\log [K_2S_2O_8]$ and fixed $[o\text{-MAPHA-Na}] = 0.50$ mol/L at 70°C in H_2O .

$$\ln R_p = \ln K + \ln[M_0] + \frac{1}{2} \ln[I_0] \quad (2)$$

The conversion increased with polymerization time and it also increased with increasing initiator concentration. The dependence of polymerization rate with respect to the $[AIBN]$ or $[K_2S_2O_8]$ is considered to be one-half, which clearly indicates that termination occurs through bimolecular interaction of growing polymer radicals.²⁹

It was possible to measure the initial reaction rate in an aqueous media and DMF for the monomer *o*-MAPHA, but for *p*-MAPHA-Na its kinetics were only followed in aqueous media.

According to the mechanism of polymerization, one expects the order with respect to the monomer concentration to be between 1 and 2. Even though rare, an order near 2.5 with respect to monomer concentration has been accounted for³⁰ and observed.

From Figure 11 it can be seen that the influence of aqueous media in the R_p of *o*-MAPHA, *p*-MAPHA-Na, and *o*-MAPHA-Na and the reaction orders found with respect to the monomers were greater than the first order in monomer concentration: 2.20, 1.77, and 2.22, respectively (Fig. 12). Values corresponding to

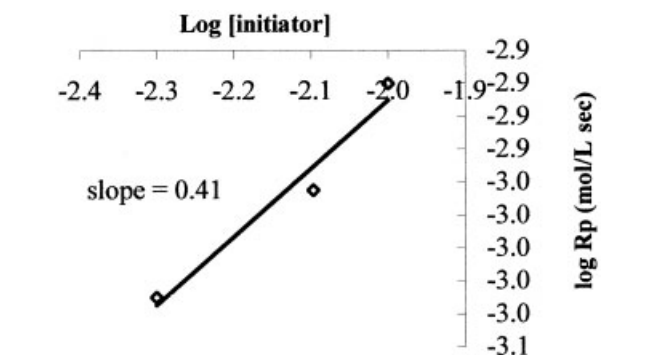


Figure 10 Variation of $\log R_p$ with $\log [K_2S_2O_8]$ and fixed $[p\text{-MAPHA-Na}] = 0.50$ mol/L at 70°C in H_2O .

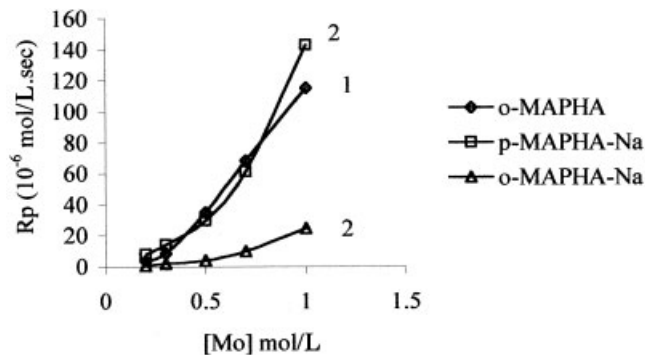


Figure 11 Dependence of the polymerization rate of the *o*-MAPHA on its concentration in DMF (1), *p*-MAPHA-Na, and *o*-MAPHA-Na on their concentration in water (2).

the slope of the linear fitting for the data were obtained. Such an increased dependence of the rate on the monomer may be an uncommon result but, from data available in the literature, one can show that, although an order of reaction of unity should be expected, a value greater than unity can be experienced in some conditions as reported for acrylic acid,^{31,32} methyl methacrylate,³³ acrylamide,³⁴ 1-vinyl-2-pyrrolidone,³⁵ and sodium acrylate.³⁶

The abnormality of the orders with respect to the monomer concentration and the change in its value as the initial concentration is increased has been previously reported for the polymerization of the *N,N*-dialkylammonium chloride and *N,N*-diallylammonium chloride and the sodium salt of *p*-styrene sulfonic acids.^{25,26} An increase in the order with respect to the monomer on going from water to aqueous-organic media has been reported in the case of sodium *p*-styrene sulfonate.³⁷ Orders greater than unity have been previously explained by solvent-transfer,^{38,39} complex⁴⁰, or cage effect⁴¹ theories.

On the other hand, the increase in the polymerization reaction is clearly connected with a corresponding increase in the ratio of the elementary kinetic constants for propagation and termination caused by the

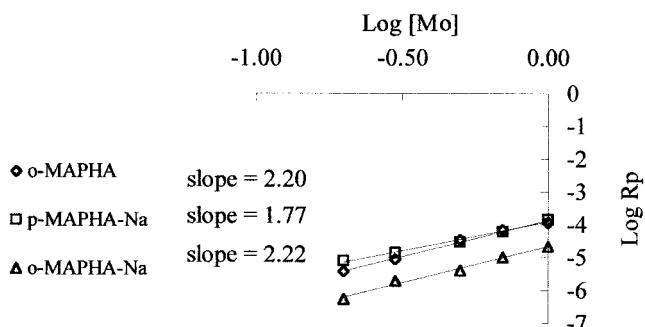


Figure 12 Variation of $\log R_p$ with $\log [M_0]$ and fixed $[I]$ at 70°C.

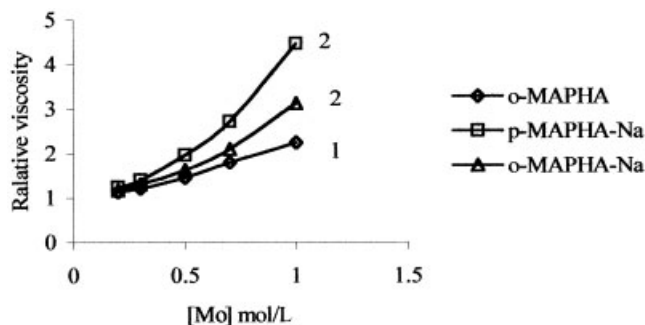


Figure 13 Concentration dependence of the relative viscosity of DMF solutions (1) and aqueous solutions (2) of *o*-MAPHA and *p*-MAPHA-Na and *o*-MAPHA-Na.

comparatively high viscosity of the initial solutions.^{24,25}

To confirm the former explanation, the dependence of the relative viscosity (η_{rel}) of the initial solutions on the monomer concentration in aqueous and DMF solutions was investigated (Fig. 13).

One can observe in Figure 13 that η_{rel} increases as the concentrations of *o*-MAPHA, *p*-MAPHA-Na, and *o*-MAPHA-Na are increased in all cases, nevertheless the increment was more abrupt for *p*-MAPHA-Na. The rate constant for bimolecular chain termination k_0 , is known to depend on the viscosity of solutions.²⁵ An increase in viscosity with an increase in monomer concentration leads to a substantial decrease in the termination rate. As a result, an abrupt and nonlinear increase in the polymerization rate (R_p) occurs in the range of monomer concentration $[M_0]$ studied. To take into account the relative viscosity of the monomers, the experimentally obtained data were presented graphically in Figure 14, using the coordinates of $\log R_p$ and $\log [M_0]\eta^{1/2}$. It may be observed that the dependence of the polymerization rate on the concentration of the initial solutions is linear and the order of the reaction with respect to the monomer is closer to unity compared to results in Figure 12.

To determine the activation energy, separate measurements were conducted at constant monomer con-

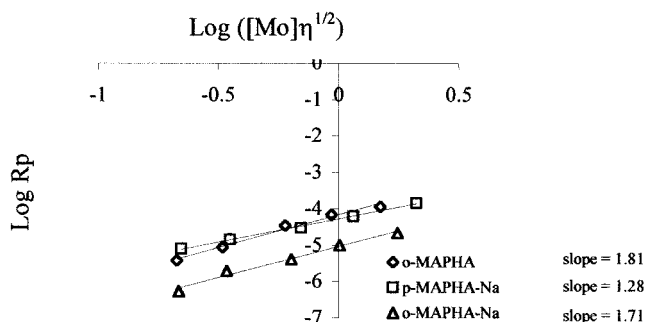


Figure 14 Variation of $\log R_p$ with $\log ([M_0]\eta^{1/2})$ and fixed $[I]$ at 70°C.

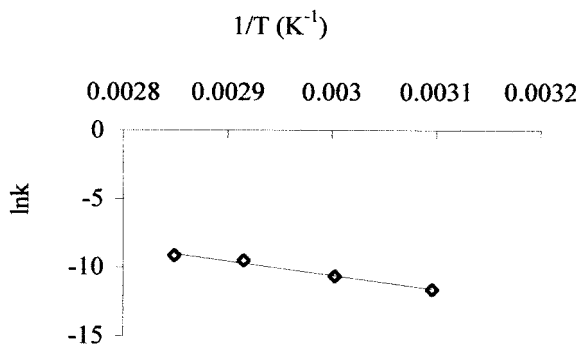


Figure 15 Plot of $\ln k$ versus $1/T$ for the *o*-MAPHA to obtain the kinetic parameter E_a of the reaction.

centration (0.50M) and initiator concentration of 2×10^{-3} mol/L while varying the temperature ($T = 50-70^\circ\text{C}$). The well known Arrhenius equation

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

gives the dependence of a kinetic constant upon the absolute temperature (T), where A and R are constants and E_a is the activation energy of the reaction.

From the logarithmic dependence of initial rate of polymerization the kinetic rate (W) of the reaction was derived:

$$W = k[I]^a[M]^b \quad (4)$$

Where $a \approx 0.50$, $b = 2.20$, 1.77 , and 2.22 for the *o*-MAPHA, *p*-MAPHA—Na, and *o*-MAPHA—Na monomers in DMF and water, $[I]$ is the initial concentration of the initiator in mol/L, $[M]$ is the initial concentration of the monomer in mol/L.

The activation energy was obtained from the slope of the curve $\ln k$ versus $1/T$, multiplied by $-R$. Experimental points for *o*-MAPHA and the corresponding linear fitting are shown in Figure 15.

The measured and calculated values for other the monomers *o*-MAPHA, *p*-MAPHA—Na, and *o*-MAPHA—Na are summarized in Table I.

The activation energy (E_a) from polymerization (Table I) changes inversely with respect to the process

TABLE I
Kinetic Parameters (rate R_p) and Activation Energy (E_a) of the Radical Polymerization of *o*-MAPHA, *p*-MAPHA—Na, and *o*-MAPHA—Na

Monomer	$R_p \times 10^6 / (\text{mol L}^{-1} \text{s}^{-1})$				E_a (Kcal mol ⁻¹)
	50°C	60°C	70°C	78°C	
<i>o</i> -MAPHA	3.22	8.55	26.21	38.41	20.66
<i>p</i> -MAPHA—Na	3.90		31.54	64.63	22.67
<i>o</i> -MAPHA—Na	0.51	1.12	3.82	8.70	23.20

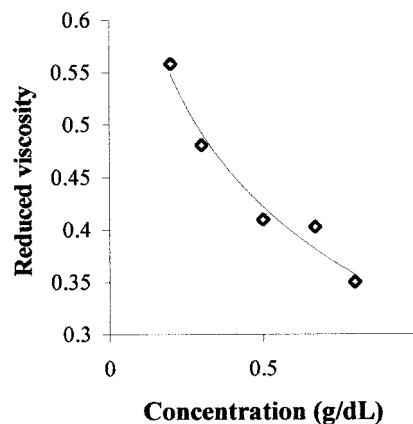
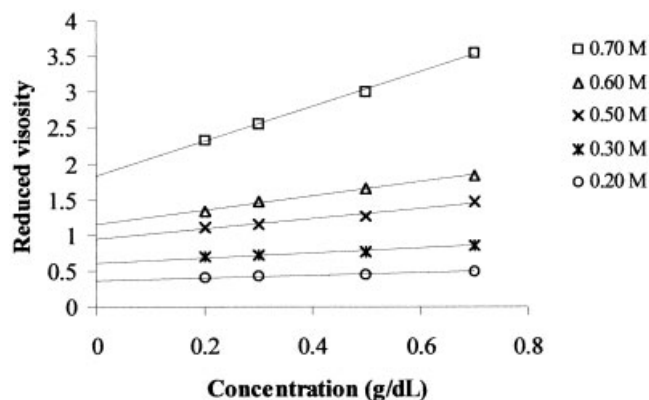


Figure 16 Dependence of the reduced viscosity versus the concentration of poly(*o*-MAPHA—Na) in water; polymer obtained at $[M] = 0.70$ mol/L and $[I] = 2 \times 10^{-3}$ mol/L.



(a)

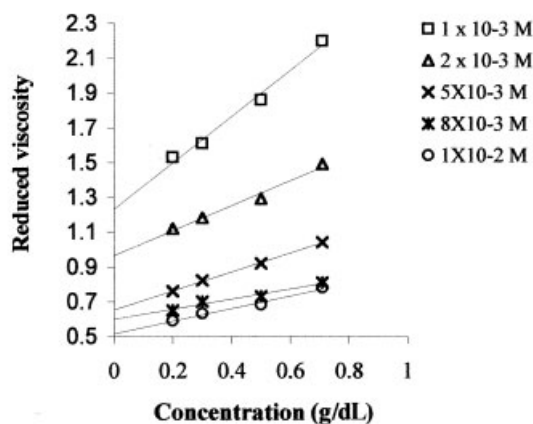


Figure 17 Dependence of the reduced viscosity from the concentration of poly-*o*-MAPHA solutions in 0.1N NaOH at (a) $[M]$ and (b) $[I]$.

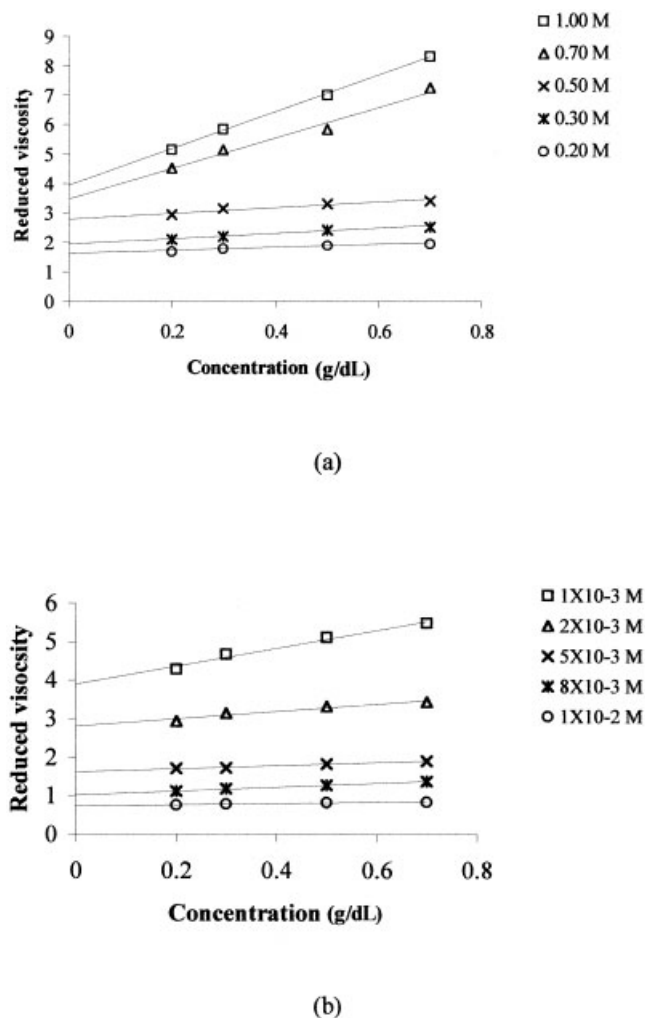


Figure 18 Dependence of the reduced viscosity from the concentration of poly-*p*-MAPHA-Na solutions in 0.1N NaOH at (a) [M] and (b) [I].

rate and for *o*-MAPHA and its salt form was observed to be an influence of the solvent in the process rate o -MAPHA > *o*-MAPHA-Na, but *p*-MAPHA-Na had a similar behavior with respect to the acid form of *o*-MAPHA monomer, which was different from the other functional monomers reported.²²

The polymer products (white powders) are readily soluble in water, dimethylsulfoxide (DMSO), or DMF. The values of the viscosity of the polymer solutions show that the synthesized high molecular weight products behave as polyelectrolytes as can be seen in Figure 16. Due to electrostatic interactions between the charged groups along the chain, the polyelectrolyte solutions show quite different behavior compared with neutral polymers regarding colligative properties (activity coefficients, osmotic coefficients) as well as transport properties (viscosity, diffusion, etc). Thus, it is well known that, in the case of pure solutions of ionic polymers or in the presence of low amounts of low molecular weight electrolytes, the η_{sp}/c versus c

curves are asymptotically against the ordinate or show a maximum.^{42,43} These η_{sp}/c versus c curves cannot be intrinsic viscosity determination. This problem can be solved in two ways: (1) by means of empirical equation;⁴⁴⁻⁴⁶ or (2) through screening of charges by addition of low molecular weight salts, i.e., NaOH, NaCl, KCl, etc. The characterization by viscometry of functionalized polymers gave the results shown in following Figures 17, 18, and 19. Obviously we chose the second way. Figures 13-15 show the variation of the

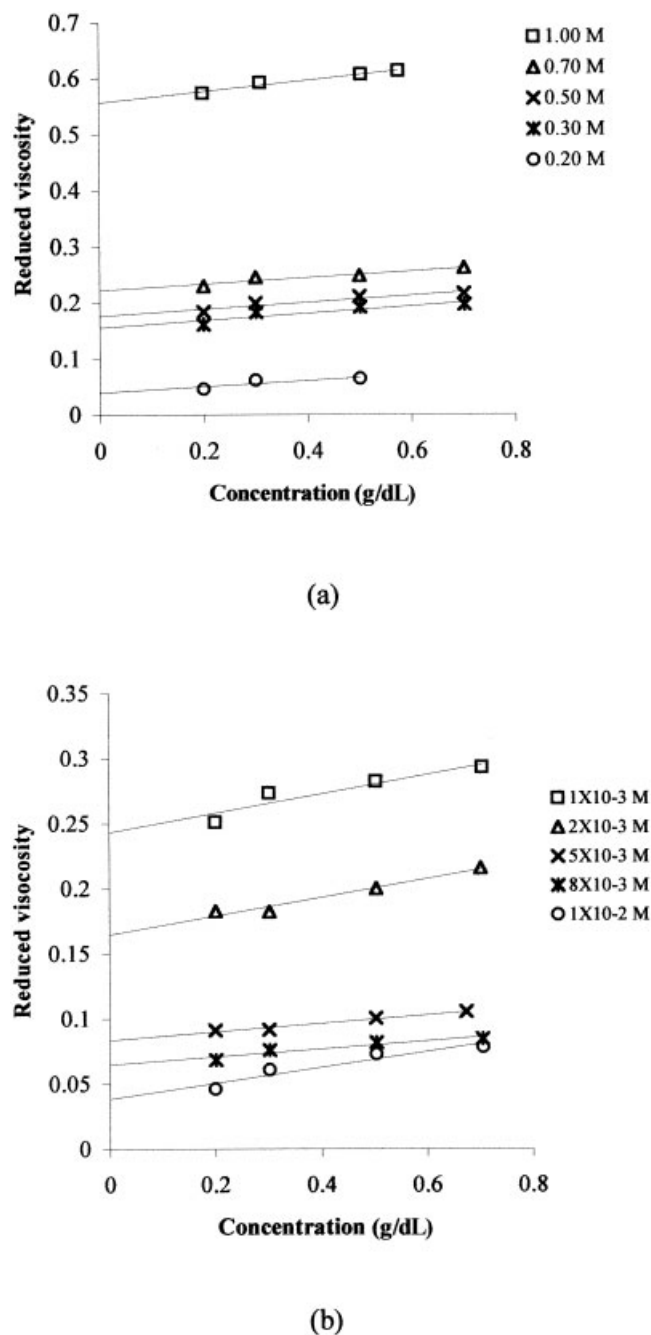


Figure 19 Dependence of the reduced viscosity from the concentration of poly-*o*-MAPHA-Na solutions in 0.1N NaOH at (a) [M] and (b) [I].

reduced viscosity versus polymer solution concentration, polymer solutions in 0.1N NaOH. It is evident from the intrinsic viscosity values from the regression of η_{sp}/c against polymer concentration obtained from viscometry that, for the poly(*o*-MAPHA) and poly(*o*-MAPHA-Na), polymerization in water can reduce the molecular weight, whereas for poly(*p*-MAPHA-Na) the water can produce an increase in the molecular weight.

CONCLUSION

The relevancy of the studied polymers is that they are polyelectrolytes having both properties of arsanilic acid derivatives with its complexing features embedded in an polymeric matrix. Results reported in this paper show clearly the importance of dilatometry to follow the polymerization kinetics reactions of anionic monomers *o*-MAPHA, *o*-MAPHA-NA, and *p*-MAPHA-NA in water and DMF. Kinetic parameters such as reaction rate and orders of reaction with respect to monomer concentration and with respect to initiator concentration can be easily derived from curves of $\log R_p$ versus $\log [I]$ and $\log [M]$. Results of R_p versus monomer concentration was greater for *p*-MAPHA-NA than for *o*-MAPHA-NA, which was an indication that the bimolecular processes rate constant k_0 depends on the viscosity of the studied solution. Also the polymers showed a typical polyelectrolyte behavior in absence of added salt, i.e., the η_{sp}/c values decreased with the concentration of polymer solution generally related to the expansion of the macroion chain. This behavior is ideal for flocculation applications mainly of heavy metal removal from wastewater.

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