Spectroscopy of Auramine Fluorescent Probes Free and Bound to Poly(Methacrylic Acid)

Robson Valentim Pereira and Marcelo Henrique Gehlen*

Instituto de Química de São Carlos, Universidade de São Paulo, 13560-590, São Carlos, SP, Brazil

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Auramines containing a vinyl group with strong electron-withdrawing substituent exhibit a π-conjugated extended effect that gives a red shift in their absorption and emission bands. The new fluorochromic dyes were bound to poly(methacrylic acid) (PMA), and their photophysical dynamics in methanol and in aqueous solution were studied. These derivatives were also used as optical probes for copolymerization process. The process was monitored by the changes in electronic absorption with a concomitant fading of the free vinyl auramine absorption band in the red and an appearance of a UV band ascribed to dye bound to the polymer chain. The conformational transition of PMA with solvent and pH was clearly observed by the drastic changes in the photophysical properties of these auramine derivatives attached to the polymer chain. Time-resolved experiments revealed an unusual long-lived decay component of about 2.2−2.6 ns in aqueous solution at low pH together with two picosecond components (50 and 570 ps). Such long decay was only reported in the literature for auramine adsorbed in solid matrices. It was ascribed to the fraction of bound auramine in a region of compact coil of PMA.

Introduction

Auramine O [(4,4'-(imidocarbonyl)bis (*N*,*N*-dimethylamine) monohydrochloride] is a diphenylmethane cationic dye which is weakly fluorescent in nonviscous solvents.[1−3] In the literature, the low quantum yield and subsequently fast dynamics of the auramine O are related to the torsion motion of the phenyl rings opening a nonradiative decay to the ground state.[1,3] Such similar effect was also observed in triphenylmethane dyes.[4] This effect reduces the fluorescence lifetime, and the excited-state dynamics occurs in a subpicosecond time scale, usually measured by fluorescence upconversion[3,5−8] or by ultrafast transient lens[3,9−10] techniques.

The excited state dynamics of Auramine O in glycerol or in alcohols was demonstrated to depend on the solvent viscosity and temperature.[1,2] Its absorption and emission spectra are known to be weakly solvent dependent.[2] When this dye is in nonviscous solvents, such as ethanol and propanol, a fast fluorescence decay dynamics is found, with a multiexponential behavior and decay times of a few picoseconds.[3,5−9] However, when this dye is dispersed in a viscous medium, such as polymeric acids and DNA, fluorescence quantum yield and lifetime increase.[1−3,11−14] For example, in the presence of DNA, a multiexponential character was found, and the longer lifetime recovered is about one ns.[2] Because of this dependence with viscosity, auramine is used as a probe for local viscosity in polymers and in micellar media.[10,15−17] In a rigid medium, long lifetimes are observed with a fluorescence dynamics occurring in nanoseconds. For example, when auramine is dispersed in a solid polymer[18] or adsorbed onto microcrystalline cellulose,[19] a long lifetime of about 2 ns in addition to a blue shift in both absorption and emission spectra have been observed.[18,20−21]

In this work, auramine was functionalized with a vinyl group containing C═O and CN electron acceptors. These derivatives have interesting photophysical properties induced by the presence of electron withdrawing groups. Moreover, auramine derivatives were studied as probes for polymerization, but in our case, the changes in electronic absorption were used to monitor the process and not the fluorescence signal, as usually reported in the literature.[22−24] These new dyes were inserted into poly(methacrylic acid), their spectroscopic studies were done in methanol and in water, and the results are correlated with the PMA conformational transition in solution.

Experimental Section

Auramine Derivative and Copolymers. Auramine O in cationic form was converted into free-base by reaction with ammonium hydroxide solution, and the product dried at low pressure in a desiccator. A sample, 1.2 mmol, of vinylene reactant (ethyl (ethoxy-methylene)cyanoacetate or ethoxymethylene-malononitrile (98%, ACROS)) was added to 1.0 mmol of auramine free-base, both dissolved in ethanol, resulting in compounds I and II respectively (see step 1 in Figure 1). The system was gently heated under reflux for 6 h, cooled, and solvent evaporated under low pressure. The crude products were purified through flash chromatography using a concentration gradient of hexane/acetone, affording an orange and a violet solid, respectively to products I and II. Analysis: ($C_{23}H_{26}N_4O_2$) Yield = 55%, mp = 195 °C. Calc.: C 70.80, H 6.67, N 14.36%. Found: C 70.60, H 6.90, N 14.10%. FTIR (cm^{-1}, KBr) signals of the vinyl substituent: 2215 (CN), 1700 (C═O), 1597 (C═C). ^{1}H NMR ($CDCl_3$): 3.10 (s, 12H), 1.35 (t), 4.27 (q), OCH_2-CH_3, 6.67 (d, 4H), 7.49 (d, 4H), 8.39 (s, −CH═C−R).

($C_{21}H_{21}N_5$) Yield = 75%, mp = 232 °C. Calc.:C 73.47, H 6.12, N 20.41%. Found: C 73.30, H 6.10, N 20.34%. FTIR (cm^{-1}, KBr) signals of the vinyl substituent: 2210 (CN), 1589 (C═C). ^{1}H NMR ($CDCl_3$): 3.20 (s, 12H), 6.65 (d, 4H), 7.47 (d, 4H), 7.89 (s, −CH═C−R).

The copolymers were synthesized by using benzyl peroxide (BP) in a thermal initiated copolymerization of methacrylic acid (previous distilled under reduced pressure) at 70 °C, and with auramine derivatives in ethanol solution (under nitrogen atmosphere), resulting in the copolymers shown in step 2 in Figure

* Corresponding author. E-mail: marcelog@iqsc.usp.br.

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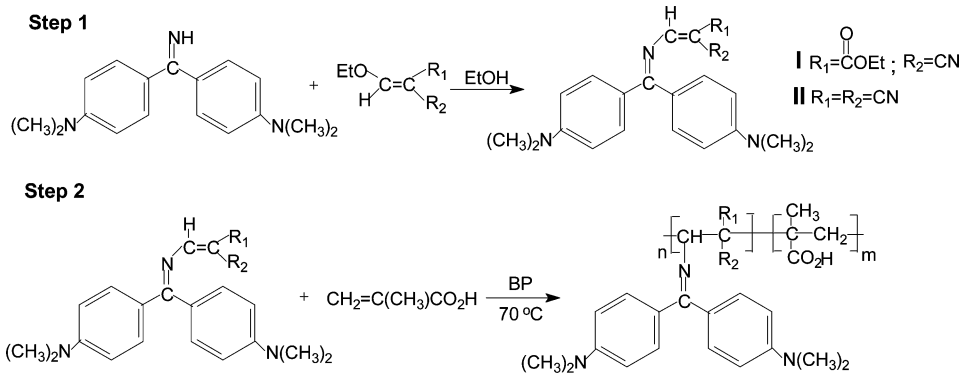

Figure 1. Synthesis of auramine derivatives (I and II) and copolymerization route with methacrylic acid ($m \gg n$). BP = benzyl peroxide.

1. These polymer materials were purified by multiple precipitations from methanol on addition of ethyl acetate. The viscosity-average molecular weights were determined by the intrinsic viscosity measurements of PMA in aqueous 0.002M HCl (T = 298 K), and using the Mark−Houwink equation and parameters given in the literature.[25] The values found are in the range of 151.000 g/mol, which are similar to those reported in the literature for PMA.[26]

Instrumentation. The FTIR and ^{1}H NMR spectra were obtained using a Bomem MB 102 and a Bruker AC 200 or DRX 400 spectrometers, respectively. Absorption measurements were performed on a Cary 5G−Varian spectrophotometer, and the corrected steady-state fluorescence spectra were recorded on a CD-900 Edinburgh spectrofluorimeter at 298 K. The pH of the aqueous solutions was measured on a Micronal pH meter. Dilute HCl and NaOH aqueous solution were used to control pH. The melting point was determined by differential scanning calorimetry (Shimadzu TA-50) under a nitrogen flow rate of 20 mL min^{-1}. Each sample was heated from 25 to 400 °C at 20 °C min^{-1}. The samples in fluorescence measurements were conditioned in a 1×1 cm quartz cuvette, thermostated by circulating fluid through a jacketed cuvette holder and in air-equilibrated conditions. Fluorescence decays in solution were measured by a time-correlated single-photon counting technique using a homemade ps spectrometer equipped with Glan-Laser polarizers in magic angle, a Peltier-cooled PMT-MCP (Hamamatsu R3809U-50) as photon detector, and Tennelec-Oxford counting electronics. The light pulse was provided by frequency doubling the 200 fs laser pulse of Mira 900 Ti−sapphire laser pumped by Verdi 5 W Coherent laser, and the pulse frequency was reduced down to 800 kHz by using a Conoptics pulse picker. The system provides an instrument response function (irf) of about 40 ps at fwhm. Decay traces were collected with 2 to 14 ps/channel over 1 kB data points. The fluorescence decays were analyzed by a reconvolution procedure with multiexponential decay models.[27] Thus, decays were fitted to a sum of the exponentials given by

$$I(t) = \sum_i b_i \exp[-t/\tau_i] \qquad (1)$$

where τ_i and b_i are the decay time and its normalized preexponential factor of the ith component (relative % is 100 b_i), respectively.

Results and Discussion

Auramine Derivatives. The electronic spectroscopy of the auramine derivatives in solution indicates that the effect of extended π-conjugation and the presence of strong electron-withdrawing groups modulate the photophysical properties of these dyes. This conjugation effect was observed early in similar compounds reported in the literature.[27−29] When compared with the precursor auramine, these derivatives have a larger red shift in the absorption spectra, with values of 25 and 35 nm for the compounds I and II, respectively. The photophysical parameters of these derivatives are reported in Table 1. The red shifts in absorption and emission spectra of the auramine derivatives and precursor are compared in Figure 2.

TABLE 1: Photophysical Properties of Auramine Derivatives (λ_{exc} = 420 nm, λ_{em} = 540 nm; T = 298 K)

system	solvent	λ_{abs} (nm)	λ_{em} (nm)	$\epsilon_{max} \times 10^3$ Lcm^{-1}1mol^{-1}	τ_1 ps (%)	τ_2 ps (%)
I	CH_3OH	459	539	50.0		
	C_2H_5OH	456	538	50.0		
	C_3H_7OH	455	538	51.0		
	C_4H_9OH	455	542	50.0	5 (92)	31 (8)
	$C_5H_{11}OH$	454	541	49.5	14 (90)	59 (10)
	$C_6H_{13}OH$	453	539	50.0	15 (86)	74 (24)
	$C_8H_{17}OH$	452	542	49.0	22 (84)	119 (26)
II	CH_3OH	471	545	42.0		
	C_2H_5OH	470	541	45.0		
	C_3H_7OH	469	543	40.0		
	C_4H_9OH	471	544	38.0		
	$C_5H_{11}OH$	469	542	37.0		
	$C_6H_{13}OH$	468	543	38.0	18 (85)	79 (25)
	$C_8H_{17}OH$	466	542	36.0	25 (84)	126 (26)

Steady state and time-resolved experiments show that the fluorescence dynamics of the derivatives is similar to that of the precursor dye. For instance, there is an increase of fluorescence with solvent viscosity in *n*-alcohols. This solvent spectral dependence for the compound I is illustrated in Figure 3, while in Figure 4 the time-resolved decays of I and II in hexanol and octanol are plotted.

The analysis of the decays shows that the deactivation of the fluorescence follows a biexpoential behavior with a transient in the ps time scale. The decay times calculated in some of the solvents used are listed in Table 1. These decay times observed are longer than those values reported for the precursor dye auramine.[5−8]

Auramine Derivatives as a Probe for Polymerization. There are several papers in the literature that describe the use of fluorescent probes to monitor polymerization rates.[22−24] Here, the absorption of the ICT band of auramine derivatives at 456 and 470 nm is used to report the copolymerization process in ethanolic solution. The fading of the red ICT band and the rise of an UV band centered on λ = 365 nm, which is ascribed to the dye bound to PMA chain, is shown in Figure 5. This color change is visible to the eye, and the solution goes from violet before reaction to pale yellow after polymerization.

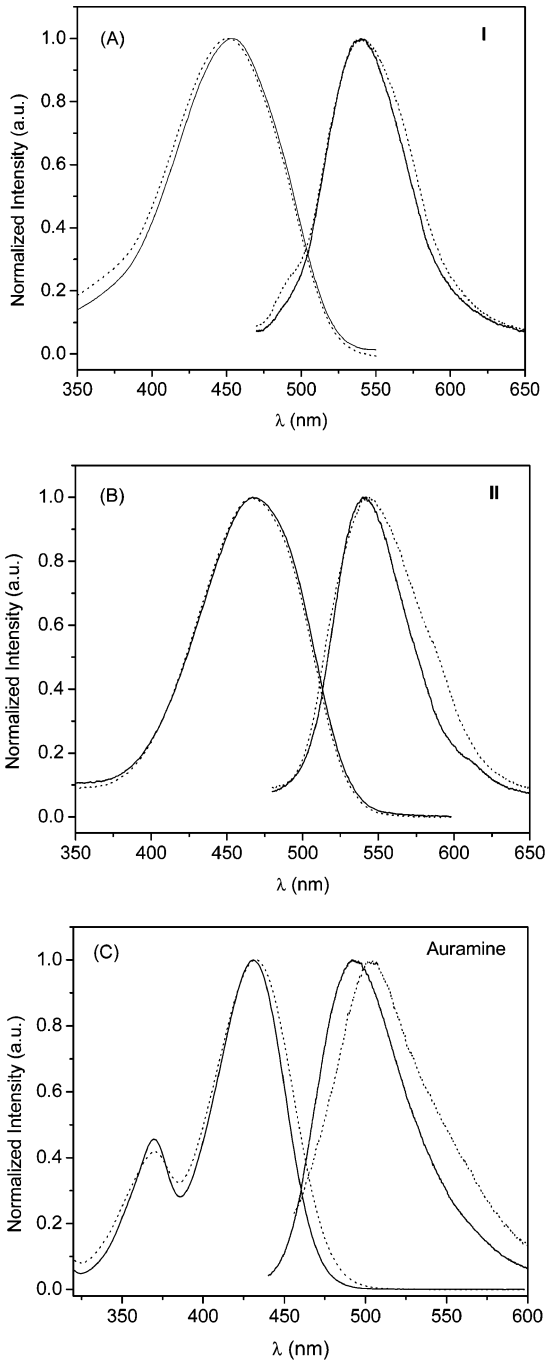

Figure 2. Normalized absorption and emission spectra of auramine derivatives. (A) compound I, (B) compound II. (—) water, (....) methanol.

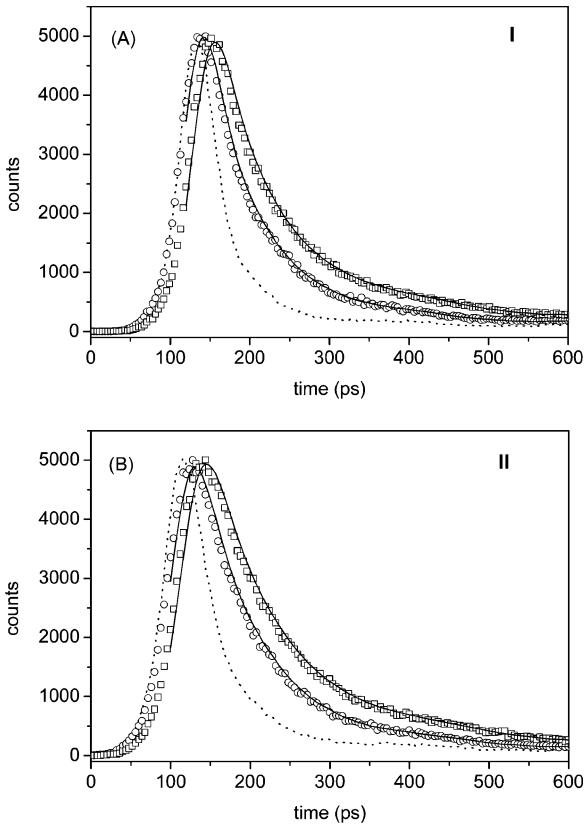

Figure 3. Fluorescence decays of (A) compound I, (B) compound II in *n*-alcohols. (....) irf, (□) octanol, (○) hexanol.

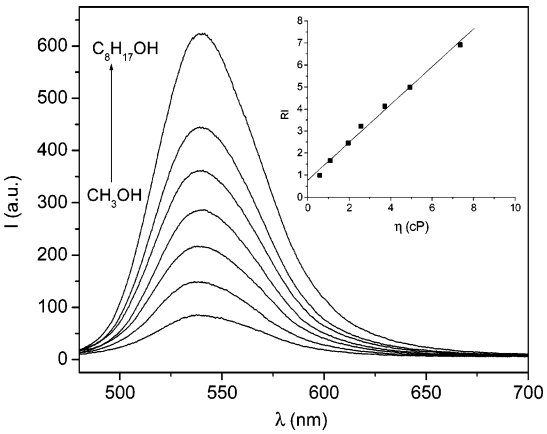

Figure 4. Emission spectra of compound II in *n*-alcohols. Inset is the relative intensity against solvent viscosity.

The blue shift is due to the break down of the charge conjugation (π-conjugation) system that precludes the optical transition with ICT character when auramine derivative is covalently bound to PMA chain. The inset in Figure 5 is the intensity of the two absorption bands with copolymerization time. The presence of a clear isosbestic point at 404 nm confirms the proposed reaction path. Also, the complete fading of the optical density at 470 nm indicates that full reaction conversion of the auramine monomer occurs.

Photophysics of Auramine Derivatives Bound to PMA. The attachment of auramine derivatives to poly(methacrylic acid) promotes significantly changes in their photophysical dynamics,[26,30−33] similar to what has been observed with some coumarin derivatives,[30] dansyl,[31] and pseudoisocyanine[32] in PMA polymer.

The first significant change observed is a large blue shift in the absorption and emission spectra upon insertion of the dye into the polymer chain. Contrasting with the precursor auramine dye and with our derivatives (I and II), which are weakly fluorescent compounds in nonviscous medium, I and II covalently bound to PMA have an appreciable emission quantum yield. The normalized absorption and emission spectra of the auramine derivatives attached to PMA in methanol and water (pH = 2) solutions are given in Figure 6.

Considering the well-known changes in conformation of the poly(methacrylic acid) with pH,[26,30−33] the emission spectra and decays of the auramine derivatives bound to PMA was evaluated within the range of pH of 2 to 8. The change in fluorescence intensity of copolymer II with pH is illustrated in Figure 7. The

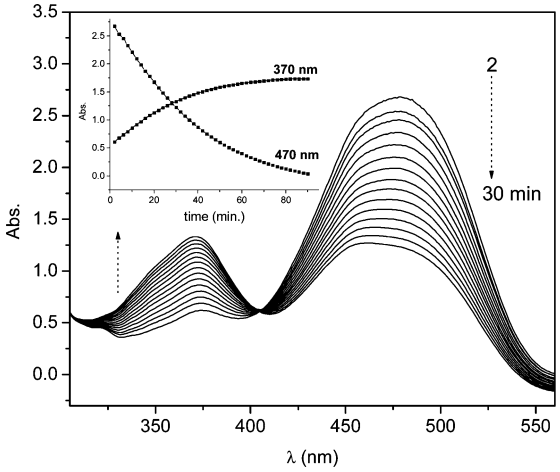

Figure 5. Change in the absorption spectrum of the compound II with polymerization time. Inset: Change the maximum of the red and UV absorption bands with polymerization time.

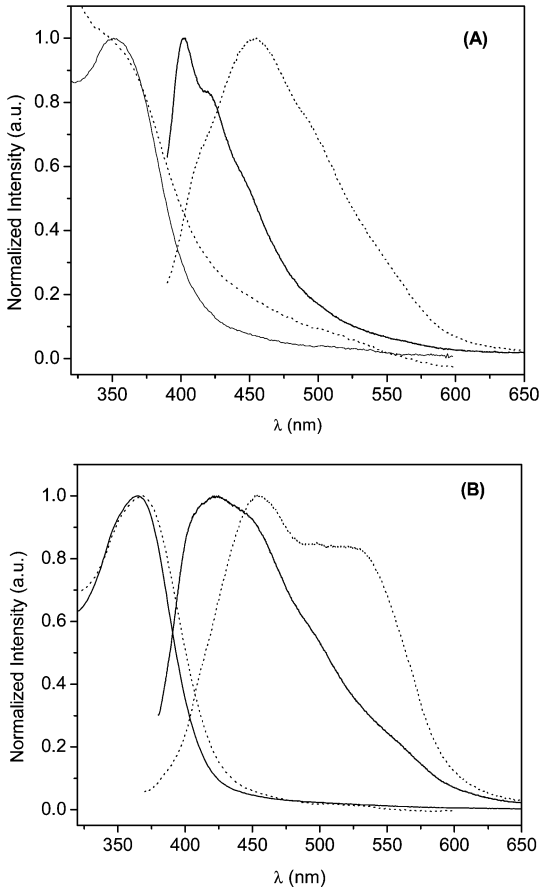

Figure 6. Normalized absorption and emission spectra of the auramine derivatives bound to poly(methacrylic acid) in methanol (—) and aqueous solutions (....). (A) copolymer I−PMA, (B) copolymer II−PMA.

inset shows the change in the maximum of the emission at λ_{em}= 455 nm with solution pH.

The high intensity of the fluorescence observed in low pH points out that this auramine probe bound to PMA is in a highly viscous microdomain. The small increase in the intensity between pH 2 and 4 occurs because PMA becomes even more compact in the initial stage of acid group ionization. This effect occurs due to the hydrogen bond interaction between deprotonated and neutral carboxyl groups.[33] This increase in emission with pH is similar to that of auramine dye in viscous medium.

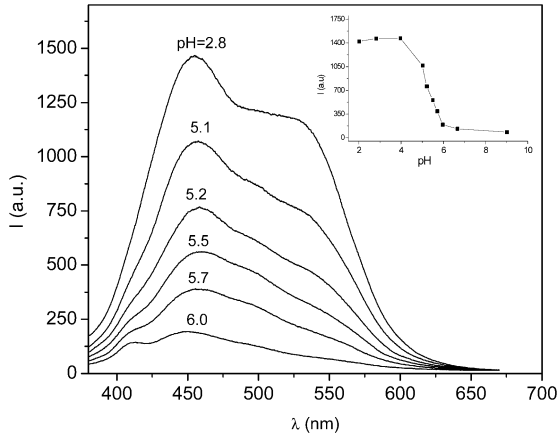

Figure 7. Change of the emission spectrum of copolymer II−PMA as a function of solution pH. Inset: change of the maximum emission intensity with pH.

TABLE 2: Fluorescence Lifetimes of Auramine Derivatives in Poly(methacrylic acid)[a]

system	solvent	λ_{em} (nm)	τ_1 ps, (%)	τ_2 ps, (%)	τ_3 ns, (%)
I−PMA	pH = 2	460	50 (58)	574 (30)	2.3 (12)
		490	72 (44)	568 (39)	2.3 (17)
		540	74 (33)	618 (43)	2.2 (24)
	pH = 6	460	17 (88)	395 (9)	2.5 (3)
	Methanol	460	7 (95)	42 (3)	1.4 (2)
		490	7 (94)	46 (5)	1.1 (1)
		540	13 (85)	55 (14)	0.6 (1)
II−PMA	pH = 2	460	35 (63)	542 (25)	2.4 (12)
		490	50 (46)	580 (36)	2.4 (18)
		540	38 (42)	578 (38)	2.4 (20)
	pH = 6	460	20 (89)	445 (8)	2.6 (3)
	methanol	460	5 (97)	45 (1)	1.4 (2)
		490	6 (95)	58 (2)	0.9 (3)
		540	7 (96)	56 (2)	0.7 (2)

[a] λ_{exc} = 380 nm, λ_{em} = 450 nm. Relative % is $100b_i$.

In addition, the quenching of auramine that is ascribed to the internal torsional relaxation motion forming a nonemissive charge transfer state (formally a twisted intramolecular charge transfer, TICT state) is precluded because of the compact chain conformation of the uncharged monomers at low pH. On the other hand, the high viscosity hinders the double bond isomerization as an additional radiationless deactivation pathway. In the region where the carboxylate starts to deprotonate, the monomers engage in an electrostatic repulsion (pH = 4−6), the polymer has a cooperative chain opening, and the local viscosity feel by auramine probe decreases. This segment dynamics of the polymer changes drastically the emission of the auramine derivative bound to PMA and leads to a decrease in its emission intensity, in part to a low viscosity effect combined with aqueous solvation of the dye.

The second important change in the dynamics of the auramine derivatives attached to PMA is revealed by time-resolved studies. Both polymer systems I−PMA and II−PMA have long-lived fluorescence decay components in aqueous solution (pH = 2 and pH = 6) as well as in methanol, as reported by the values in Table 2 obtained from triexponential fitting of the fluorescence decays.

This long lifetime found in methanol is similar to the value reported in the literature when auramine is in the presence of DNA (τ = 1.0 ± 0.1 ns). It could be explained by high viscosity probed by auramine located inside biopolymers or synthetic polymer coils. The fluorescence decay of the copolymer I−PMA in methanol is shown in Figure 8.

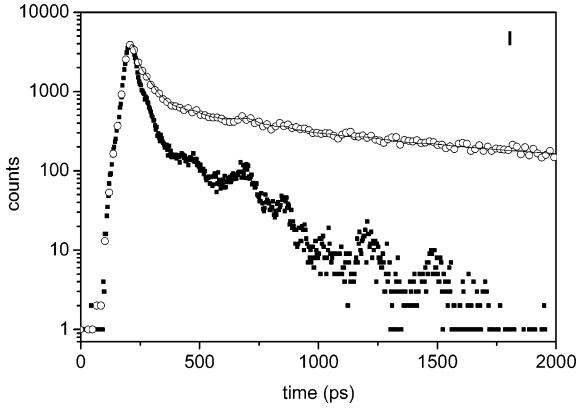

Figure 8. Emission decay of the copolymer I−PMA in methanol. λ_{exc} = 380 nm, λ_{em} = 450 nm. (■) irf, (○) decay, (—) fit.

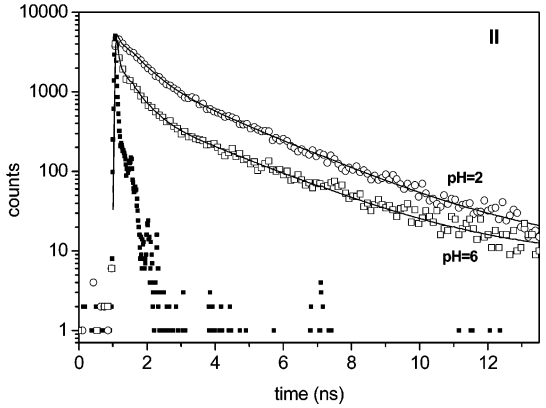

Figure 9. Emission decay of the copolymer II−PMA in water at pH = 2 and 6. (■) irf, (○) decay at pH = 2, (□) decay at pH = 6, (—) fit. λ_{exc} = 380 nm, λ_{em} = 450 nm.

Concerning aqueous solution, the values of decay time found are extremely different from those reported for auramine. The results obtained can be compared only with the fluorescence lifetime of auramine adsorbed in solid matrices, where lifetime is about 2.3 ns when the dye is adsorbed onto microcrystaline cellulose,[19] or it falls in the range of 1.9−2.4 ns in solid polymer when the external pressure varies from 0 to 80 Kbar.[18] Thus, it follows that auramine derivatives bound to PMA are in a deeply buried site of the polymer chain that provides a significantly rigid environment comparable with a solid state.

Another interesting behavior of our systems is the dependence of the lifetimes with the emission wavelengths. In the blue region (λ_{em} = 460 nm) there is a great contribution of the short lifetime (τ_1 in the Table 2) and a small contribution of the long lifetime. However, in the red region (λ_{em} = 540 nm) the situation is reversed. This fact shows that the shoulder at about 525 nm in the emission spectrum is related to the fraction of auramine bound to the poly(methacrylic acid) in a more compact polymer environment.

The fluorescence decay of I−PMA and II−PMA in aqueous solution are pH dependent with an increase of the relative % of the shorter decay components (τ_1 and τ_2) allied with a decrease of the weight of the larger one (τ_3) when the solution pH changes from 2 to 6. As shown in Table 2, the long decay component of 2.2 ns (24%) at λ_{em} = 540 nm has a significant contribution at pH = 2, but a small contribution at pH = 6, when the PMA chain has performed a coil transition from compact to an elongate conformation. These decay traces in aqueous solution at pH = 2 and at pH = 6 are shown in Figure 9 for copolymer II−PMA for comparison.

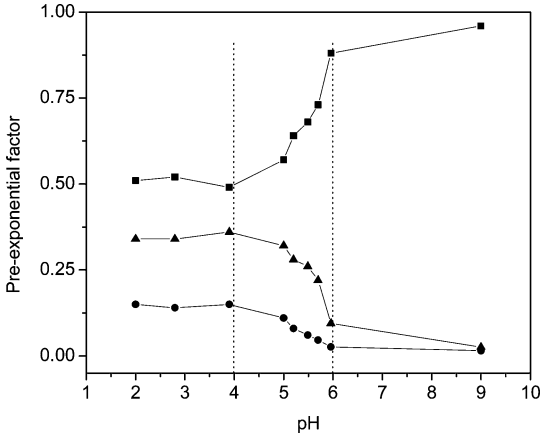

Figure 10. Plot of the preexponential factors b_i of the fluorescence decay components (■ τ_1, ▲ τ_2, and ● τ_3) of II−PMA as a function of pH. Parallel traces indicate the conformational transition region of PMA. λ_{exc} = 380 nm, λ_{em} = 450 nm.

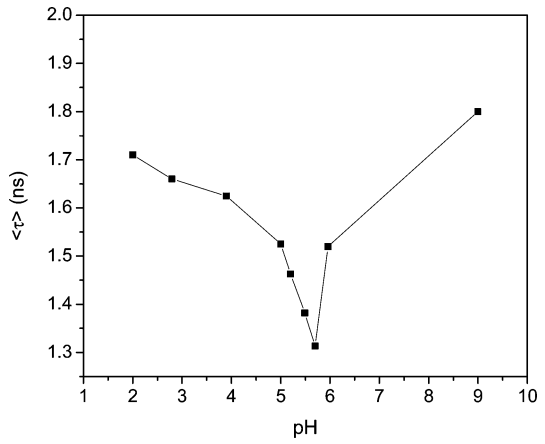

Figure 11. Behavior of the average fluorescence lifetime of copolymer II−PMA with pH. λ_{exc} = 380 nm, λ_{em} = 450 nm.

The behavior of fluorescence decay components with pH (in the range of pH 2 to 8 for the copolymer II) can also be analyzed by the change of the of the preexponential factors b_i (see eq 1) as illustrated in Figure 10.

Similar to what was observed with the fluorescence total intensity given in the inset of Figure 7, the changes in the preexponential factor b_i with pH are significant in the transition region of conformation of PMA of pH 4−6. On the other hand, the average lifetime which is calculated by

$$\langle\tau\rangle = \frac{\sum b_i \tau_i^2}{\sum b_i \tau_i} \qquad (2)$$

has also an abrupt change within this pH interval as shown in Figure 11.

These results are explained by the change in the polymer conformation that affects the fluorescence of auramine dye. PMA is a compact coil at low solution pH that leads to a significant contribution of the long lifetime component by precluding the dye excited-state relaxation motions. When the carboxylate groups become charged, electrostatic repulsion takes place and induces a cooperative expansion of the coil against the hydrophobicity. This causes a decrease in local viscosity and aqueous solvation of the dye that favors fluorescence deactivation of the bound auramine (by rotational relaxation and solvent dissipation), thus increasing the percent of the short lifetime component. On the other hand, *N*,*N*-dimethylamine of

the auramine-PMA will be protonated at low pH, and this effect should inhibit the ICT process and contribute to the observed increase of the % of τ_3 and emission intensity in acid medium.

Conclusions

The auramine vinyl derivatives have π-extended conjugation effect combined with intramolecular charge transfer providing a low energy absorption band and an ICT character in excited state. The dual absorption band behavior of these dyes upon loss of the unsaturated carbon bond was used as a spectral probe for copolymerization process with methacrylic acid. On the other hand, the time-resolved studies reveal a long emission lifetime in solution that is ascribed to the bound auramine surrounded by a compact coil of the polymer chain. Similar values for free auramine were observed only in solid matrices. In addition, the lifetime components are indicating the conformation transition region of PMA aqueous solution with pH. The changes in the emission intensity, preexponential factors, and average lifetime point out that the pH-induced conformational transition of PMA occurs progressively between pH 4 and 6 at 298 K, but the larger change takes place near pH = 5.5.

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