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### A Fluorescence Probe Study of Low Molecular Weight Poly(Methallyl Sulfonate-Vinyl Acetate) Copolymers

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## A FLUORESCENCE PROBE STUDY OF LOW MOLECULAR WEIGHT POLY(METHALLYL SULFONATE-VINYL ACETATE) COPOLYMERS

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### ABSTRACT

When vinyl acetate is copolymerized with sodium methallyl sulfonate, low molecular weight polymers are produced. By controlling the starting mixture composition, the negatively charged monomer content of the polymer chain was varied between 2.5 and 10%. The effect of these copolymers on the fluorescence properties and quenching of pyrene was investigated. It was found that fluorescence intensity and lifetimes increase when the polymer concentration increases. Quenching by nitromethane, Cu(II) ions, and oxygen was greatly reduced compared to quenching in water. The effect is more pronounced for the copolymers with a lower charge content. The results can be interpreted by an aggregation of the polymer chains. These aggregates provide sites for the pyrene molecules, where the radiationless decay processes are reduced, and they are also protected from impurity quenching.

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## INTRODUCTION

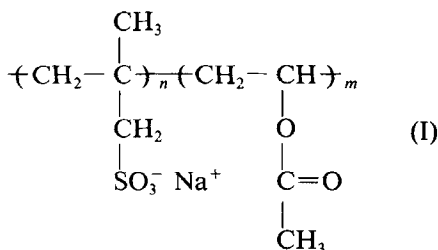
Fluorescence techniques have been very useful for understanding the micellization process of low molecular weight surfactants [1]. These methods were employed with great success for the determination of the cmc and aggregation numbers of micelles, and also for studying the binding of small neutral molecules.

Similarly, phosphorescence and fluorescence emission techniques were successfully used for studying reactions occurring in the presence of weak and strong polyelectrolytes. In this way, information was obtained on the conformation of water-soluble polymers and the interaction with small molecules, neutral or charged [2].

Recently these studies were extended to low molecular weight polyelectrolytes [3] and to block copolymers [4] which can form aggregates when dissolved in water.

In the study of conformation of polyelectrolytes, in general, polymers derived from carboxylic acids were used, typically PMA and PAA homo- and copolymers [5]. Charge density, i.e., the amount of ionized groups along the backbone, which may be thought to be responsible for the conformation of the chain, and therefore, for the amount and extension of the hydrophobic domains, are regulated in those polymers by adjusting the pH of the solution [6].

We present here results obtained from a fluorescence probe study of water solutions of low molecular weight methallyl sulfonate-vinyl acetate copolymers (I) with different charge densities on the chains.



In these polymers the ionic groups are permanent and the charge density is regulated by the percentage of sulfonated monomers copolymerized with vinyl acetate. Even the uncharged monomer units contribute to the water solubility due to the polar ester group. Thus, these polymers are water soluble even with a very low percentage of charged groups, and therefore micelle-like behavior can be expected, since the low charged chains can form hydrophobic domains which will dissolve nonpolar probes like pyrene. In this sense they will present a behavior similar to that of micelle-like polyelectrolytes and block copolymers, although the structures of these are different, normally containing sections or blocks of the polymer chain formed by hydrophobic groups or monomer units [4].

## EXPERIMENTAL

### Chemicals

Commercial vinyl acetate, VA, was distilled under N<sub>2</sub> after treatment with CaCl<sub>2</sub>. Sodium methallyl sulfonate, MAS, was recrystallized twice from methanol-water 70:30. Azobisisobutyronitrile, AIBN (Merck), was recrystallized from methanol and pyrene, Py (Aldrich), twice from benzene. Nitromethane (Merck) and copper sulfate (Merck) were used as received.

### Copolymers

The copolymers were synthesized by free radical polymerization initiated by 1% AIBN in ethanol-water (80:20 g/g) solutions. The reaction mixture was purged with nitrogen for 30 min, and then heated up to the boiling point (70°C) for 10 h. After leaving the mixture at room temperature for another 10 h, 15 mL of the mixture was diluted with water and dialyzed for 7 days. The dialyzed solution was evaporated to dryness in vacuum, dissolved in methanol, and precipitated with ether. After centrifugation and separation, the copolymers were kept in a desiccator.

In order to determine the amount of sulfonation (or of MAS) incorporated into the polymer, a known amount was eluted through an ion-exchange column (Amberlite IR-120). The acid form of the polymer obtained in this way was titrated with NaOH. The degrees of sulfonation, together with the average molecular weights determined by osmometry, are shown in Table 1. The last row in the table shows the mean number of MAS per polymer chain.

### Fluorescence Measurements

All measurements were done using  $10^{-6}$  M solutions of Py, made up by two different procedures. In one, equal amounts of a stock solution ( $1.04 \times 10^{-3}$  M in methanol) were added with a microsyringe to the polymer solutions. The other way was to add to a volumetric flask a known volume of a stock solution of pyrene in acetone and then the acetone was evaporated. A known volume of the copolymer stock solution of copolymer was added and diluted to volume. In both procedures the mixtures were equilibrated for 24 h before measurement. Excitation wavelength was 310 nm and emission intensity was measured at 373 nm ( $I_1$ ) and 384 nm ( $I_3$ ).

The quenching experiments were performed by adding known amounts of stock solutions ([nitromethane] = 0.0503 M and  $[\text{Cu}^{2+}] = 0.05$  M) with a microsyringe to the Py-COP mixtures. The points on the plots correspond to the average of two independent sets of measurements. All experiments were performed at room temperature ( $25 \pm 2^\circ\text{C}$ ).

Fluorescence spectra were measured on an Aminco-Bowman J4 spectrofluorimeter, absorption spectra were taken on a Beckman DU-7 spectrophotometer, and molecular weights were determined on a Knauer mod. 11.00 thermistor vapor pressure osmometer.

### Lifetime Measurements

The determination of excited pyrene lifetimes was carried out with a nitrogen laser (FWHM = 5 ns), a TRW 75A filter fluorimeter, and a digital oscilloscope which transmitted the data to a PC-XT for analysis and plotting.

TABLE 1. Properties of MAS-VA Copolymers

	COP1	COP2	COP3	COP4	COP5
% MAS	3.5	4.7	5.4	8.4	9.8
$\overline{M}_n$	2500	2800	1800	1500	1400
MAS/chain	1.0	1.5	1.1	1.3	1.5

## RESULTS

### Fluorescence Intensities and Spectra

Figure 1 shows the fluorescence spectra of Py in the presence of increasing amounts of copolymer. It can be seen that the intensity of the peaks increases gradually with the concentration of the polyelectrolyte.

In Fig. 2 the fluorescence intensity at 373 nm is plotted vs the polymer concentration for the five copolymers of Table 1. A plateau is reached in all cases at high polymer concentrations. The lower the charge densities on the backbone, the higher is the intensity at the plateau. The ratio  $I_1/I_3$ , which corresponds to the intensity ratio of the (0,0) band to the (0,2) band in the fine structure of the pyrene fluorescence spectrum, remains constant at  $1.70 \pm 0.03$  when the plateau is reached for all systems. This ratio is usually taken as indicative of the polarity of the medium surrounding the pyrenyl group. It goes from 1.9 for water to 0.6 for aliphatic hydrocarbons [7].

The region of increasing intensities in Fig. 2 at low polymer concentration is shown in detail in Fig. 3 for COP2 together with the change in  $I_1/I_3$  ratio vs the log of the polymer concentration. Both quantities show a similar transition region from the values corresponding to the aqueous media to those of the high concentration region.

### Fluorescence Lifetimes

The fluorescence lifetimes of Py in the presence of the various MAS copolymers are shown in Table 2.

The measurements for polyelectrolyte concentrations of 1.1 g/L are the average of the values obtained for Py concentrations of  $5 \times 10^{-7}$  and  $2 \times 10^{-6}$  M. All

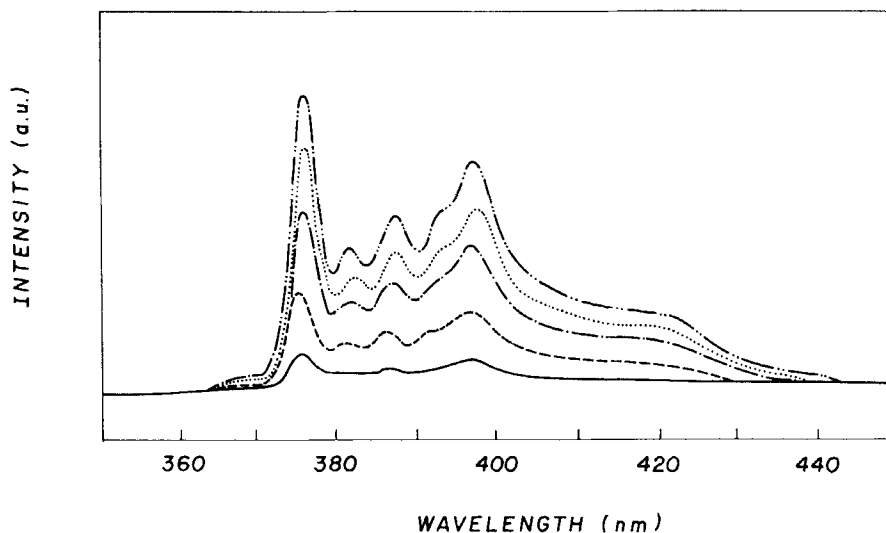


FIG. 1. Fluorescence spectra of pyrene in water (—) and solutions of COP2: 0.02 g/L (---); 0.08 g/L (-·-·-); 0.22 g/L (·····); and 0.40 g/L (- - - -).

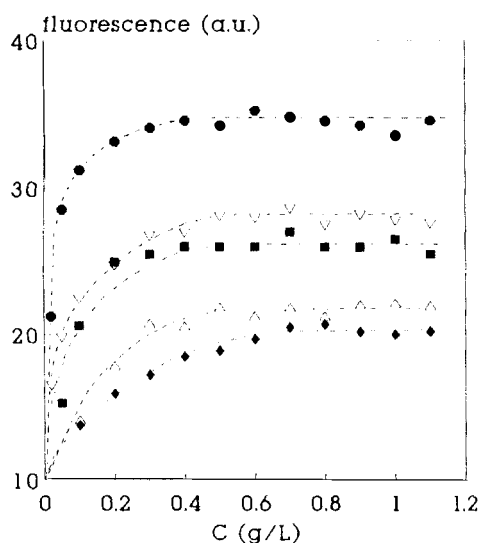


FIG. 2. Fluorescence intensity of pyrene in solutions containing MAS-VA copolymers. COP1 (●); COP2 (▽); COP3 (■); COP4 (△); and COP5 (◆).

decays were monoexponential. When using a lower polyelectrolyte concentration (0.6 g/L), the decays were not monoexponential, except for COP1. Measurements in pure water gave a value of 152 ns, in good agreement with that reported in the literature [8].

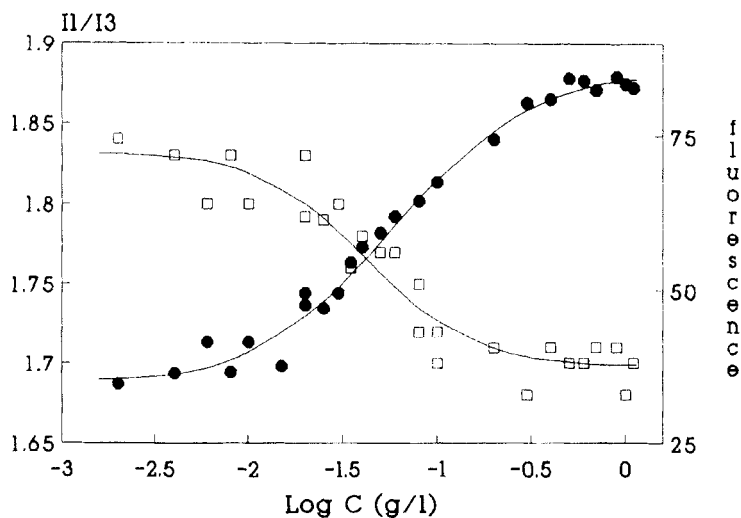


FIG. 3. Plot of the fluorescence intensity (arbitrary units) (●) and the intensity ratio  $I_1/I_3$  (□) as a function of COP2 concentration.

TABLE 2. Lifetime (in nanoseconds) of Pyrene Fluorescence in Air Equilibrated Aqueous Solutions Containing MAS-VA Copolymers

	Polymer				
	COP1	COP2	COP3	COP4	COP5
1.1 g/L	360	336	333	309	297
0.6 g/L	344	310 <sup>a</sup>	303 <sup>a</sup>	294 <sup>a</sup>	260 <sup>a</sup>

<sup>a</sup>Mean lifetimes, non-monoexponential decays.

Oxygen has a negligible effect on the fluorescence lifetime of pyrene in the presence of the polymer at 1.1 g/L. The lifetimes measured in deoxygenated solutions were the same, within experimental error, as those in air equilibrated conditions.

### Fluorescence Quenching

Quenching of the Py fluorescence by Cu(II) ions and the polar quencher nitromethane in the presence of MAS-VA copolymers was performed to obtain information regarding the pyrene microenvironment. In Fig. 4 the results for nitromethane are presented in the form of Stern-Volmer plots. It can be seen that the quenching efficiency of nitromethane was greatly reduced in the presence of the

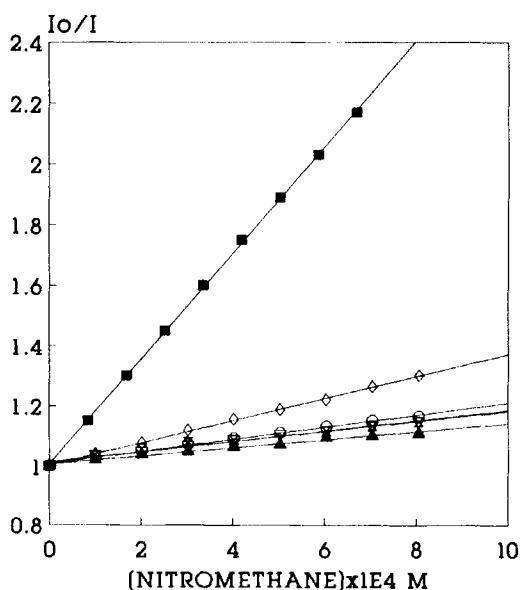


FIG. 4. Stern-Volmer plots for the quenching of pyrene fluorescence by nitromethane in water (■) and in the presence of MAS-VA copolymers (1.0 g/L). COP1 (▲); COP2 (X); COP3 (▽); COP4 (○); and COP5 (◇).

copolymers. The slopes decrease with the sulfonation degree of the polymer chain. The effect of copolymer concentration is shown in more detail in Fig. 5. A two-slope behavior is apparent for low polyelectrolyte concentrations. The extension of the initial slope diminishes as the polyelectrolyte concentration is increased, and it eventually disappears, leaving only the second branch of the curve, which is the same at all concentrations. This effect can be taken as evidence of more than one environment for probe location. Lifetime measurements of the quenching by nitromethane afford results which are dependent upon the charge density on the chain. For the less charged polymer, COP1, no effect of nitromethane on the lifetime could be detected with a COP1 concentration of 1.1 g/L. Thus, in this case the quenching can be considered as totally static. For the other copolymers the lifetime decreases with nitromethane concentration, but with  $\tau_0/\tau$  always lower than  $I_0/I$  by a factor of 2 in most cases. Cu(II) ions, which could be expected to be at the polymer-water interface, showed a low efficiency quenching with saturation-type Stern-Volmer plots (Fig. 6). In this case the quenching is most probably totally static. The plateau attained in each case is a function of the polymer concentration.

## DISCUSSION

All results indicate the presence of two or more different environments for the probe in the presence of MAS-VS in the polymer. At low copolymer concentrations (<0.1 g/L), most of it would be in the form of single chains. Since even in the low

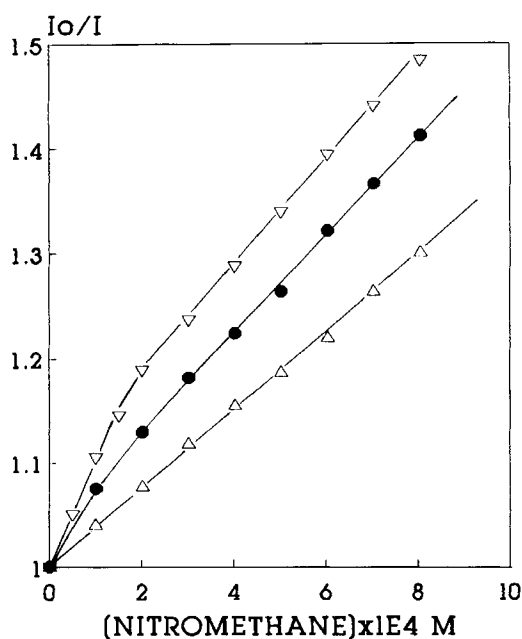


FIG. 5. Stern-Volmer plots for the quenching of pyrene fluorescence by nitromethane in the presence of COP4 as a function of copolymer concentration: (▽) 0.4 g/L; (●) 0.7 g/L; (△) 1.0 g/L.



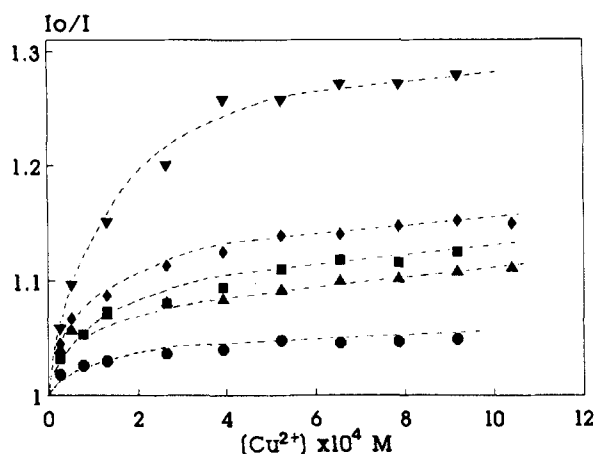


FIG. 6. Stern–Volmer plots for the quenching of pyrene fluorescence by Cu(II) ions in the presence of MAS-VA copolymers (1.0 g/L). COP1 (●); COP2 (▲); COP3 (■); COP4 (◆); and COP5 (▼).

concentration range studied the molar ratio chain/probe is always greater than 10, and in most cases  $> 100$ , and due to the less polar nature of the chains compared with water, they can offer to the probe a hydrophobic domain in proximity to the aqueous phase. At higher concentrations various polymer chains may interact or aggregate to form larger hydrophobic domains in which the probe may dissolve. In these domains the probes are better protected from the external environment than in the “single chain” hydrophobic domains.

From the plots in Fig. 3 it is clear that the abrupt variation of the ratio  $I_1/I_3$  with increasing amounts of polymer in the solution takes place in the same concentration region in which the fluorescence intensity increases. This region can be considered as a “cmc” for aggregation of the polymer chains. As can be observed in Fig. 2, this region moves to higher concentrations when the charge density on the chain increases. When the plateau in Fig. 2 is reached, the micelle-like aggregates permit the partitioning of pyrene into protected hydrophobic environments where the radiationless decay processes are reduced, resulting in higher fluorescence quantum yields and longer lifetimes (Table 2). At high polymer concentrations (1.1 g/L) the Py decays are monoexponential for all copolymers, indicating that the total amount of the probe is placed in hydrophobic domains with similar properties, irrespective of its concentration being changed by a factor of 4 (from  $5$  to  $20 \times 10^{-7} M$ ). The difference in the lifetimes, from 360 to 297 ns, can be ascribed to the different structures of the polymer chains, which may confer to the domains more or less rigidity or oxygen permeability. When the amount of polyelectrolyte is decreased, the aggregate structure of the hydrophobic domains will disentangle, leaving the chains more or less individual (or forming smaller aggregates), so that a certain amount of the probes will be placed in this new environment. This can explain the non-monoexponential behavior of the decay and the shorter mean lifetimes for the lower polymer concentration if it is assumed that the pyrene molecules

associated with single chains sense a more polar microenvironment. Under this condition, the probes may also be more prone to oxygen quenching. For COP1 the decay remains monoexponential at the lower polymer concentration, which can be an indication that in this case the polymer is mostly in the aggregated form even at the lower concentration. Thus, the variation in the decay behavior when the probe/polymer ratio is changed by decreasing the polymer or increasing the probe can only be explained by assuming the formation of aggregates at a certain "critical aggregate concentration," which might be different for each type of polyelectrolyte.

The quenching of Py fluorescence by nitromethane in the presence of MAS-VA copolymers presents two features. The first is the reduced efficiency of nitromethane as compared with that in the absence of the polymer. The second is the presence of two regions with different slopes in the Stern-Volmer plots. The extent of the first slope depends on the concentration of the polymer, and eventually disappears at higher concentrations. These results also point to the existence of two types of environments where the probe can be placed. The first one, which corresponds to the initial slope and only exists when the polymer concentrations are relatively low, is in a region where the access of the quencher is facilitated compared with that when all the probe is in the aggregates. In this situation the probes may be quenched dynamically by the nitromethane remaining in the aqueous phase [9, 10]. The other region for the probes is obtained only when a certain concentration of the polymer is reached. In this region the quenching always proceeds at the same rate and may be assumed to be due to the interaction of the nitromethane molecules partitioned into the hydrophobic aggregates, yielding a mixture of dynamic and static quenching because the slope of the  $I_0/I$  plot in this region is about two times that of  $\tau_0/\tau$ .

The Stern-Volmer plots for the quenching of Py fluorescence by Cu(II) ions in the presence of MAS-VA copolymer are curved, reaching a plateau at high Cu(II) concentrations. This may indicate that the Cu(II) ions are partitioned between the aqueous phase (from where they may easily reach the probes placed in the "single chain" microenvironments) and the anionic sites in the chain aggregates. The plateau should correspond to the complete saturation of the anionic sites and will be different for each type of polymer, being higher for the polymer with higher MAS content, due to its configuration being more open, and the higher concentration of anionic sites in, or near, the hydrophobic regions. An additional complication may arise with this quencher at sufficiently high concentrations, when all anionic sites are saturated. In this condition a change of the conformation of the aggregates can eventually occur, producing variations of the properties of the polymers and of the environments where the probes may be located.

An unexpected result is the inefficient oxygen quenching of Py incorporated in the polymer aggregates. Oxygen quenching of pyrene in organized systems is well documented. Kalyanasundaram [11] reported lifetimes of Py in micellar systems and in water, with values of 440, 281, and 210 ns for SDS, CTAC, and water, respectively. The corresponding values in air equilibrated solutions are 244, 157, and 150 ns. This means a quencher efficiency of oxygen in SDS or CTAC micelles very much higher than in the polymer aggregates studied here. This implies that in our case the probe is placed either into a higher microviscosity microenvironment or in a location which oxygen cannot access. On the other hand, this location is expected to have a relatively high water content, as indicated by the value of the  $I_1/I_3$  ratio.

## CONCLUSION

All our results point to an aggregation process of the MAS-VA copolymers which results in a micelle-like behavior. This aggregation creates sites where a hydrophobic probe like pyrene can remain protected from being deactivated by small quencher molecules. Also of interest is the fact that excimer emission was not observed in these systems, which implies that there is no more than one Py molecule per site.

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