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### Fluorescence of Pyrene Derivatives in the Presence of Poly(Methallyl Sulfonate-Vinyl Acetate) Copolymers. Effect of Charge Density

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## **FLUORESCENCE OF PYRENE DERIVATIVES IN THE PRESENCE OF POLY(METHALLYL SULFONATE-VINYL ACETATE) COPOLYMERS. EFFECT OF CHARGE DENSITY**

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### **ABSTRACT**

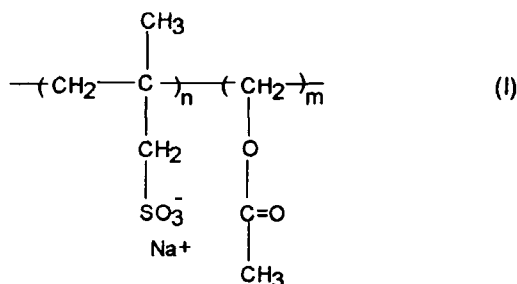
When vinyl acetate is copolymerized with sodium methallyl sulfonate (MAS), low molecular weight polymers are produced. The negatively charged monomer content of the polymer was varied by controlling the starting mixture composition. Copolymers with 19% (COP19) and 77% (COP77) MAS content in the chains were investigated. Three fluorescence probes were employed: a neutral one, pyrene, and two positively charged, 1-pyrene-methyltrimethylammonium (PyMe) and 1-pyrene-undecyltrimethylammonium (PyUnd). The fluorescence spectrum and lifetimes of the three probes were determined at different concentrations of the copolymer. Pyrene showed a biexponential decay in either of both copolymers, and excimer emission could also be observed. For PyMe the fluorescence intensity and lifetimes increase in the presence of COP19, whereas only minor changes are observed with COP77. PyUnd shows both a monoexponential monomer decay and excimer emission. The results can be interpreted by assuming aggregation of the polymer

chains to form micelle-like structures in the case of COP19. This aggregation is less important for COP77, but it can be induced by the presence of the hydrophobic probe PyUnd.

## INTRODUCTION

Fluorescence techniques have been widely used for understanding the solution behavior of polyelectrolytes, especially conformation changes and the interaction with small neutral molecules [1, 2]. These studies were recently extended to low molecular weight polyelectrolytes [3] and to block copolymers [4] which can form aggregates when dissolved in water.

In general, the conformation of polyelectrolytes was studied for polymers containing weak acid groups in the chain, typically poly(methacrylic acid) and poly(acrylic acid) homo- and copolymers [5]. Charge density on the chain was varied by adjusting the pH of the solution [6]. Otherwise, charge density can also be adjusted by controlling the composition of the polymerization reaction mixture when monomers containing a strong electrolyte are copolymerized with neutral monomers. In a previous paper [7] we presented results obtained from a fluorescence probe study of aqueous solutions of low molecular weight methallyl sulfonate-vinyl acetate copolymers (I) with different charge densities on the chains.



Pyrene was employed as the fluorescent probe, and the charge density was controlled by varying the percentage of sulfonated monomers in the chain between 3.5 and 9.8%. It was found that fluorescence intensities and lifetimes of pyrene increase when the polymer concentration increases. The effect was more pronounced for copolymers with a lower charge content. The results were interpreted by assuming aggregation of the polymer chain. In the present paper we extend those studies to copolymers with higher charge contents, 19.2 and 77%. For these copolymers a lower tendency to aggregation can be expected, and less hydrophobic domains will be formed. Therefore, in addition to neutral pyrene, charged derivatives were used as fluorescence probes.

## EXPERIMENTAL

### Chemicals

Commercial vinyl acetate (VA) was distilled under  $\text{N}_2$  after treatment with  $\text{CaCl}_2$ . Sodium methallyl sulfonate (MAS) was recrystallized twice from methanol-water 70:30. Azobisisobutyronitrile (AIBN, Merck) was recrystallized from methanol,

and pyrene (Py, Aldrich) was recrystallized twice from benzene. The pyrene derivatives employed were pyrene (Aldrich), 1-pyrene-methyltrimethylammonium iodide (PyMe, Molecular Probes), and 1-pyrene-undecyltrimethylammonium iodide (PyUnd, Molecular Probes). The concentration of the charged probes was  $1 \times 10^{-5}$  M in all cases and that of Py was  $1 \times 10^{-6}$  M.

### 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 minutes and then heated to the boiling point (70°C) for 10 hours. After leaving the mixture at room temperature for another 10 hours, 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 next to last row in the table shows the mean number of MAS per polymer chain.

### Fluorescence Measurements

The measurements with pyrene were carried out as described previously [7]. The concentrations of the probes in the copolymer solutions were  $1 \times 10^{-5}$  M except for pyrene in water which was  $1 \times 10^{-6}$  M. All measurements were carried out in air-equilibrated solutions at  $25 \pm 2$  °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 model 11.00 thermistor vapor pressure osmometer. The determinations of excited pyrene derivatives lifetimes were carried out with a nitrogen laser (FWHM = 5 ns), a TRW 75A filter fluorimeter, and a digital oscilloscope that transmitted the data to a PC for analysis and plotting.

TABLE 1. Properties of MAS-VA Copolymers

	Copolymer	
	COP19	COP77
% MAS (mol/mol)	19.2	77
$M_n$	1000	1000
MAS/chain	2.0	5.5
VA/chain	8.0	1.5

## RESULTS

Fluorescence spectra and lifetimes of the probes were determined for different concentrations of the copolymers. The concentrations were expressed as normality of monomer units, based on an average monomeric molecular weight calculated from the compositions given in Table 1. The results of the lifetime measurements are given in Table 2.

## COP19

## Pyrene

At a low concentration of the polyelectrolyte, the fluorescence decay of this probe, shown in Fig. 1, was biexponential with two components of around 70 and 136 ns. At higher concentrations of the polyion (0.002 and 0.02 N), the decay became monoexponential with a lifetime of 155 ns. No excimer emission was detected under these conditions. It is well known that the fluorescence lifetime of pyrene increases on going from a polar to a nonpolar solvent. 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, is 1.65 for [COP19] = 0.002 N and 0.02 N. This value is very similar to that found for the less charged MAS-VA copolymers,  $1.70 \pm 0.03$  [7], and is clearly smaller than the value of 1.9 for water [8]. These results indicate that the probe is localized in a less polar environment than pure water. This capability of dissolving an aromatic hydrocarbon suggests a micelle-like structure for this polyelectrolyte.

TABLE 2. Lifetimes (in nanoseconds) of Pyrene Derivatives in Air-Equilibrated Aqueous Solutions Containing MAS-VA Copolymers<sup>a</sup>

Copolymer	Monomer decay		Excimer decay
	Monoexponential	Biexponential	
Pyrene	H <sub>2</sub> O	152	
	COP19	$2.0 \times 10^{-4}$ N	70 + 136
	COP19	0.002–0.02 N	155
	COP77	0.006 N	85 + 160
PyMe	H <sub>2</sub> O	55	No
	COP19	$2.0 \times 10^{-4}$ N	56
	COP19	0.02 N	67
	COP77	0.0048 N	59
PyUnd	COP19	$2.0 \times 10^{-4}$ N	81 + 140
	COP19	$2.0 \times 10^{-3}$ N	130
	COP19	0.02 N	145
	COP77	$4.8 \times 10^{-5}$ N	80
	COP77	$4.8 \times 10^{-4}$ N	77
	COP77	0.0048 N	—

<sup>a</sup>Probe concentrations were  $1 \times 10^{-5}$  M except for pyrene in water which was  $1 \times 10^{-6}$  M.

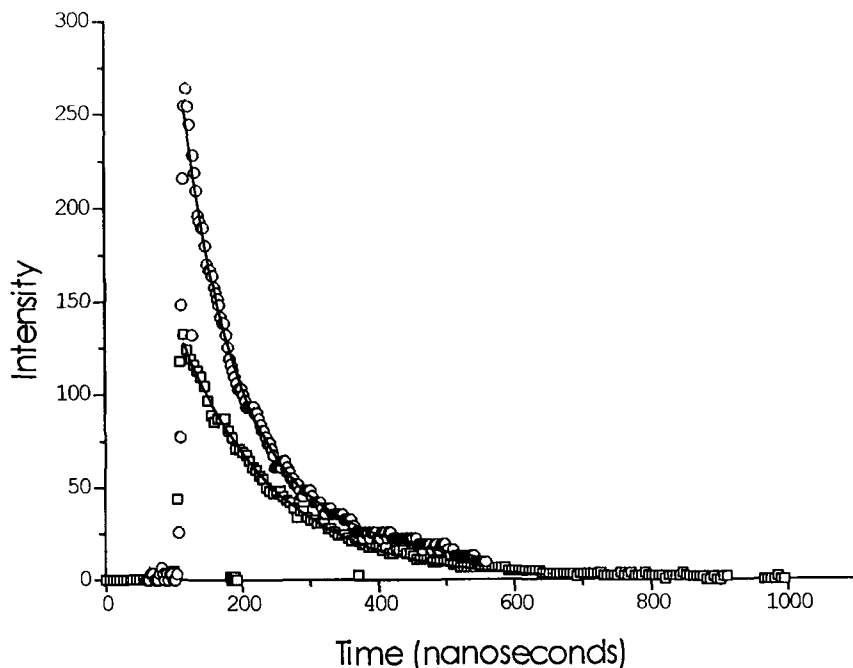


FIG. 1. Pyrene ( $1 \times 10^{-5}$  M) fluorescence emission decays in aqueous solution ( $\square$ ) and in the presence of COP19 ( $2 \times 10^{-4}$  N) ( $\circ$ ).

### PyMe

The fluorescence spectrum of this probe in the presence of COP19 is shown in Fig. 2. An increase in the emission intensity can be observed when the copolymer concentration is increased, as well as a small red shift of 2 nm in the more intense band for the more concentrated solution. The probe shows a monoexponential decay with lifetime increasing from 56 to 67 ns when the polyion concentration increases from  $2.0 \times 10^{-4}$  N to  $2.0 \times 10^{-2}$  N. Excimer emission was not observed. The absorption spectrum shows a slight red shift (4 nm) on going from pure water to 0.02 N in the polymer. These results could be interpreted by considering a partitioning of PyMe between the water pseudophase (lifetime in pure water: 55 ns) and the polymer charged interface. The existence of two populations requires two lifetimes; however, we observed a monoexponential decay for all the concentrations of COP19. This may reflect either the inability of our setup to resolve two close lifetimes or that the probe molecules constitute a single and homogeneous population. The higher lifetime, 67 ns, for 0.02 N corresponds to an observed monoexponential decay for near three lifetimes. In this condition, all the probe is probably localized in the water-macroion interface.

### PyUnd

This probe forms aggregates in pure water, even at  $10^{-5}$  M. The fluorescence spectrum in the absence of the copolymer presents a contribution from excimer emission. The fluorescence spectrum in the presence of COP19 shows the character-

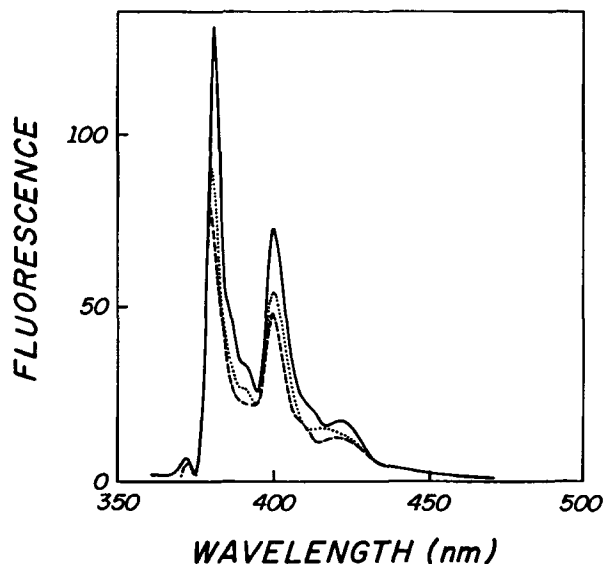


FIG. 2. Fluorescence emission spectrum of PyMe ( $1 \times 10^{-5}$  M) in the presence of COP19:  $2 \times 10^{-2}$  N (—),  $2 \times 10^{-3}$  N (···), and  $2 \times 10^{-4}$  N (- - -).

istic excimer emission at low polymer concentration that disappears at the highest normality (0.02 N), as can be seen in Fig. 3. The monomer emission is also red shifted by 2 nm. Since the monomer emission dominates in all cases, the lifetime measurements were carried out only for this species. A biexponential decay was obtained for the lower concentration with lifetimes of 81 and 140 ns, while at 0.02 N a monoexponential decay of 145 ns was observed. The absorption spectrum presents a red shift with respect to pure water by about 4 nm at the highest concentration. When these results are compared with those for PyMe, a similarity is readily apparent in the sense that the fluorescence intensity of the probe increases with copolymer concentration. However, excimer emission is present only for PyUnd. This can be rationalized by assuming a deeper localization of the pyrene group in this case. This penetration in the polymer domain will also render excimer formation more favorable.

## COP77

### Pyrene

This probe could not be dissolved at low polymer concentrations. At [COP77] = 0.006 N the decay is biexponential with lifetimes similar to those in the presence of COP19 at low concentrations. The emission spectrum can be seen in Fig. 4, where the typical excimer band is evident.

### PyMe

The fluorescence spectrum of this probe in the presence of COP77 is very similar to that in water. No excimer emission is observed and a red shift of the bands is not apparent, but the emission intensity is slightly higher. The decay of

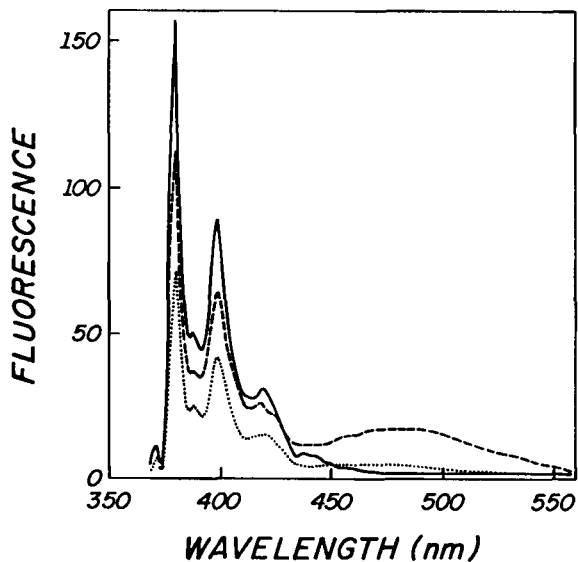


FIG. 3. Fluorescence emission spectrum of PyUnd ( $1 \times 10^{-5}$  M) in the presence of COP19:  $2 \times 10^{-2}$  N (—),  $2 \times 10^{-3}$  N (···), and  $2 \times 10^{-4}$  N, scale  $\times 4$  (- -).

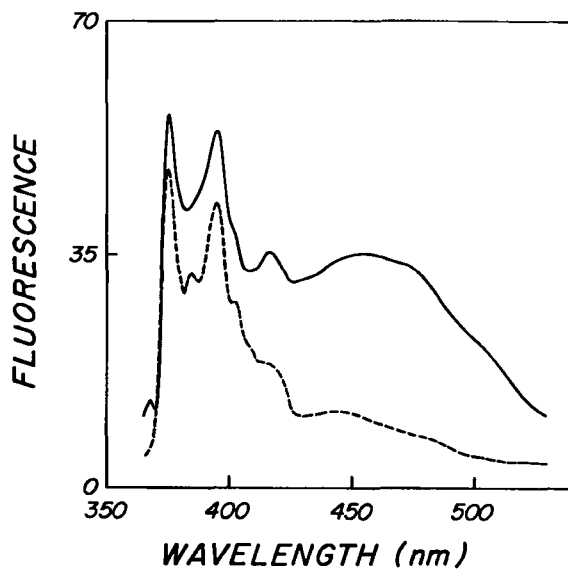


FIG. 4. Fluorescence emission spectrum of pyrene ( $1 \times 10^{-5}$  M) in the presence of COP77:  $4.8 \times 10^{-4}$  N (—) and  $4.8 \times 10^{-3}$  N (- -).



the probe is monoexponential. The lifetime increases to only 59 ns for the higher polyelectrolyte concentration, 0.0048 N. This indicates that this probe is located mainly in an aqueous ambient.

### PyUnd

Excimer emission was observed for this probe at all the polymer concentrations used, as can be seen in Fig. 5. The total emission decreases when the polymer concentration increases. Within experimental error, the maxima of the bands of the monomer species remain at the same wavelength as in pure water. At the highest concentrations, the excimer dominates the emission. The fluorescence decays were measured at the wavelengths of maximum excimer and monomer emissions. The decay curves could be fitted by a single exponential in all cases. The emission profile at 500 nm did not show the characteristic growth of excimer dynamics. This suggests that the broad emission centered at around 480 nm is not due to a true excimer but to a ground state aggregate of two or more pyrene derivatives with adequate orientation of the pyrene groups.

## DISCUSSION

For the MAS-VA copolymers with a lower charge content, the formation of micelle-like aggregates of the oligomer chains was proposed to explain the behavior of the probes [7]. In the present case, due to the higher charge density on the chain, this effect is expected to be less important. The three probes that were used (pyrene,

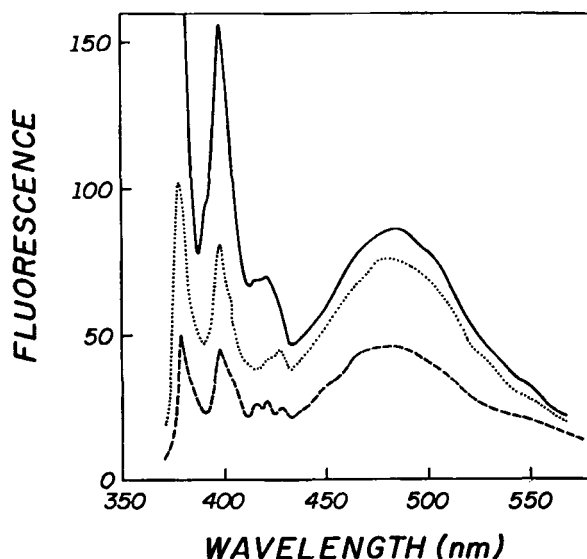


FIG. 5. Fluorescence emission spectrum of PyUnd ( $1 \times 10^{-5}$  M) in the presence of COP77:  $4.8 \times 10^{-5}$  N (—),  $4.8 \times 10^{-4}$  N (···), and  $4.8 \times 10^{-3}$  N (- - -).

PyMe, and PyUnd) have different degrees of charge and hydrophobicity which allow them to be placed in different environments.

Pyrene, which is reasonably hydrophobic, will tend to be located in the more hydrophobic regions. Thus, in polymers with a low sulfonic group content, its behavior resembles that of micelles, showing monoexponential decays with lifetimes around 300 ns [7], well above those found for pyrene in water (152 ns) [9]. On the other hand, the decay of this probe in solutions containing COP19 at low concentrations, and COP77 at all concentrations, shows a biexponential behavior. Our experimental setup does not allow us to resolve precisely the two components of the decay; however, one of them is similar to the decay of pyrene in air-equilibrated water solutions while the other one is much shorter, around 80 ns. Since pyrene is insoluble in water at the concentrations of these experiments, probably it will be totally incorporated in the polymer domain. As its concentration in the pseudophase will be much higher, the observed shorter lifetimes could be ascribed to self-quenching. Excimer emission is clearly observed for COP77, and its magnitude decreases with concentration, indicating a dilution effect. For COP19 at high concentration the excimer emission is absent and the monomeric species decays with a single lifetime like that in pure water. These results point to a larger extension of the hydrophobic microdomain accessible to pyrene in the case of COP19. Although the  $I_1/I_3$  ratio is lower than in water, from the lifetime values it is concluded that these regions must be of high water content. The behavior of this probe suggests that both copolymers aggregate to some extent. Due to its lower charge density, COP19 is more prone to aggregation than COP77, and therefore pyrene senses a larger hydrophobic region.

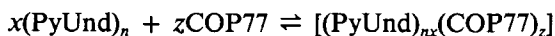
If the COP19 aggregates are thought as micelle-like structures, with the negative groups forming a negative interface, then the positive probes PyMe and PyUnd would be totally associated with the aggregates. Due to its short side chain, the pyrenyl group of PyMe would be located near the surface of the aggregate. The distance between the groups would be large enough to prevent the formation of dimers, and only the monomer emission will be observed. As the concentration of copolymer increases, the aggregates can become larger in size, increasing their hydrophobic character. This can explain the increase in fluorescence intensity and lifetime of PyMe.

Excimer emission is observed with using PyUnd. This can be evidence of a deeper localization of the pyrenyl group, where it may find a nearby second pyrene ring, giving place to excimer emission. When the COP19 concentration increases, the excimer emission decreases due to a dilution effect. It is important to note that the lifetime of the monomer emission at the highest concentration corresponds to that in a medium of reduced polarity. It must also be considered that the hydrophobic probe PyUnd could induce aggregation of the copolymer, even at very low concentrations [10].

For PyMe a similar effect can be observed with the COP77 copolymer, but here the increase in the lifetime and intensity due to the presence of the polymer is smaller. This reflects the more extended conformation of the chains and the lesser tendency of this copolymer to aggregate. No excimer emission is found for the PyMe probe under the conditions used in this investigation.

The larger hydrophobicity of the PyUnd probe is responsible for the differentiated behavior when placed in the presence of COP77. At low concentrations the

copolymer probably does not aggregate and will not compete with the self-aggregation of the amphiphilic probe molecules. When the polymer concentration increases, the following equilibrium can be established:



The excimer/monomer ratio, measured as the quotient of intensities of the two bands ( $I_E/I_M$ ), in the absence of the copolymer is 0.3; at higher concentrations it is approximately 1.0. If the mixed aggregates contain a higher number of PyUnd ions per aggregate than those formed by PyUnd alone, the observed behavior could be explained by assuming that the total emission quantum yield per pyrene group is lower in the right-hand aggregates.

## CONCLUSIONS

The results discussed above show that polymer chains containing a lower proportion of charges (as in COP19) are more likely to aggregate to form micelle-like structures, although the polarity of the polymer domain is larger than that in the less charged copolymers. Aggregation processes are less important for COP77 due to the presence of a larger number of charged groups in the chains (~25%), which confer a less hydrophobic character to the copolymer, increasing the electrostatic repulsion between the chains. Nevertheless, under appropriate conditions, aggregation can be induced by the presence of the hydrophobic probe PyUnd.

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