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Spectral characteristics of probes based on ionic derivatives of pyrene in polar polymer matrices

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Abstract

The spectral properties of pyrene probes with ionic carboxylate or ammonium groups have been investigated in water and in polar polymer matrices like poly(vinyl alcohol) and the sodium salt of poly(acrylic acid). An ionic carboxylate group directly linked to pyrene influences significantly the absorption and emission spectra. Separation of pyrene and the ionic group by one methylene also causes changes in the spectral properties of pyrene. Spectral properties of the ionic pyrenyl compounds in methanol and water in concentration range 10^{-5} – 10^{-4} mol dm⁻³ and in poly(vinyl alcohol) in range 10^{-3} – 10^{-2} mol kg⁻¹ indicate the presence of monomeric species. In methanol, quenching of fluorescence of the ionic probes by molecular oxygen was observed. In water solution, the effect of oxygen was small. No effect was observed on the fluorescence intensity or temporal decay when 1 M sodium acetate was added to water as well. Two effects were observed for the ionic pyrenyl probes in films of sodium salt of poly(acrylic acid): a decrease of fluorescence intensity and the presence of aggregates. The fluorescence intensity and rate constants of decay of ionic probes in the polyelectrolyte matrix were decreased (about 10 times) as compared with poly(vinyl alcohol). The decrease of fluorescence intensity of all the ionic probes in the sodium salt of poly(acrylic acid) is attributed to the opening of radiationless decay channel due to the ionic field. The ionic probes based on 4-(1-pyrenebutyric acid) exhibit surfactant-like behaviour due to the presence of hydrophilic and hydrophobic parts. As a result of hydrophobic interactions during film preparation by casting, aggregates form and provide excimer-like emission. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Spectral characteristics; Pyrene; Ionic derivatives

1. Introduction

Aggregation of large chromophores occurs in homogeneous solutions, in the presence of surfactants or polyelectrolytes, in micelles, in amorphous or semicrystalline bulk polymers and on surfaces. If a chromophore aggregates its applicability as the probe may be compromised; in any case, its state in an environment must be known if the emission from it are to be useful. On the other hand, it can be employed for characterisation of its environment. Pyrene, itself, or in the form of more complex probes is widely used for monitoring polarity and viscosity of environments. Pyrene as an isolated chromophore exhibits strong, well-resolved absorption and emission and a long singlet life time. Therefore, static and dynamic monitoring can be employed [1–3].

Recently, we have described the application of water soluble, more complex probes based on pyrene and a protonated, sterically-hindered amine for characterisation of

premicellar aggregates of surfactants and polyelectrolytes [4]. Similarly, a probe based on pyrene and an oxidised sterically hindered amine exhibiting internal quenching has been characterised as well [5]. In both studies, the conditions were found under which aggregates which exhibit excimer-like emission in the premicellar solutions or in the solid state are formed.

Suitable aggregation in the solid phase might lead to interesting technical applications. For instance, the exceptionally high sensitivity of a Novolak-diazoquinone resist is due to controlled diffusion of base through the penetration zone. The transport of the base through the zone can be modulated not only by changing the overall density of the hydrophilic sites, but also altering their spatial distribution by clustering. Phenolic clusters are formed in the coating solution used to make resist films by an inductive polarisation effect of the diazoquinone function. Hydrophilic site clusters modulate the diffusive flux of base. On exposure to light, this prearranged structure is destroyed due to photochemical reaction and the dissolution of the exposed area is increased [6].

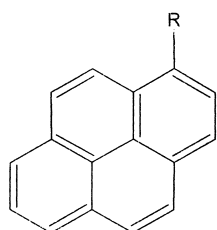
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The effect of aggregation plays a role in another type of photoresist based on poly(vinyl alcohol) modified by a small amount of styrylpyridium salts. The high photosensitivity is due to aggregation of the highly polar styrylpyridium group in the poly(vinyl alcohol) matrix [7].

In this paper, we demonstrate that under certain conditions, the ionic probes based on pyrene aggregate in strongly polar polymer matrices, yielding excimer-like emission.

2. Experimental

The structures of the fluorescent probes used in this paper are shown in Scheme 1. Anthracene and pyrene(I) were zone refined (Lachema n.e., Brno, CR). 1-Pyrenecarboxylic acid(II), 1-pyreneacetic acid(III), 4-(1-pyrene)butyric acid(IV) and 1-pyrenemethylammonium chloride(V) were from Aldrich-Chemie, Steinheim, F.R.G. 2,2,6,6-Tetramethyl-4-piperidinyl-4-(1-pyrene)butyrate was prepared by transesterification of the methyl ester of 4-(1-pyrene)-butyric acid with 2,2,6,6-tetramethyl-4-piperidinol as described in [4]. 2,2,6,6-Tetramethyl-4-hydroxypiperidinium 4-(1-pyrene)butyrate(VI) chloride m.p.: 220–230°C [4] was prepared as described previously.



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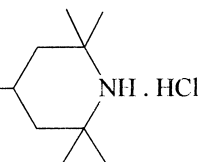
II -COOH / Na

III -CH₂COOH / Na

IV -CH₂CH₂CH₂COOH / Na

V -CH₂NH₂ · HCl

VI -CH₂CH₂CH₂COO-



Scheme 1.

Methanol (Slavus, Bratislava, SR) was UV spectroscopy grade. Chloroform, (Lachema n.e., Brno, CR) was analytical reagent grade. Water was distilled.

Polymer films doped with probes were prepared by casting from solution. Films of poly(methyl methacrylate) (PMMA) (Diacon, ICI, England) were prepared by casting 0.02–2 mg of probe in 1 ml chloroform solution of polymer (5 g 100 ml⁻¹) on a quartz or glass plate (28×35 mm²). Films of poly(vinyl alcohol) (PVA) (Mowiol, F.R.G) and sodium salt of polyacrylic acid (PAANa) (DEGAPAS 4104, Degusa, FRG) were prepared by casting water solutions (5 g 100 ml⁻¹) similarly. Probe concentrations were 0.001–0.01 mol kg⁻¹. The films of PMMA and PVA were self-supporting whereas films of PAANa were on quartz plates.

UV-VIS absorption spectra were recorded on a model M-40 Zeiss spectrophotometer.

Emission spectra were recorded on a Perkin-Elmer MPF-4 spectrofluorimeter which was connected through an interface and an A/D convertor to a microcomputer [8] for data collection, processing and plotting on an XY plotter. Emission of solution was measured in 1 cm cuvettes using a right-angle arrangement. The quantum yields for emission were determined relative to anthracene in methanol [5]. Emission of polymer films was measured in a front-face arrangement using a Perkin-Elmer solid sample holder. The quantum yield for emission of each probe in each polymer films was determined using anthracene in the same polymer as standard.

The quantum yields in film were determined according to the relation [9],

$$\phi = \phi_F^S \frac{\int_0^\infty I_F(\tilde{\nu}) d\tilde{\nu}}{\int_0^\infty I_F^S(\tilde{\nu}) d\tilde{\nu}} \left(\frac{1 - 10^{-A^S}}{1 - 10^{-A}} \right) \left(\frac{n}{n^S} \right)^2$$

where ϕ_F^S is the quantum yield of the standard, $\int_0^\infty I_F(\tilde{\nu}) d\tilde{\nu}$ and $\int_0^\infty I_F^S(\tilde{\nu}) d\tilde{\nu}$ are the areas under fluorescence curve of the probe and standard respectively, A and A^S are absorptions of the probe and standard, and n and n^S are the refractive indices of probe and standard, respectively.

Fluorescence lifetime measurements were performed on a LIF 200 (Lasertechnik, Berlin, F.R.G.) which operates as a stroboscope. The excitation is performed by nitrogen laser $\lambda=337$ nm and the emission is selected by cut-off filters. The output signal was digitized and transferred to a microcomputer [10]. Since the fluorescence lifetimes of pyrene and its derivatives are >10 times the halfwidth of the nitrogen laser (0.5 ns), simple linear least-square fits of the data without deconvolution were applied to mono- and biexponential functions [11]. The standard deviation $G^{1/2} = \Sigma((I_{\text{exp}} - I_{\text{calc}})^2/n)^{1/2}$, where I_{exp} and I_{calc} are experimental and calculated intensities of emission, respectively, was used to judge the goodness of fit. It was assumed that the decay curve is monoexponential if $G^{1/2}$ is < 5%.

Steady-state and time-resolved measurements were performed either on deaerated solutions (argon bubbling for

10 min) or on aerated solutions. All measurements on polymer films were in the presence of air.

3. Results and discussion

Absorption spectra of ionic derivatives of pyrene (Scheme 1) preserve the main features of the unsubstituted parent chromophore. They exhibit vibrationally well-resolved absorption spectrum in methanol and water, although in methanol the carboxyl group is protonated while in water it is ionized. Absorption spectra of ionic probes in non-ionic polar polymer matrix of PVA were basically the same as in water, but slightly bathochromically shifted. The red shift is larger in PAANa than in PVA (Table 1). Moreover, the absorption spectra in PAANa are more diffuse than in water or PVA (Fig. 1). All the ionic probes exhibit an additional red shift in the excitation spectra of ca. 2–5 nm. It indicates that some aggregates (microcrystallites) emit with spectra like those of monomeric species.

Fluorescence spectra of ionic derivatives exhibit bands at 380, 385, 400 and 417 nm; 380 nm band is the most intense and the second is often not resolved. The main features of fluorescence of all derivatives except IV and VI are nearly

Table 1
Characteristics of absorption, excitation and emission spectra of ionic probes of pyrene

Probe ^a	M ^b	$\lambda_{\text{abs}}^{\text{c}}$ (nm)	$\log \epsilon^{\text{d}}$ ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)	$\lambda_{\text{exc}}^{\text{e}}$ (nm)	$\lambda_{\text{em}}^{\text{f}}$ (nm)	$\Delta\nu^{\text{g}}$ (cm)
II	MeOH	341	4.52		382	
	H ₂ O	340	4.50		383	
	PVA	352	4.52	355	382	2060
	PAANa	352		355	387	2330
III	MeOH	341	4.59		378	
	H ₂ O	342	4.70		378	
	PVA	348	4.32	350	379	2186
	PAANa	350		352	383	2300
IV	MeOH	342	4.70		378	
	H ₂ O	340	4.65		378	
	PVA	346	4.38	349	379	2268
	PAANa	347		355	385	2195
V	MeOH	340	4.69		378	
	H ₂ O	339	4.52		379	
	PVA	345	4.30	349	379	2268
	PAANa	350		350	383	2482
VI	MeOH	341	4.67		378	
	H ₂ O	341	4.67		378	
	PVA	344	4.30	348	379	2450
	PAANa	346		351	466	7031

^a Probe designated according to Scheme 1.

^b Medium: MeOH – methanol, H₂O – 0.1 M NaOH in water, PVA – poly(vinyl alcohol), PAANa – sodium salt of poly(acrylic acid).

^c The longest wavelength absorption maximum.

^d The decadic extinction coefficient.

^e The maximum of excitation spectrum.

^f Emission maximum.

^g Stoke's shift.

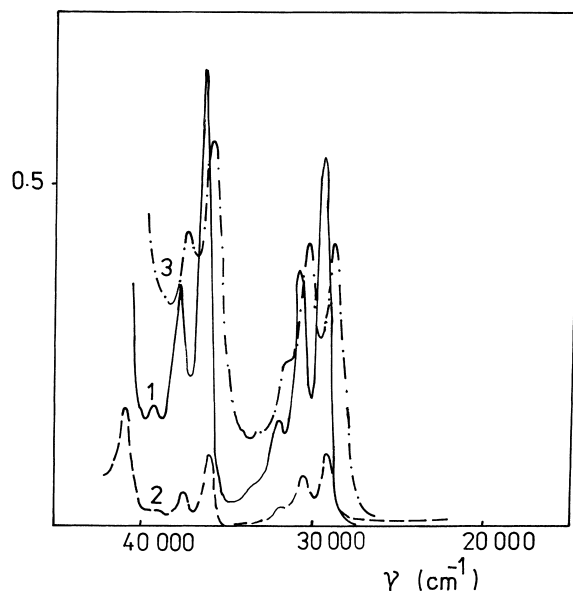


Fig. 1. Absorption spectrum of VI: (1) water, $10^{-5} \text{ mol dm}^{-3}$; (2) PVA, $10^{-3} \text{ mol kg}^{-1}$; (3) PAANa, $10^{-3} \text{ mol kg}^{-1}$.

the same in water, PVA and PAANa (See for instance III, Fig. 2). In the polyelectrolyte matrix of PAANa, a broadening of emission bands, a slight bathochromic shift and substantially lower intensity are observed. Fluorescence of II in protonated and ionic forms is red-shifted even more. The Stokes shift for most derivatives in both matrices is more than 2000 cm^{-1} . In cases where there is some aggregation, this value is substantially higher. The quantum yields of the ionic probes doped in PVA relative to anthracene in

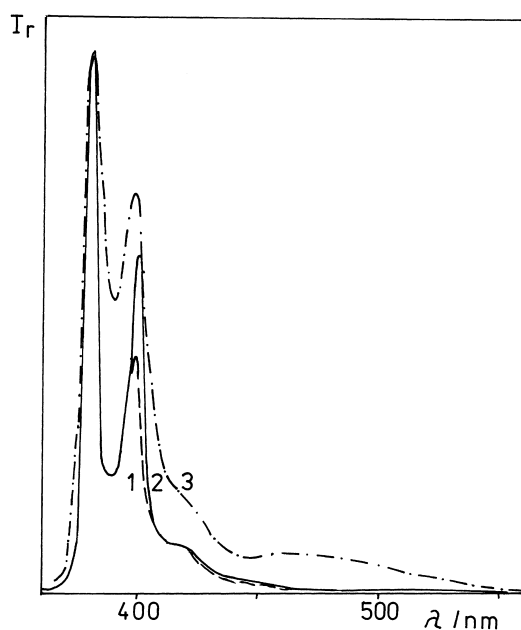


Fig. 2. Emission spectrum of sodium salt of III: (1) 0.1 N NaOH, $10^{-5} \text{ mol dm}^{-3}$; (2) PVA, $10^{-3} \text{ mol kg}^{-1}$; (3) PAANa, $10^{-3} \text{ mol kg}^{-1}$.

Table 2
Characteristics of emission spectra of ionic probes of pyrene

Probe ^a	Medium ^b	λ_{exc}^c (nm)	$\lambda_{\text{em}} (I_r)^d$ (nm)	ϕ_r^e	$\phi_{\text{PVA}}/\phi_{\text{PAANa}}^f$
I	PMMA	335	375(0.95)386(0.61) 395(1.00)	1.13	
II	PVA	350	383(1.00) 403(0.750) 422(0.08)	3.21	10.7
	PAANa	350	387(1.00) 404(0.58)	0.30	
III	PVA	347.5	379(1.00) 399(0.61)	2.65	8.3
	PAANa	347.5	383(1.00) 399(0.74)	0.32	
IV	PVA	345	379(1.00) 399(0.40) 418(0.08)	2.36	4.5
	PAANa	345	385(0.65) 401(1.00) 418(0.82) 465(0.91)	0.52	
V	PVA	345	379(1.00) 399(0.67) 418(0.10)	1.83	13.1
	PAANa	345	383(0.95) 398(1.00)	0.14	
VI	PVA	338	379(1.00) 399(0.52)	3.53	12.2
	PAANa	350	466(1.00)	0.29	

^a Probes designed according to Scheme 1.

^b Medium designed as in Table 1.

^c Excitation wavelength.

^d Emission wavelength (relative intensity).

^e Quantum yield relative to anthracene in poly(methyl methacrylate) film at 0.002 mol kg⁻¹.

^f Ratio of quantum yields in PVA and PAANa matrices.

PMMA are higher than 1 (Table 2). In polar ionic matrices, the quantum yields relative to anthracene are substantially lower. The quantum yield of pyrene in PMMA relative to anthracene taken under identical conditions is 1.2. The ratio of quantum yields in PVA and PAANa matrices is about 10, but a lower value is calculated for IV. Since the determination of relative quantum yields is laden with large experimental errors, the ratio reflects the imprecision even more.

The lifetime measurements are based on decay of emission selected by cut-off filters. Therefore, mixing of the emission from different excited species using short wavelength cut-off filters at higher chromophore concentration cannot be completely excluded. The fluorescence lifetimes of ionic derivatives of pyrene in deaerated methanol and water are clearly different at 10⁻⁴ mol dm⁻³ (Table 3). In methanol the lifetimes are longer (about 250 ns for all derivatives) than in water (about 150 ns). The decay curves of all derivatives in methanol show an initial slight rise followed by a decay which can be fitted to monoexponential function; since the initial experimental intensity is taken arbitrary as 100, the fitted pre-exponential factor A_0 is higher than 100 in most cases. 1-Pyrenecarboxylic acid (II) exhibits shorter lifetime under the same conditions: 30 ns in methanol and 40 ns in water. Most decay curves in water decreased initially more steeply. Therefore, the calculated values of A_0 are lower than 100. The reason for faster decay in water than in methanol is not well understood. The fluorescence decay in aerated methanol is about 10 times faster than in deaerated water, while in aerated water the decay is only about 20% faster. Moreover, addition of 1 M sodium acetate does not influence the decays in deaerated solutions either. Sodium acetate was chosen as a model for carboxylate group in ionic PAANa.

The fluorescence decay curves of fluorescence of the ionic probes of pyrene can be fit to a monoexponential function at concentration of 0.01 mol kg⁻¹ in PVA (Table 4. There is

Table 3
Decay constants and related information for fluorescence from ionic probes of pyrene in solution

Probe ^a	M ^b	A^c	τ^d (ns)	$k \times 10^6, ^e$ (s ⁻¹)	$G^{1/2, f}$	r^g
I	MeOH	126.7	189.9	5.3	6.0	0.9957
	H ₂ O	74.2	30.7	32.5	6.1	0.9895
	NaAc	73.6	41.8	23.9	5.8	0.9935
II	MeOH	104.8	45.0	22.2	1.0	0.9996
	H ₂ O	109.6	259.9	3.8	2.0	0.9986
	NaAc	87.6	145.0	6.9	2.6	0.9977
III	MeOH	82.8	151.6	6.6	3.1	0.9981
	H ₂ O	120.7	234.0	4.2	4.8	0.9962
	NaAc	102.6	136.2	7.3	0.9	0.9994
IV	MeOH	104.9	140.0	7.1	0.9	0.9996
	H ₂ O	110.0	235.4	4.2	2.5	0.9986
	NaAc	88.5	153.4	6.5	2.7	0.9967
V	MeOH	80.6	179.4	5.8	3.8	0.9964
	H ₂ O	109.31	252.9	3.9	2.4	0.9986
	NaAc	103.0	159.5	6.3	1.1	0.9990
VI	MeOH	98.2	158.2	6.3	0.9	0.9983
	H ₂ O					
	NaAc					

Data were fitted to monoexponential function.

^a Probe designed as on Scheme 1.

^b Medium: MeOH – methanol, H₂O – 0.1 M NaOH in water, NaAc – 1 M sodium acetate in water.

^c Calculated value of preexponential factor. The experimental value is set to 100.

^d Lifetime.

^e Decay constant $k=1/\tau$.

^f Standard error.

^g Correlation coefficient of the dependence of $\log I$ on t .

Table 4
Decay constants and related information for fluorescence from ionic probes of pyrene in polymer matrices

Probe ^a	M ^b	D ^c	A _{1,2} ^d	τ^e (ns)	$k \times 10^{6,f}$ (s ⁻¹)	G ^{1/2,g}	r ^h	$\tau_{\text{PVA}}/\tau_{\text{PAANa}}$ ⁱ
I	PMMA	M	73.1	172.5	5.8	4.8	0.9866	
II	PVA PAANa	M B	86.4	41.5	24.1	4.2	0.9947	5.3
			89.5	7.8	128.3	1.3		
			10.5	62.4	16.0			
III	PVA PAANa	M B	87.8	128.9	7.8	2.4	0.9983	19.8
			86.5	6.5	153.9	1.2		
			13.5	48.2	20.7			
IV	PVA PAANa	M B	97.2	153.5	6.5	1.4	0.9992	21.3
			75.5	7.2	138.9	1.0		
			25.5	49.4	20.3			
V	PVA PAANa	M B	91.7	151.6	6.6	2.2	0.9977	22.6
			95.5	6.7	148.8	1.7		
			5.5	386.5	2.6			
VI	PVA PAANa	M B	83.0	166.8	6.0	2.7	0.9960	15.5
			73.1	10.8	92.6	0.9		
			20.9	45.9	21.8			

Data were fitted to monoexponential or biexponential function.

^a Structure of probes according to Scheme 1.

^b Medium: PMMA – poly(methyl methacrylate), PVA – poly(vinyl alcohol), PAANa – sodium salt of poly(acrylic acid). Concentration of probe 0.01 mol kg⁻¹.

^c Type of decay: M – monoexponential, B – biexponential.

^d Preexponential factor for mono- and biexponential fitting.

^e Lifetime.

^f Decay constant $k=1/\tau$

^g Standard error.

^h Correlation coefficient for log *I* on *t*.

ⁱ Ratio of lifetimes in PVA and the fast component in PAANa.

initial fast component of decay which is about 20%. This estimation is based on the calculated value of A which is usually lower than 100. The initial experimental value was arbitrary set to 100. The decays in the PAANa matrix deviate strongly from monoexponential. A biexponential fit has a fast component with a decay constant shorter than 10 ns (80%) and a longer component roughly in the range 40–400 ns. This imprecision is due to the fact that the set of data is not adequate to give a reliable biexponential fit. The ratio of the decay times in PVA to those in PAANa is about 20, higher than the ratio of the fluorescence spectral intensities. A lower value for this ratio from 1-pyrene carboxylic acid (II) is due to its much shorter longer decay components in the PVA matrix (only 40 ns). Moreover, the value of faster component is very imprecise because the kinetic analysis was performed without deconvolution. In any case, static as well as dynamic data indicate a decrease of fluorescence intensity and shortening of lifetime in the polyelectrolyte matrix. As mentioned, up to 1 M acetate anion does not reduce the lifetime or intensities of the pyrenyl fluorescence. In PAANa film, the concentration of carboxylate groups is near 10 M. It is difficult to imagine that carboxylate group acts as a quencher only at higher concentration. On the other hand, some specific quenching

cannot be excluded. Comparison of spectral properties of the probes under study in polar, non-ionic PVA and polar, ionic PAANa indicates that the decrease in the fluorescence intensity and shortening of lifetime are due to the polyelectrolyte matrix. If quenching by carboxylate ion is not involved, then the effect of ionic field must be considered. Possibly, the ionic field opens a new radiationless channel for deactivation of the first excited state of the pyrene chromophore.

Recently Umeuchi et al. [12] investigated the influence of a modulated electric field on absorption and fluorescence spectra of pyrene doped in PMMA. They demonstrated that the electric field causes changes in absorption and fluorescence intensity as a result of a Stark effect, leading to a change of molecular polarizability of ground and excited states. The polarizability of excited states was larger than the ground state, as expected. The net result is enhanced absorption and diminished emission intensities. The effect of a modulated electric field may not be comparable to a static field produced by ions in a polyelectrolyte. At present, the influence of ionic field on photophysical processes in pyrene chromophore seems to be a reasonable explanation of the results in the polyelectrolyte matrix. If correct, this effect should be quite general and observed for other chromo-

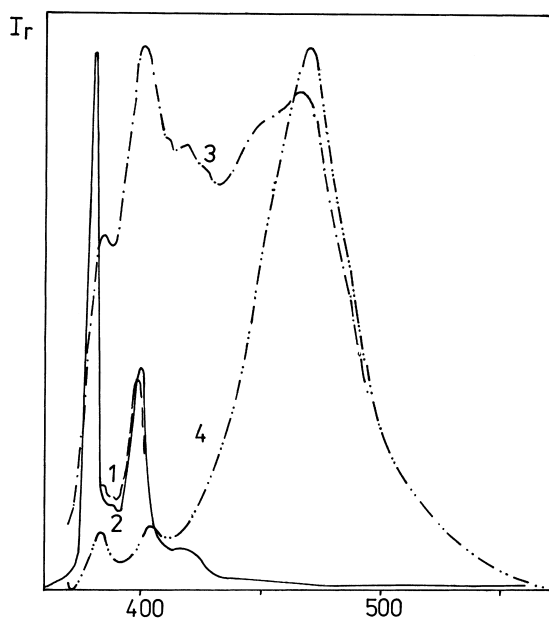


Fig. 3. Emission spectrum of sodium salt of IV: (1) 0.1 N NaOH, 10^{-5} mol dm^{-3} ; (2) PVA, 10^{-3} mol kg^{-1} ; (3) PAANa, 10^{-3} mol kg^{-1} ; (4) PAANa, 10^{-2} mol kg^{-1} .

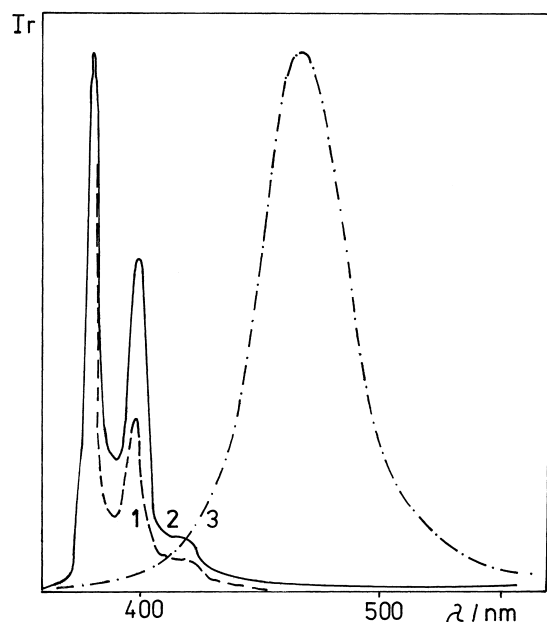


Fig. 4. Emission spectrum of VI: (1) water, 10^{-5} mol dm^{-3} ; (2) PVA, 10^{-3} mol kg^{-1} ; (3) PAANa, 10^{-3} mol kg^{-1} .

phores doped in different polyelectrolytes in the solid state as well.

Another effect, which was observed for derivatives of 4-(1-pyrene)butyric acid (IV and VI), is the formation of aggregates emitting excimer-like emission under certain conditions. Even at low concentrations of IV and VI in PAANa matrix (Table 2), excimer-like emission is observed. These aggregates are formed nearly completely for VI and partially for IV at 0.001 mol kg^{-1} . At higher concentration (0.01 mol kg^{-1}), the formation is complete in both cases (Figs. 3 and 4). In this concentration range, no excimer-like emission is observed in the PVA matrix for the same probes. For probes II, III, and V, where the polar and non-polar ends are not separated by a long distance, no excimer-like emission is observed in the PAANa matrix either. It is remarkable that the formation of aggregates is similar when the ionic group has a positive (VI) or negative (IV) charge. In both cases, due to hydrophobic interactions, the aggregates are formed in an arrangement which allows excimer-like emission upon excitation. Since there is a bathochromic shift in absorption and excitation spectra of all the probes when matrix is changed from PVA to PAANa, the spectral evidence for aggregate formation is not unequivocal. The quenching effect of the polyelectrolyte matrix appears to be decreased at higher concentration of probe VI. Moreover, the longer component of decay data of VI and IV in PAANa matrix corresponds to excimer (about 50 ns, Table 4).

In a previous paper [5], we demonstrated that similar aggregation of probe VI occurs in atactic polypropylene at a much higher concentration (0.2 mol kg^{-1}). In this case, the ionic interactions of the probe in the non-polar environment are responsible for aggregation.

Regardless, it is clear that probe VI is quite useful in monitoring non-polar as well as polar polymer environments.

Acknowledgements

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