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## Photophysical studies of functionalised polyionene complexes in solutions and in the solid state

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### Abstract

Fluorescence steady state and time-resolved studies of hydrophobically modified polyionene systems prepared by exchange reaction with counterions of aromatic and aliphatic character in the parent polymer were conducted in DMF and water solutions as well as in solid films cast from these solvents. The effect of polyionene composition on excimer formation and energy transfer has been examined for different types of counterions, that is: 1-pyrenesulfonate, 1-pyrenebutyrate, 2-naphthalene sulphonate and sodium dodecyl sulphate. In a DMF solution, excimer formation was observed only for hydrophobically modified parent polyionene samples. In an aqueous solution, excitation spectra and instantaneous decay of fluorescence monitored at 480 nm suggest that excimer originates from paired chromophores in the ground state. For solid samples prepared from different solvents, the results indicate that various structures produced by solvent as the result of the self-organising interactions may be trapped in the solid state by polyelectrolyte. Such findings might be interesting for a variety of new optically active materials. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:** Polyionenes; Hydrophobically modified polymers; Fluorescence; Pyrene derivatives

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### 1. Introduction

Polyelectrolyte–surfactant complexes formed in aqueous solutions are very attractive systems due to the presence of ordered structures with a wide variety of properties brought about by a self-assembling behaviour of the surfactant molecules (see e.g., Ref. [1]). Also their solid solution compositions draw attention giving opportunity to fabricate ordered thin films with different functions suitable for electronic, nonlinear optical or electroluminescent devices, since a structure organisation induced by a surfactant–water mixture may be trapped in the solid state by polyelectrolyte network [2]. Previous studies reported in the literature indicated that particularly useful and promising materials for these purposes could be polyionenes—an integral type of polyelectrolytes with dimethylammonium charge centres in the main chain. They show useful optical parameters that are difficult to reach with inorganic materials and can be obtained by convenient preparation techniques [3,4].

Non-modified polyionenes in water solution show many structure-related properties depending on the hydrophilic site density. Ionenes with short  $-\text{CH}_2-$  segments and with high

charge concentration at the same time show expanded conformation in aqueous solution. Non-symmetrical polyionenes, i.e., those with variable length between  $\text{N}^+$  centres demonstrate length dependent change in conformation and, above 14 methylene groups, they display marked similarity to micelles formed from ammonium amphiphiles [5]. Symmetrical polyionenes by self-assembly can even be formed for the length of segments above 20 methylene units a monolayer vesicle [6].

Recently, we have found another simple way of changing hydrophobicity in the parent macromolecule by binding a surfactant to polyion [7]. This modification combined with a concurrent dye ion exchange reaction gives structures of interesting properties. It turned out that polyionene with aromatic hydrocarbons, which adopted an open conformation after modification with long aliphatic counterions in aqueous solutions, forms microdomains. This was evidenced by an increase in excimer emission due to hydrophobic interaction. Such polyionene easily interacts with excessive surfactant molecules and effectively forms polymer–surfactant aggregates, where electrostatic repulsion between aggregates dominates hydrophobic interaction, and is responsible for chain conformational changes.

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Different structures that are found in polyelectrolyte–surfactant complexes are formed by self-organising interactions, which generally depend on a mutual balance between hydrophobic and electrostatic forces competing in this system. Relatively, an abundant body of research has been focused on the binding properties of the local field in the specific nonpolar regions of the complexes of surfactant and polyelectrolytes using fluorescence probe method (see Ref. [1]). Only a few papers discuss solution and solid-state properties of polyionenes with exchanged counterions [8–10].

In the present work, we would like to report on further studies on aggregation behaviour for several kinds of hydrophobically modified polyionene–anionic dyes–surfactant systems investigated in both solution and solid state. Fluorescence and UV absorption spectroscopy are very powerful methods in the study of these materials owing to a wealth of photophysical processes, which are sensitive to environment. In particular, pyrene derivatives as hydrophobic labels exhibit photophysical features that make them the chromophores of choice. The polyionenes studied have different pyrene molar content and different spacer length between pyrene moiety and ammonium centre in the ionene chain. We conducted absorption and fluorescence (steady-state and time-resolved) studies to observe some characteristic microscopic structure evolution of these complexes in the solid state obtained from various solvents and composition, which was manifested by characteristic changes in the spectra. Photophysical steady-state and time-resolved properties of spin-coated thin films cast from different solutions were analysed in terms of pyrene excimer formation, as well as the resonance energy transfer from naphthalene to pyrene.

## 2. Experimental

### 2.1. Materials

The structure of the starting polyionene (I) prepared as bromide and exchanged counterions used in this study are shown in Fig. 1. 1-Pyrenesulphonic acid (PySNa) 1-pyrene-

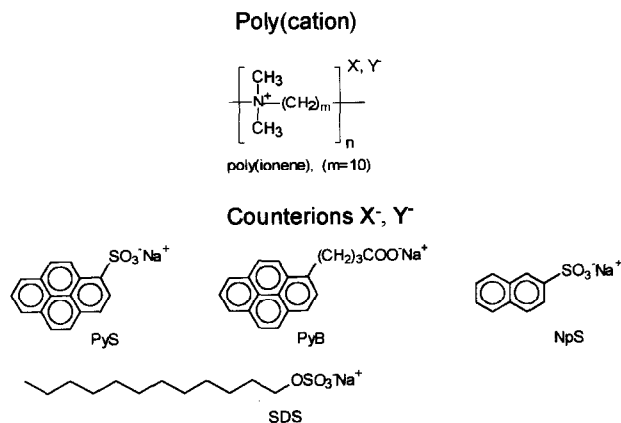


Fig. 1. Chemical structures of the investigated polyionene and counterions.

Table 1

The investigated molecular composites of polyionene and dye/surfactant complexes

Counterion X <sup>-</sup> [10%]	Counterion Y <sup>-</sup> [90%]	Abbreviation
PyS	BF <sub>4</sub> <sup>-</sup>	I-Py
PyB	BF <sub>4</sub> <sup>-</sup>	I-PyB
PyS	SDS	I-PyS-SDS
PyB	SDS	I-PyB-SDS
SDS	PyS	I-SDS-PyS
PyB	NpS	I-PyB-Np

The percentage indicates the molar loading of the appropriate counterion with respect to N<sup>+</sup>-charged ammonium groups.

butyric acid (PyBNa), 2-naphthalenesulfonic acid (NpSNa), dodecyl sulphate sodium salt (SDS) and cetyltrimethylammonium bromide (CTAB) of fluorescence grade were purchased from Aldrich, and were used without further purification. The exchange of bromide counterions in the parent polycation was made by a method previously reported for the preparation of complex salts of ionenes [3]. The investigated polycations containing different counterions as well as their abbreviations are presented in Table 1.

### 2.2. Sample preparation

Samples for the spectroscopic measurements were deaerated by bubbling either their water or dimethylformamide (DMF) solutions of polyionene by nitrogen in quartz cells for 20 min. The polyionene films were prepared by casting the polyionene solution on glass slide followed by gradual evaporation of the solvent under the nitrogen stream at elevated temperature. The measured lifetimes of such samples were the same for an air- or nitrogen-filled cells.

### 2.3. Measurements

Absorption spectra were observed using Specord M40 UV-Vis spectrophotometer. Steady-state fluorescence and excitation spectra (uncorrected) both of liquid and solid solutions were measured on a Perkin-Elmer LS-50 Luminescence Spectrometer equipped with front face accessory. Time-resolved fluorescence measurements were performed with the system consisting of a nitrogen laser (Laser Photonics, USA model LN 120C) producing single light pulses (duration about 300 ps, energy up to 78 μJ), a monochromator (Bausch and Lomb), a photomultiplier (Hamamatsu 1P28) with 2 ns response time, a digitising oscilloscope (Hewlett-Packard 54510A) and a computer for data storage and analysis. All the measurements were carried out at room temperature.

## 3. Results and discussion

Before photophysical studies of functionalised polyionenes will be discussed some fluorescence properties of ionic

pyrenyl probes are presented in order to elucidate the solvent effect on their absorption and emission properties.

### 3.1. Photophysical properties of free ionic pyrene derivatives in solutions

Ionically substituted pyrenes, independent of the aliphatic spacer length separating ionic group from pyrene moiety, show well-resolved fluorescence emission and excitation spectra. Examples of those spectra are presented in Fig. 2. The excitation spectrum of sulfonated pyrene matches the absorption one and is shifted to longer wavelength as compared to pyrene with butyric linker. The red-shift effect is also observed for each chromophore when DMF solvent is replaced by water. It is well established that for unsubstituted

pyrene, a polarity-dependent emission band is correlated by its  $I_1/I_3$  ratio of the characteristic vibronic peaks at 377 nm ( $I_1$ ) and at 385 nm ( $I_3$ ) with vibronic coupling [11]. Usually, for unsymmetrically substituted pyrenes the substituent itself breaks the vibronic symmetry and the immediate environment has little influence on vibronic coupling, which is well represented by PyBNa fluorescence spectrum with almost no solvent effect on  $I_1/I_3$  values:  $I_1/I_3 = 3.25$  in DMF and 3.20 in water (Fig. 2a). In the case of PySNa molecule, the fluorescence spectrum is very sensitive to solvent. When it is dissolved in a mixture of water and DMF as solvent with the different specific solute–solvent interactions, the relative ratio  $I_1/I_3$  increases with increasing water content (inset in Fig. 2b.) from 1.23 in pure DMF to 4.5 in water. This effect can be explained by the influence of solvation forces in dipolar

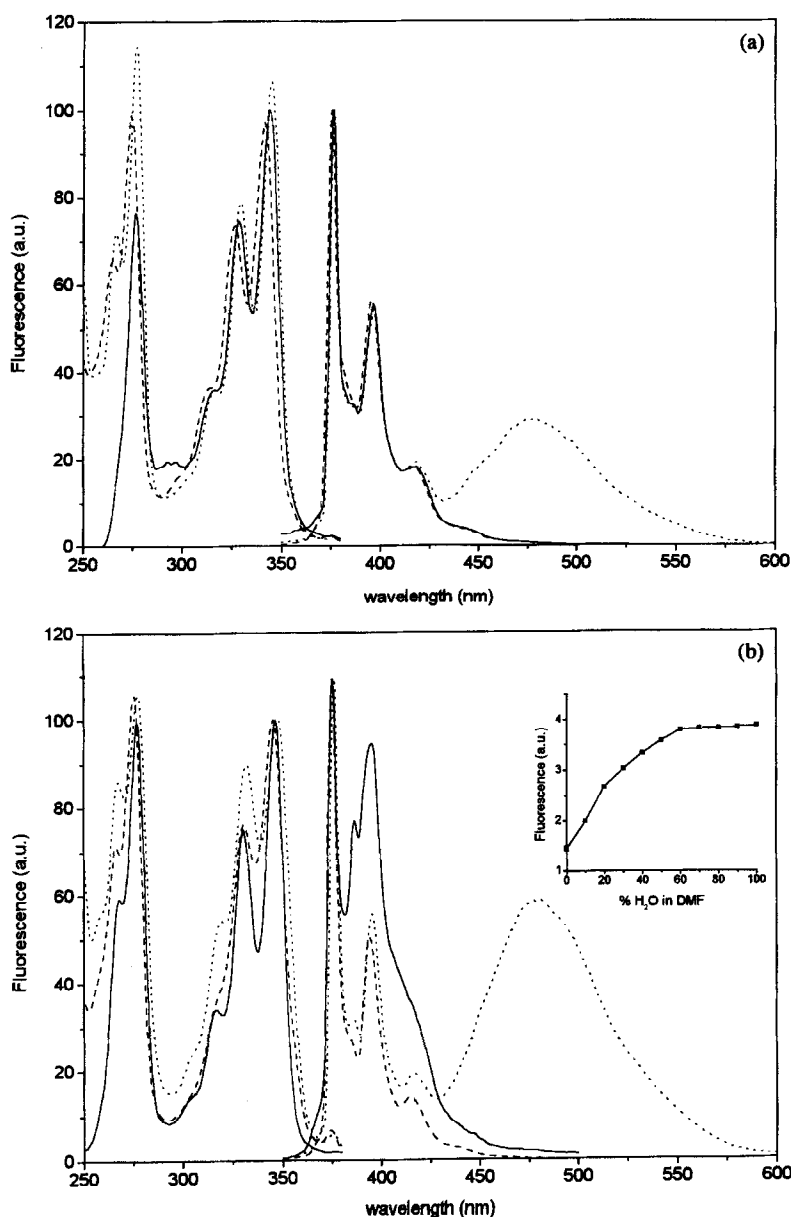


Fig. 2. Excitation and fluorescence spectra (normalised) of (a) PyBNa and (b) PySNa in DMF (solid), water (dash) and CTAB micelles (dot). Excitation was carried out at 340 nm. Inset: plot of  $I_1/I_3$  relative intensity ratio for PySNa vs. the volume fraction of water content in binary DMF/H<sub>2</sub>O mixtures.

Table 2

Fluorescence lifetimes obtained by fitting time-resolved data to one- ( $e^{-t/\tau}$ ) or two ( $A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2}$ )-exponential decay for PyBNa and PySNa in DMF, water, CTAC micelles and solid polyionene (I–Br) films

Solvent	PyBNa (ns)	PySNa (ns)
DMF	$\tau = 175$	$\tau = 206$
Water	$\tau = 124$	$\tau = 67$
CTAC micelles [13]	$\tau = 194$	$\tau = 125$
I–Br film (2 mol%)	$\tau_1 = 10$ $\tau_2 = 76$	$\tau_1 = 19$ $\tau_2 = 68$
I–Br film (10 mol%)	$\tau = 13$	$\tau = 20$

aprotic DMF on an ionic group in which it is much less solvated and hence the electrostatic forces of attraction are strong enough to prevent dissociation of  $\text{Na}^+$  ion [12]. The substitution of DMF for protic water in solution results in very close matching of  $I_1/I_3$  values for two examined compounds.

The fluorescence lifetime of the free probes (see Table 2) in water solution can be fitted by single exponential yielding a lifetime of 67 ns and 124 ns for PySNa and PyBNa, respectively [13], and they are longer than reported previously for an air-equilibrated solution [14]. In DMF solution, fluorescence decays are also well described by a one-exponential decay pattern of  $\tau = 206$  ns for PySNa, and  $\tau = 175$  ns for PyBNa. The addition of an anionic surfactant (SDS) to water solution has no observed influence on the UV spectra and fluorescence parameters of examined fluorophores, which means that negatively charged pyrene moieties are pushed out from anionic micelles. On the contrary, profound changes occur in the presence of CTAB, a hydrocarbon cationic surfactant. Monomer intensity drastically decreases, and simultaneously, excimer emission centred at around 480 nm is observed. The radical drop in intensity cannot be exclusively due to the excimer formation, but must be related to a heavy atom effect, too. The excimer emission is detected not only above critical micelle concentration (cmc) (Fig. 2), but also a few orders of magnitude below this value. The ratio of excimer to monomer fluorescence (E/M), which is a measure of aggregate concentration in the excited state, depends on the type and molarity of anionic pyrene; PyBNa forms aggregates more efficiently, and this ratio increases as CTAB concentration decreases in the case of the sub-cmc of CTAB. This fact explains also a dynamical process of decreasing E/M ratio with time observed above cmc of CTAB which can take place due to an intermicellar exchange mechanism (e.g., collisions). Above cmc one can observe, besides an excimeric band, a small red shift of the monomeric peaks probably as a result of drastic changes in polarity of the fluorophore environment arising from the contact with surfactant interface layer or interior. This fact is also reflected in the lifetime of the examined compounds.

In the solid I–Br solution of ionic pyrene (2% by mol), spectra were observed with maxima at the same wavelengths as those of the DMF solution. The decay profiles of monomer

emission were analysed by a two-exponential function with characteristic lifetimes  $\tau_1$ ,  $\tau_2$  shorter than for the DMF solution. It indicates of at least two photophysical processes taking part in the deactivation process of excited state. Short-living component may suggest quenching of the fluorescence probe, probably by interactions evoked by the presence of polyionene matrix. The lifetimes measured for samples with higher concentration of pyrenes (10% by mol) suggest that concentration effects are responsible for fluorescence behaviour of free ionic derivative of pyrene in the polyelectrolyte solid film.

To summarise, the photophysical studies on free ionic derivatives of pyrene indicate that only pyrene moiety with directly substituted ionic group shows pronounced effect of solvent on  $I_1/I_3$  ratio, opposite to pyrene derivative containing aliphatic spacer between ionic head and chromophore. Nevertheless, the characteristic changes in absorption and excitation spectra, formation of excimers and long fluorescence lifetimes show that examined systems containing pyrene derivative are sensitive to environment and enable probing polyionene behaviour in solution and in solid state.

### 3.2. Fluorescence behaviour of polyionenes in solution

Polyionenes modified by different counterions and having various compositions show different solution properties from the parent I–Br polycation. Figs. 3 and 4 illustrate absorption and fluorescence spectra of I–PyB, I–PyB–SDS and I–SDS–PyS in a ‘good’ (DMF) and a ‘poor’ ( $\text{H}_2\text{O}$ ) solvent respectively, at a concentration of  $4 \cdot 10^{-4}$  M. The fluorescence spectra depend on the solvent ( $I_1/I_3$  changes), in the same way as for free probes, but additionally they show excimer bands on various emission intensities depending on a solution and polyionene composition. In DMF for I–SDS–PyS the intensity ratio  $I_1/I_3$  has a value of 1.34, the same as for free molecule while for that of I–PyB and I–PyB–SDS it equals 2.85 and 3.93, respectively. At the same time, the absorption spectrum of I–SDS–PyS is red-shifted. In water solution, the emission fine structure ratio  $I_1/I_3$  is less scattered and assumes the values between 3.31 and 4.5 for all investigated samples. The samples show excimer bands change with the formation efficiency evaluated at 480 nm from normalised fluorescence at 377 nm in the order I–PyB < I–PyB–SDS < I–SDS–PyS. The excitation spectra correspond closely to the absorption ones. The excitation spectra were independent of the wavelength at which the emission was monitored. The excitation spectrum of I–PyB and I–SDS–PyS in water shows band broadening as well as a small shift to the red. This behaviour can be distinctly discerned by comparison of the peak intensity at 345 nm to the adjacent valley at a shorter wavelength. In the case of I–PyB, i.e., at low concentration of Py on polyionene, the excitation spectrum is still sharp, indicating that almost all pyrene species are separated from each other both in their ground and excited states. This occurs in contrast to the two samples with completely hydrophobically filled up ammonium centres (I–PyB–SDS and I–SDS–PyS), where

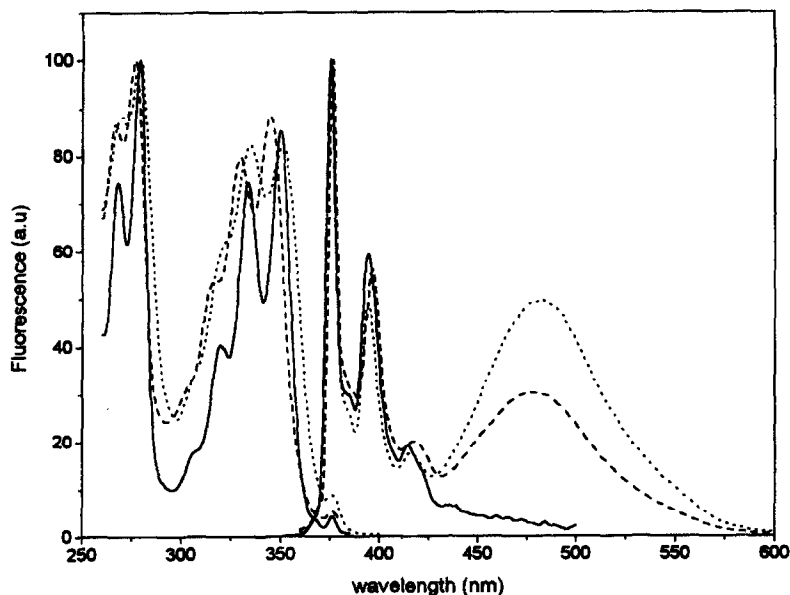


Fig. 3. Absorption and fluorescence spectra (normalised) of I-PyB (solid), I-PyB-SDS (dash), I-SDS-PyS (dot) in DMF. Excitation was carried out at 350 nm.

even the hydrophobic attraction in the ground state is evident. Previous measurements suggested that the association among pyrenes had intrapolymeric origin and polycation might form unimolecular micelles at high level of exchange of aromatic counterions on parent macromolecule [7]. The picture obtained from steady-state measurements remains in good agreement with time-resolved experiments presented below.

Both the monomer and the excimer emissions data in a nanosecond time domain were analysed by a single- ( $\tau$ ) or double-exponential ( $\tau_1$ ,  $\tau_2$ ) function. The  $\tau$ ,  $\tau_1$  and  $\tau_2$  parameters for various systems are collected in Table 3. The values of the decays were associated with fast-decaying com-

ponents,  $\tau_1 \approx 7 \div 30$  ns, components with the rate in the range of  $\tau_2 \approx 60 \div 200$  ns or slowly decaying components above  $\tau_2 \approx 200$  ns, depending on polyionene composition. Fig. 5 shows examples of the decay profiles of I-PyB-SDS and I-SDS-PyS for the monomers and excimers monitored at 400 nm and 480 nm, respectively, in DMF solution. For the monomer emissions, a long-lived component of the decays was observed approximately with the same lifetime ranges as for free salts of pyrene in contrast to a shortlived component for which it increased by one order of magnitude. For both samples monitored at 480 nm a rising portion appears in the time domain  $0 \div 50$  ns: 52 ns and 18 ns for I-PyB-

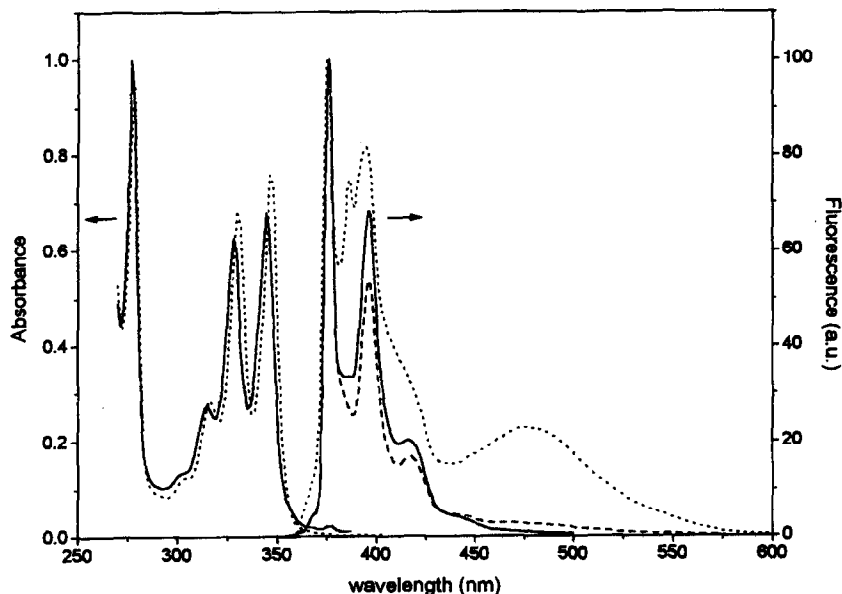


Fig. 4. Excitation and fluorescence spectra (normalised) of I-PyB (solid), I-PyB-SDS (dash), I-SDS-PyS (dot) in water. Excitation was at 350 nm and emission was monitored at 400 nm.

Table 3  
Fluorescence lifetimes (in ns) of I-PyB-SDS, I-PyB and I-SDS-PyS in DMF, water and solid films monitored at 400 and 480 nm

Solvent	I-PyB		I-PyB-SDS		I-SDS-PyS	
	400 nm	480 nm	400 nm	480 nm	400 nm	480 nm
DMF	$\tau = 175$	—	$\tau_1 = 78$ $\tau_2 = 172$	$\tau = 169$	$\tau_1 = 45$ $\tau_2 = 172$	$\tau_1 = 64$ $\tau_2 = 348$
Water	$\tau_1 = 31$ $\tau_2 = 112$	$\tau = 45$	$\tau_1 = 15$ $\tau_2 = 132$	$\tau = 172$	$\tau = 62$	$\tau_1 = 132$ $\tau_2 = 385$
Solid films:						
DMF	$\tau_1 = 19$ $\tau_2 = 104$	—	$\tau_1 = 13$ $\tau_2 = 93$	$\tau_1 = 7$ $\tau_2 = 96$	$\tau = 13$	$\tau_1 = 6$ $\tau_2 = 34$
H <sub>2</sub> O	$\tau_1 = 22$ $\tau_2 = 85$	—	$\tau_1 = 13$ $\tau_2 = 78$	$\tau_1 = 8$ $\tau_2 = 84$	$\tau = 12$	$\tau_1 = 7$ $\tau_2 = 40$

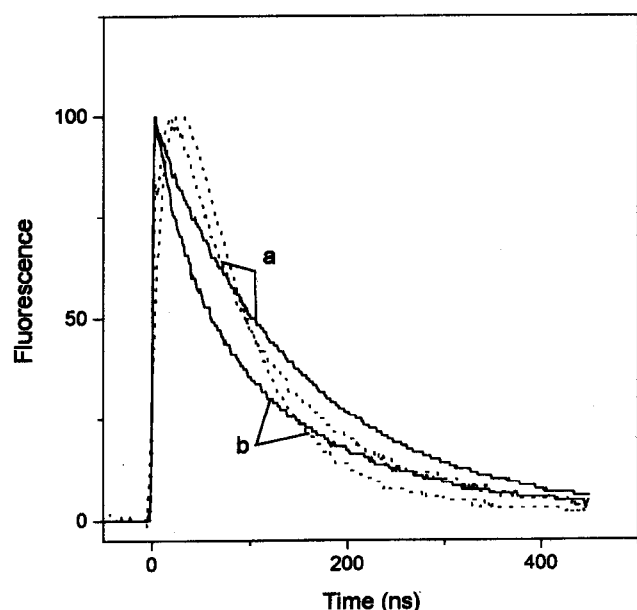


Fig. 5. Monomer (solid) and excimer (dot) emission decay profiles of (a) I-PyB-SDS and (b) I-SDS-PyS in DMF solution.

SDS and I-SDS-PyS, respectively. The decay of excimers was also described by two exponential functions, but for I-SDS-PyS with the second lifetimes once more as long as for I-PyB-SDS. A dependence of the kinetic data upon the solvent is also observed in water with a more complicated characteristic. The main differences occur for the fast decaying component as compared to DMF solution, which becomes again much shorter. The decay profiles of the excimer emission for all samples in water solutions have no rising component under the nanosecond time resolution. This suggests that for sample with high pyrene loading excimers are formed from paired pyrenes what, in fact, was observed in perturbed excitation spectra.

### 3.3. Effects of polyionene composition and morphology on fluorescence behaviour in the solid state

Fig. 6 shows fluorescence spectra of polyionene in solid state (films obtained from DMF solution). The monomeric

emission of PyB moiety is red-shifted for I-PyB with respect to I-PyB-SDS and the excimer fluorescence is strongly depressed for both samples. For I-PyB, only the monomer emission was observed. For I-SDS-PyS, the excimer band is strongly enhanced, and the loss in monomeric emission intensity was observed with respect to solution. These results indicate that the composition of the polyionene affects the excimer formation. In I-SDS-PyS, at high loading of aromatic counterions, pyrenes seems to be prealigned to each other, so that the face-to-face conformation necessary for the excimer formation is easily attained with only a small reorientation of the pyrene moiety. On the other hand, for polyionene composites with lower mole content in polyionene, larger movements are required for Py to adopt a face-to-face configuration. However, in the solid solution, such a dynamic process is strongly depressed.

Table 3 also collects fluorescence lifetimes of thin films cast from DMF or water solution. Fast excimeric decay for I-SDS-PyS, unrelated to the decay of monomer, confirms the instantaneous formation of excimer and indicates that Py moieties are present in a glassy film as a ground state dimer. It is interesting to note the different behaviour of the excimer formation of PyB in the polyionene with and without SDS counterions. In I-PyB-SDS films, because of the presence of SDS molecules, the PyB-counterions are more mobile, while in the I-PyB they have restricted mobility owing to the influence of stiff ionene chain.

In solution depending on solvent (DMF, water or surfactant-water), different structures are formed by self-organising interactions of polyionene-surfactant complexes [1]. The question is whether a phase produced by a solvent may be trapped in the solid state by polyelectrolyte network. Fig. 7 compares fluorescence spectra of I-SDS-PyS films obtained from various solutions. Ground-state interactions between pyrene molecules, presented in all samples, show that pyrene associates can form different configurations (e.g., head-to-head or tail-to-tail) depending on the solvent used. Water enhances the excimer formation in solid film, decreases its decay rate markedly and blue-shifts the excimeric maximum by about 14 nm as compared to other investigated samples. The presence of additional SDS molecules reduces the excimer formation and increases the decay of monomer fluorescence.

Differences in morphology of the solid-state samples brought about by various solvent-dependent interactions are also observed for other samples comprised of aromatic counterions with high loading. Fig. 8 shows the fluorescence spectra obtained by selective excitation of naphthalene at 290 nm of I-PyB-NpS solid films cast from DMF, water or a mixture with SDS surfactant at concentration below and above critical micelle concentration (cmc). The fluorescence of PyB chromophore does not show specific interaction related with excimer formation. The ratio  $I_1/I_3$  increases from 2.5 for the sample blended with additional SDS to 3.4 for the samples obtained from pure DMF, thus indicating changes in polarity of pyrene environment. The emission band at the blue side

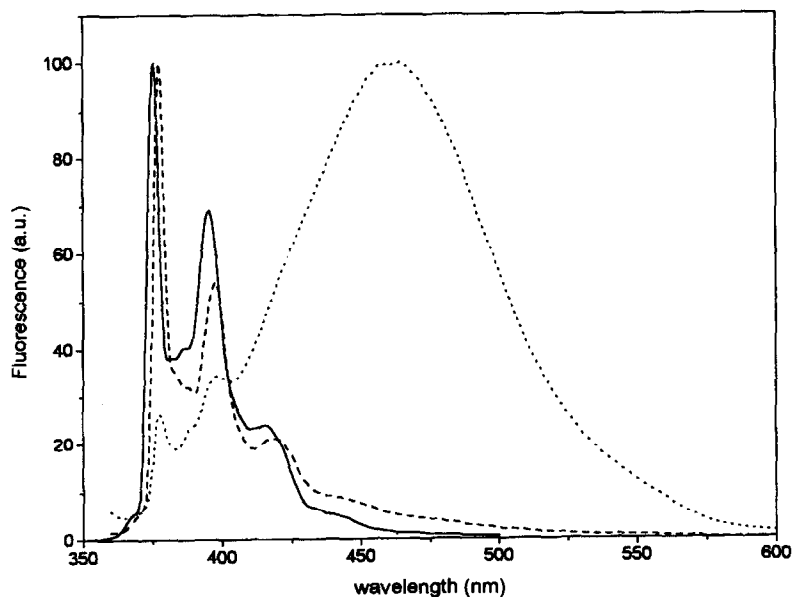


Fig. 6. Emission spectra of thin films of I-PyB (solid), I-PyB-SDS (dash) and I-SDS-PyS (dot) obtained from DMF solution.

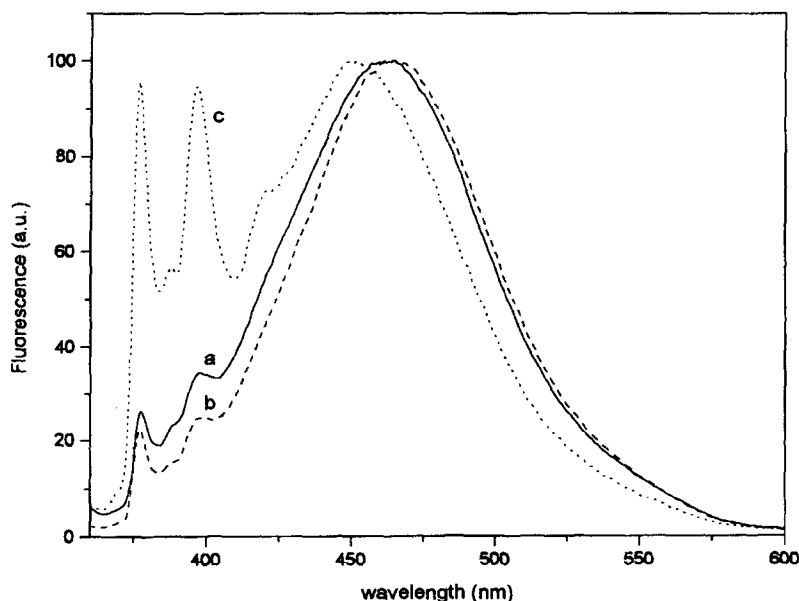


Fig. 7. Thin film fluorescence spectra (normalized) of I-SDS-PyS poured out from DMF (a) or water solution (b) and in the presence of additional SDS surfactant molecules (c).

of pyrene spectrum is the monomer fluorescence of Np chromophore. The intensity of the naphthalene band, related to the intensity of pyrene, indicates on the extent of energy transfer between two chromophores. For DMF cast samples, a complete quenching of Np emission by Py is observed. Aqueous solution-cast samples show a decrease of energy transfer. Water is responsible for worse organisation of chromophores in the films, which further decreases with increasing additional surfactant concentration. Due to the presence of SDS molecules, the chromophores are separated from each other and more expanded, inducing further separation and change in relative orientation between Py and Np. These spectra completely reflect the aggregation of ionene with SDS

in water solution when SDS is added to water [7], and suggests that there is no phase separation.

#### 4. Conclusion

The result presented show that hydrophobically modified ionene polymers form different aggregates depending on solution, degree of molar loading on ammonium groups, and the character of the counterions. Polyionene aggregates are formed not only from samples with long aliphatic counterions, but also as a result of ground-state interactions between aromatic counterions such as pyrene or naphthalene. This

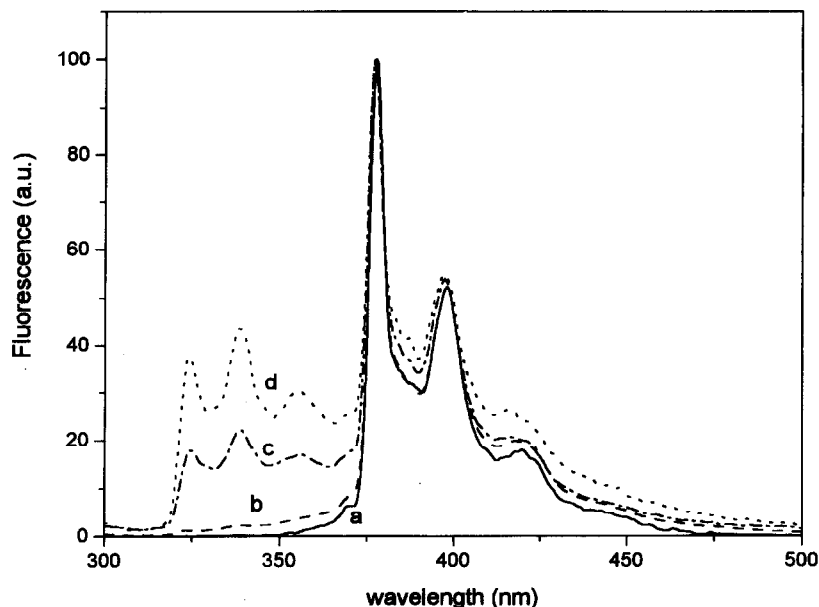


Fig. 8. Steady-state fluorescence emission spectra of I-PyB-Np film cast from DMF (a), water (b) or water-surfactant mixture in a presence of varying concentration of SDS, (c)  $[SDS] = 10^{-5}$  M, (d)  $[SDS] = 10^{-3}$  M.

behaviour manifests by spectral and fluorescence decays changes of pyrene derivatives used for monitoring the relationship between the composition of polyionene complexes and their solution dependent properties.

Excimer formation dynamics was observed in the nano-second time-domain only for DMF solutions of polyionene modified by aliphatic SDS counterions or for samples with high loading of pyrene moiety. In water solution, a decay of emission was registered, with a resolution of our time-resolved set-up, which suggests that excimers may originate directly from the excitation of the paired chromophores in the ground state. Pyrene fluorescence indicates that hydrophobically modified polyionenes contract in water and try to encapsulate their counterions into detached components. The solvent, as well as a composition of polyionene, has an influence on the morphology of the solid-state samples. I-PyB-SDS, i.e., polyionene of the highest aliphatic character, although might be considered as micelle-forming polyelectrolyte, it forms less organised structures in the solid films. Polyionenes samples with high aromatic counterion contents preserve their compact morphology from liquid solution. All observed photophysical parameters, i.e., the broadening of the excitation spectra, the very fast formation of excimer and changes in efficiency of energy transfer indicates that Py moieties are present in glassy films in a close proximity of other aromatics. This suggests that the latter form compact structures similar to unimolecular micelles. Such findings suggest that polyionenes with high degree of exchanged counterions might be interesting for various optical applications.

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