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Spectral characteristics of fluorescence probes based on pyrene in solution and in polymer matrix

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Abstract

Spectral properties of four types of bifunctional probes based on pyrene and sterically hindered amines (HAS) were compared in solution of cyclohexane and methanol and in polymer matrices as isotactic polypropylene (iPP), polystyrene (PS), poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC). Absorption spectra of these probes strongly depend on the type of linkage. When the carbonyl group in the linkage is in α-position to pyrene ring, the absorption bands are broader with rather poor vibrational resolution. The carbonyl group in α-position influences the emission spectra as well. For derivatives of 4-oxo-4-(1-pyrene)butanoic acid (I), the broad emission band was observed. Some vibrational resolution was observed for probes based on 1-pyrenecarboxylic acid (IV). Lifetime of these probes is in the range 1–10 ns. When methylene group instead of carbonyl is attached to pyrene and forms the link, the absorption spectra are the same as that of alkyl-substituted pyrene. This behaviour was shown for derivatives of 1-pyreneacetic acid (III) and 4-(1-pyrene)butyric acid (II). The emission spectra of these probes are similar as parent alkyl pyrene. The lifetime is in the range above 100 ns. The influence of solvent polarity and polymer matrix on spectra was not very pronounced for probe of parent amine types Ic–IVc. The decay of fluorescence of probes of this type was satisfactorily fitted to monoexponential function. The efficiency of intramolecular quenching observed for oxidised probes Id–IVd is in the range from about 1.5 for derivative Id to value of about 10 for IIId. It was influenced by type of linkage and medium. The decay of fluorescence of linked pyrene chromophore of probes Id–IVd is better fitted by biexponential function. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Probes; Pyrene; Hindered amine stabilisers; Absorption; Emission; Polymer matrices; Intramolecular fluorescence quenching; Solvent effect

1. Introduction

Fluorescence spectroscopy of low molecular mass compounds added to polymers can yield valuable information concerning the physical properties of macromolecules. Suitable probes can be applied to study the microenvironment of otherwise macroscopically homogeneous solutions for characterisation of polymeric media and for correlation of changes of photophysical parameters, which respond to different structural modifications. Singlet probes are suitable for monitoring of processes in nanosecond range. Triplet probes are suitable for monitoring of processes in more ordered systems in microsecond up to millisecond time range [1,2]. Fluorescence probes are important tools in biophysical studies of aggregates as micelles, membranes and vesicles [3,4]. The advantage of this approach lies in its high sensitivity, since the probes are to be applied at low concentration, which does not disturb at all or only slightly the original structures.

Studies with pyrene as fluorescence probe are of special importance [5,6]. Pyrene exhibits several valuable photophysical parameters such as high quantum yield of fluorescence $\Phi = 0.6$, long lifetime $\tau = 450$ ns in deaerated cyclohexane, sensitivity of its vibrational structure in the fluorescence spectra on polarity of the solvent and the ability to form excimers [6,7]. All these properties make it suitable for probing rather complex system as whole or their non-polar part. Monomer emission can serve as a starting point to monitor processes in which excitation localised on pyrene is transferred to other chromophore due to dipole–dipole interaction or electron exchange [1,8]. Pyrene molecules were used in many experiments employing excimer formation limited by diffusion to monitor some other processes mainly in liquid phase [1,7]. In solid phase, the yield of excimer fluorescence on pyrene concentration was established in low-temperature matrices [9]. The concentration effect of pyrene in poly(methyl methacrylate) (PMMA) indicates the formation of ground state dimers

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with suitable conformation for excimer formation [10]. Formation of ground state dimers or higher aggregates was observed in polystyrene (PS) at higher pyrene concentration [11]. These dimers serve as traps in the case of energy migration in highly doped polymer matrices with pyrene. Their absorption spectrum is red shifted resulting in larger overlap with monomer emission.

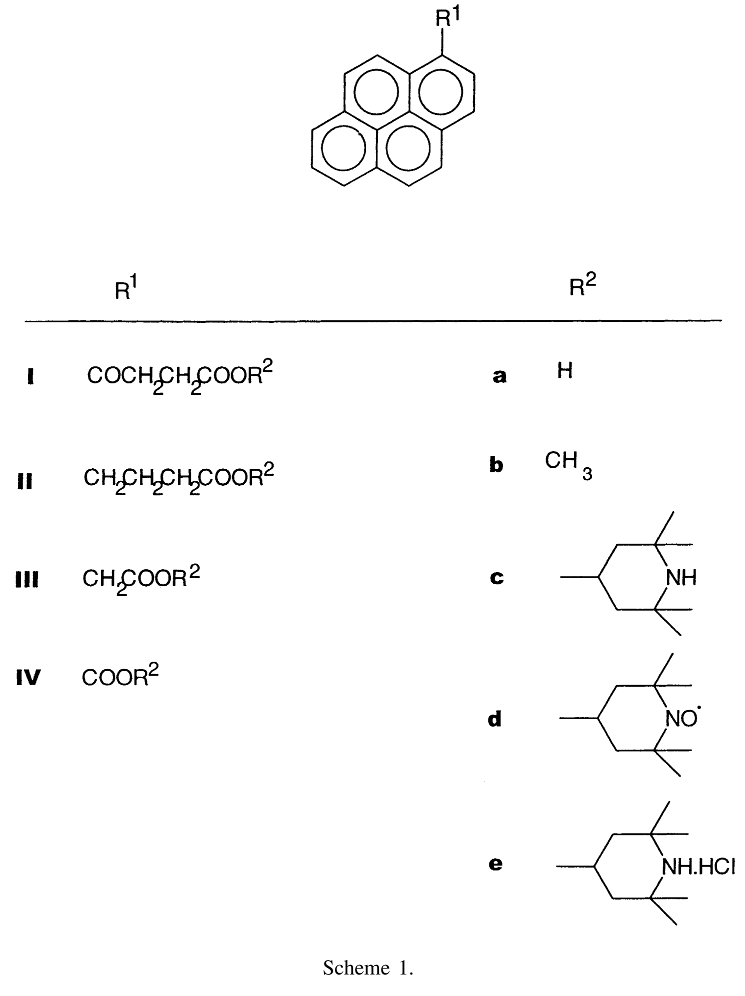
Sterically hindered amines (HAS) are at present the most effective stabilisers for long-term stabilisation of polyolefins, polystyrene, polydienes and its copolymers and terpolymers [12,13]. HAS are multifunctional stabilisers based on transformation of parent amine to nitroxyl radical. Oxidation products of HAS as nitroxyls, hydroxylamines and hydroxylaminoethers are active species in photoprotecting processes and regeneration cycles. Scavenging of radicals by nitroxyls is amplified by the ability of parent amines and oxidised products to form complexes with peroxides and peroxy radicals. Nitroxyls can form complexes with metals and take part in redox reactions. They influence the photo-oxidation of ketones by preventing the decarbonylation of acyl radicals.

During the last decade, fluorescence probes have been prepared and characterised in which simple chromophore as naphthalene [14–16], 1,8-naphthaleneimide [17], and pyrene [18–20] were linked with nitroxyls derived from HAS. In such probes, the intramolecular quenching of fluorescence is operated by different mechanisms depending on the structure of quencher–quenchee couple. The intramolecular quenching could be utilised to monitor oxidation processes accompanied by transformation of parent amine to nitroxyl [20]. This might be important for understanding processes during induction period of polyolefins stabilised by HAS provided that the chromophore withstands the harsh conditions of photo-oxidation.

In this paper, we compare the spectral properties of fluorescence probes derived from pyrene and HAS connected with a short link as carboxyl and with a longer one as *n*-butyl carboxyl. The absorption, emission spectra and decay of fluorescence are measured for four different types of probes in various solvent and polymer matrices. The extent of intramolecular quenching of pyrene fluorescence by nitroxyls in oxidised form of probes is quantified by static and dynamic measurements.

2. Experimental

Structures of bifunctional fluorescence probes used for spectral measurements are given in Scheme 1. Probes of



Scheme 1.

IIb–IIe are the same as used in [18,19]. The details of synthesis of the probes Ib–Ie, IIIb–IIIe and IVb–IVd have been described recently in [20]. The following derivatives were used: methyl-4-oxo-4-(1-pyrenyl)butanoate (Ib) mp 105–108°C, (2,2,6,6-tetramethyl-4-piperidyl)-4-oxo-4-(1-pyrenyl)butanoate (Ic) mp 117–122°C, (1-oxo-2,2,6,6-tetramethyl-4-piperidyl)-4-oxo-4-(1-pyrenyl)-butanoate (Id) mp 95–99°C, [(2,2,6,6-tetramethyl-4-piperidyl)-4-oxo-4-(1-pyrenyl)-butanoate]ium chloride (Ie) mp 117–125°C, methyl-4-(1-pyrenyl)butanoate (IIb) mp 43–45°C, (2,2,6,6-tetramethyl-4-piperidyl)-4-(1-pyrenyl)butanoate (IIc) yellow oil, (1-oxo-2,2,6,6-tetrametyl-4-piperidyl)-4-(1-pyrenyl)butanoate (IId) mp 110–112°C, [(2,2,6,6-tetramethyl-4-piperidyl)-4-(1-pyrenyl)butanoate]ium chloride (IIe) mp 220–230°C, methyl-2-(1-pyrenyl)acetate (IIIb) mp 90–92°C, (2,2,6,6-tetramethyl-4-piperidyl)-2-(1-pyrenyl)acetate (IIIc) mp 35–40°C, (1-oxo-2,2,6,6-tetrametyl-4-piperidyl)-2-(1-pyrenyl) acetate (IIId) yellow oil, [(2,2,6,6-tetramethyl-4-piperidyl)-2-(1-pyrenyl)acetate]ium chloride (IIIe) mp 264–266°C, methyl-1-pyrenylcarboxylate (IVb) mp 81–83°C, (2,2,6,6-tetramethyl-4-piperidyl)-1-pyrenylcarboxylate (IVc) mp 126–128°C, 1-oxo-2,2,6,6-tetramethyl-4-piperidyl-1-pyrenylcarboxylate (IVd) mp 174–176°C.

Anthracene was zonnally refined (Lachema n.e., Brno, CR). Cyclohexane (Merck, Darmstadt, FRG) was for UV spectroscopy. Methanol (Slavus s.r.o., Bratislava, SR), chloroform and THF (Lachema n.e., Brno, CR) were analytical reagents.

Polymer films doped with probes were prepared by casting from chloroform or THF solution or by hot-pressing of impregnated powders. The following polymers were used as matrices: PS (Krasten, Kaučuk Kralupy a.s., CR, SEC (chloroform), $M_n = 9.37 \times 10^4$, $M_w/M_n = 2.7$), polymethyl methacrylate (PMMA, Považské Chemické Závody a.s., Žilina, SR, $M_v = 1.01 \times 10^5$), polyvinyl chloride (PVC, Neralit 628, Spolana Neratovice a.s., CR, $M_v = 1.11 \times 10^5$) and atactic polypropylene (aPP, Slovnaft a.s., Bratislava, SR, $M_v = 9.3 \times 10^3$). Films were prepared for all polymers by casting 0.02–2 mg of probe in 1 ml chloroform or tetrahydrofurane solution of polymer (5 g per 100 ml) on a quartz or glass plate (28 mm × 35 mm). Isotactic polypropylene (iPP, Borealis, Schwechat, Austria, MFI = 3.5 g per 10 min) films were prepared by hot-pressing of impregnated powder (200°C for 1 min) in two concentrations of probe 0.002 and 0.02 mol kg^{-1}. Probe was dissolved in 1 ml of chloroform and added to 1 g of non-stabilised powder. After 24 h of impregnation, solvent was removed and powder was hot-pressed.

UV–VIS absorption spectra were recorded on M-40 (C. Zeiss, Jena, FRG) and UV 160 (Shimadzu, Japan) spectrometers. Emission spectra were recorded on a Perkin-Elmer MPF-4 spectrofluorimeter, which was connected through an interface and an A/D converter to a microcomputer [21] for data collection, processing and plotting on an X–Y plotter. The excitation wavelength was in the range 335–350 nm. 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 [16,19]. Emission of polymer films was measured in a front-face arrangement using a Perkin-Elmer solid sample holder. The relative quantum yield for emission of each probe in each polymer film was determined using anthracene in the same polymer as standard.

The relative quantum yields in films were determined according to the following relation [22]:

$$\Phi_F = \Phi_F^S \frac{\int_0^\infty I_F(\nu)\,d\nu}{\int_0^\infty I_F^S(\nu)\,d\nu} \left(\frac{1 - 10^{-A^S}}{1 - 10^{-A}} \right),$$

where Φ_F^S is quantum yield of anthracene as standard which was assumed to be 0.25 for all environments. For relative quantum yield, the value of Φ_F^S for anthracene was put as 1. Integrals $\int_0^\infty I_F(\nu)\,d\nu$ and $\int_0^\infty I_F^S(\nu)\,d\nu$ are areas under emission curve of investigated compound and standard, A and A^S the absorbances of investigated compound and standard, respectively. Excitation wavelength was set to reach the maximum of emission. The excitation of anthracene was in the range of 355–360 nm depending on the medium.

Fluorescence lifetime measurements were performed on a LIF 200 (Lasertechnik Ltd., Berlin, FRG) which operates as a stroboscope. The excitation source is nitrogen laser with $\lambda = 337$ nm. The emission is selected by cut-off filter. The output signal was digitised and transferred to a microcomputer [23]. When the fluorescence lifetime of pyrene and its derivatives was >20×, the half-width of the nitrogen laser (0.5 ns), simple linear least-square fits of the data without deconvolution were applied to mono- and biexponential functions [24]. When the fluorescence lifetimes is shorter than 20× of half-width of the nitrogen laser, phase plane method was used for analysis of decay curves [25]. The standard deviation $G^{1/2} = \sum((I_{exp} - I_{calc})^2/n)^{1/2}$, 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 function, if $G^{1/2} < 5\%$.

Static and time-resolved measurements were performed in deaerated solutions (argon bubbling for 5 min). All measurements on polymer films were in the presence of air.

Spectral characteristics and lifetimes of four pyrene/HAS probes in the form of parent amine and stable nitroxyl radical are summarised in Tables 1–4.

3. Results and discussion

The medium effect of solvent (solvatochromism) which surrounds the solute in ground and excited state is well established for liquids [26]. This effect is often used to estimate the excited state dipole moment in combination with ground state dipole moment. The effect of solid matrix is important, because many compounds (such as dyes, stabilisers and others) are applied as components of a more

Table 1
Spectral characteristics and lifetime of 2,2,6,6-tetramethyl-4-piperidyl-4-oxo-4-(1-pyrenyl)butanoate Ic and its amino-oxide Id

Probe	Medium[a]	λ_{abs}[b] (nm)	$\log \varepsilon$[c]	λ_{exc} (nm)	λ_{em} (I_r)[d] (nm)	Φ_r[e]	τ[f] (ns)	$G^{1/2}$[g]
Ic	CY	354	4.3	292	381 (1.00)	0.161	–	
	MeOH	354	4.13	350	439 (1.00)	0.018	0.8	8.3
	PS	357	4.22	363	422 (1.00)	0.122	1.3	6.1
	PMMA	355	4.19	360	413 (1.00)	0.066	0.9	8.7
	PVC	358	4.15	365	423 (1.00)	0.030	1.4	5.9
Id	CY	355	4.3	292	380 (1.00)	0.115	–	–
	MeOH	353	4.19	360	435 (1.00)	0.014	–	–
	PS	358	4.01	363	421 (1.00)	0.040	1.0	4.1
	PMMA	355	4.13	360	414 (1.00)	0.052	0.6	9.1
	PVC	357	4.14	365	418 (1.00)	0.019	1.6	6.9

[a] CY: cyclohexane; MeOH: methanol; PS: polystyrene; PMMA: poly(methyl methacrylate); PVC: poly(vinyl chloride).
[b] Wavelength of absorption band with maximum intensity.
[c] Decadic logarithm of extinction coefficient.
[d] Wavelength of emission maximum (relative intensity compared with emission band of maximum intensity).
[e] Relative quantum yield to anthracene measured at the same conditions.
[f] Lifetime determined by phase plane method [25].
[g] S.D.

Table 2
Spectral characteristics and lifetime of 2,2,6,6-tetramethyl-4-piperidyl-4-(1-pyrenyl)butanoate IIc and its amino-oxide IId

Probe	Medium[a]	λ_{abs}[b] (nm)	$\log \varepsilon$[c]	λ_{exc} (nm)	λ_{max} (I_r)[d] (nm)	Φ_r[e]	τ[f] (ns)	$G^{1/2}$[g]
IIc	CY	343	4.41	342	378 (1.00), 398 (0.25)	0.18	235.9	1.7
	MeOH	341	4.63	340	378 (1.00), 398 (0.26)	0.34	248.9	2.3
	aPP	344	4.61	342	378 (1.00), 398 (0.28)	1.39	208.0	0.9
	PS	348	4.44	347	380 (1.00), 399 (0.67)	0.86	159.3	3.3
	PMMA	345	4.36	345	379 (1.00), 398 (0.47)	0.97	157.0	4.0
	PVC	348	4.29	347	380 (1.00), 399 (0.51)	3.20	100.5	2.3
IId	CY	343	4.42	342	378 (1.00), 398 (0.38)	0.11	M[h]: 139.9 B[i]: 7.7 158.6	7.6 0.7
	MeOH	342	4.59	340	378 (1.00), 398 (0.33)	0.27	M[h]: 132.6 B[i]: 19.35 154.8	6.5 1.2
	aPP	344	4.55	342	378 (1.00), 398 (0.29)	0.58	M[h]: 157.7 B[i]: 85.3 203.1	3.5 0.3
	PS	348	4.36	347	380 (1.00), 399 (0.63)	0.52	M[h]: 153.6 B[i]: 74.8 180.8	3.3 0.4
	PMMA	345	4.23	345	379 (1.00), 397 (0.49)	0.63	M[h]: 96.5 B[i]: 13.1 105.9	6.9 0.5
	PVC	348	4.37	347	379 (1.00), 399 (0.48)	0.126	M[h]: 82.9 B[i]: 20.04 91.2	5.0 0.6

[a] CY: cyclohexane; MeOH: methanol; PS: polystyrene; PMMA: poly(methyl methacrylate); PVC: poly(vinyl chloride); aPP: atactic polypropylene.
[b] Wavelength of absorption band with maximum intensity.
[c] Decadic logarithm of extinction coefficient.
[d] Wavelength of emission maximum (relative intensity compared with emission band of maximum intensity).
[e] Relative quantum yield to anthracene measured at the same conditions.
[f] Simple fitting without deconvolution.
[g] S.D.
[h] Monoexponential fitting.
[i] Biexponential fitting.

Table 3
Spectral characteristics and lifetime of 2,2,6,6-tetramethyl-4-piperidyl-2-(1-pyrenyl)acetate IIIc and its amino-oxide IIId

Probe	Medium[a]	λ_{abs}[b] (nm)	log ε[c]	λ_{exc} (nm)	λ_{max} (I_r)[d] (nm)	Φ_r[e]	τ[f] (ns)	$G^{1/2}$[g]
IIIc	CY	343	4.62	342	391 (1.00)	1.32	299.8	1.7
	MeOH	341	4.56	340	378 (1.00), 398 (0.81)	0.81	230.0	3.1
	iPP	344	4.66	342	378 (0.56), 389 (1.00), 398 (0.96)	1.46	297.3	1.7
	PS	347	4.28	347	381 (0.57), 398 (1.00)	0.63	220.7	0.6
	PMMA	345	4.39	345	379 (0.79), 399 (1.00)	1.22	198.3	3.3
	PVC	347	4.27	347	380 (0.65), 399 (1.00)	0.74	146.4	5.1
IIId	CY	343	4.62	344	392 (1.00)	0.10	M[h]: 203.8 B[i]: 44.2 232.6	4.3 1.4
	MeOH	341	4.49	342	378 (0.79), 396 (1.00)	0.43	M[h]: 234.1 B[i]: 23.7 248.9	4.4 0.5
	iPP	344	4.53	345	378 (0.63), 389 (1.00)	0.47	M[h]: 257.1 B[i]: 68.3 302.6	3.5 6.5
	PS	347	4.31	348	381 (0.73), 399 (1.00)	0.75	M[h]: 168.7 B[i]: 48.7 197.8	5.9 0.5
	PMMA	345	4.36	345	378 (0.90), 398 (1.00)	1.13	M[h]: 157.4 B[i]: 50.3 198.6	7.5 0.6
	PVC	347	4.37	348	379 (0.79), 398 (1.00)	0.98	M[h]: 71.6 B[i]: 12.1 82.7	10.1 0.6

[a] CY: cyclohexane; MeOH: methanol; PS: polystyrene; PMMA: poly(methyl methacrylate); PVC: poly(vinyl chloride); iPP: isotactic polypropylene.
[b] Wavelength of absorption band with maximum intensity.
[c] Decadic logarithm of extinction coefficient.
[d] Wavelength of emission maximum (relative intensity compared with emission band of maximum intensity).
[e] Relative quantum yield to anthracene measured at the same conditions.
[f] Simple fitting without deconvolution.
[g] S.D.
[h] Monoexponential fitting.
[i] Biexponential fitting.

Table 4
Spectral characteristics and lifetime of 2,2,6,6-tetramethyl-4-piperidyl-1-pyrenecarboxylate IVc and its amino-oxide IVd

Probe	Medium[a]	λ_{abs}[b] (nm)	log ε[c]	λ_{exc} (nm)	λ_{em} (I_r)[d] (nm)	Φ_r[e]	τ[f] (ns)	$G^{1/2}$[g]
IVc	CY	385	3.87	354	387 (1.00), 406 (0.25), 428 (0.06)	1.64	15.5	0.7
	MeOH	386	3.87	354	395 (1.00), 411 (0.47)	3.90	8.6	4.8
	iPP	385	3.65	358	388 (0.63), 408 (1.00), 428 (0.08)	2.04	17.3	3.3
	PS	387	3.56	359	393 (1.00), 413 (0.57)	2.21	8.4	1.6
	PMMA	386	3.90	359	392 (1.00), 412 (0.88)	5.13	8.2	2.2
	PVC	387	3.93	360	393 (1.00), 413 (0.84)	5.98	6.5	0.7
IVd	CY	386	3.90	356	388 (1.00), 407 (0.26)	0.11	1.0	14.9
	MeOH	385	3.87	353	395 (1.00), 410 (0.50)	0.36	4.3	8.0
	iPP	385	3.65	358	388 (0.88), 408 (1.00)	1.09	14.5	2.7
	PS	387	3.61	359	393 (1.00), 413 (0.51)	0.18	4.3	8.7
	PMMA	386	3.86	359	391 (1.00), 411 (0.83)	0.82	5.6	3.7
	PVC	386	3.98	360	393 (1.00), 412 (0.62)	1.13	4.1	5.8

[a] CY: cyclohexane; MeOH: methanol; PS: polystyrene; PMMA: poly(methyl methacrylate); PVC: poly(vinyl chloride); iPP: isotactic polypropylene.
[b] Wavelength of absorption band with maximum intensity.
[c] Decadic logarithm of extinction coefficient.
[d] Wavelength of emission maximum (relative intensity compared with emission band of maximum intensity).
[e] Relative quantum yield to anthracene measured at the same conditions.
[f] Simple fitting without deconvolution.
[g] S.D.

complex system in the solid phase. Therefore, it is important to evaluate the medium effect for these systems as well. The solvatochromic effects of rigid matrices are complex and as yet less understood as compared with solvents. It is important to take into account not only the matrix itself but its mode of preparation and the way in which the solute has been incorporated into the matrix.

At the analysis of the influence of the medium on spectral properties of doped molecules in the polymer matrix two limiting cases are to be considered: (i) the polymer matrix is more or less inert; (ii) the polymer matrix exhibits equal or similar effect as low molecular solvent containing the same structural units. In the case of (ii), the main difference between low molecular solvent and polymer matrix is in the mobility of the solvent shell. This effect plays minor role in absorption spectra. Therefore, small differences are observed in absorption spectra of the probes under study in polymer matrices as compared to solvents. It can be however more important at other spectral properties.

Absorption spectra of pyrene derivatives substituted with carbonyl group directly on pyrene ring — derivatives of 4-oxo-4-(1-pyrenyl)butanoic acid (I) or carboxylic group — derivatives of 1-pyrenylcaboxylic acid (IV) substantially differ from the spectra of unsubstituted pyrene or alkyl-substituted pyrene — derivatives of 4-(pyrenyl)-butanoic acid (II) or derivatives of 1-pyreneacetic acid (III). Presence of carbonyl group in α-position to pyrene causes that absorption bands are broader with less-resolved vibrational structure (Fig. 1). The longest wavelength band is extended to the red. The spectrum has got the same feature as that of 1-heptanoylpyrene [27]. The longest wavelength band of derivatives I has got shoulder at 380 nm on band with maximum at 350 nm. At derivatives IV this band has got maximum at 385 nm ($\log \varepsilon \sim 3.5$). The solvent polarity has got small influence on this band for both series (I and IV) of derivatives; small hypsochromic shift (1–2 nm) is observed in going from non-polar cyclohexane to polar methanol, but mostly bathochromic shift in going to polymer matrices (Tables 1 and 4).

Absorption spectra of bifunctional probes where pyrene is connected with sterically hindered amine through methylene bridge on pyrene (derivatives of II and III) exhibit well-resolved spectra in the same fashion as pyrene. Probes based on 4-(1-pyrenyl)butanoic acid (II) exhibit maximum around 345 nm. In going from non-polar cyclohexane to polar methanol, hypsochromic shift of absorption bands is observed for derivatives of II (Table 2). Absorption spectra of derivatives III are slightly influenced by solvent polarity. In the case of a polymer matrix for both series, a bathochromic shift of absorption bands is observed in going from non-polar iPP to polar PVC. Probe IIIc (parent amine) exhibits at longest wavelength edge weakly resolved transition $S_0 \rightarrow S_1$ at concentration 10^{-3} mol dm^{-3} in methanol. On the other hand, this transition at 368 (shoulder), 376, and 400 nm of IIId (amino-oxide) is better resolved in cyclohexane than in methanol (Fig. 2).

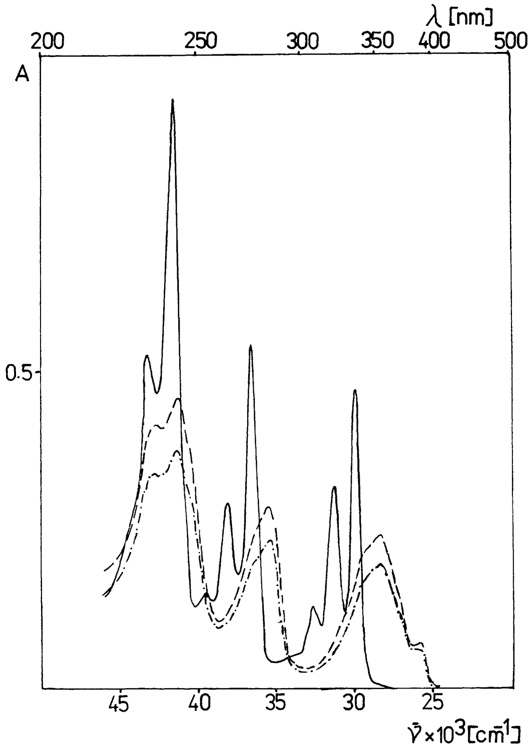


Fig. 1. Absorption spectra of pyrene (—) and derivatives I in cyclohexane ($c = 10^{-5}$ mol dm^{-3}): Ib (– – –) and Id (– · – · –).

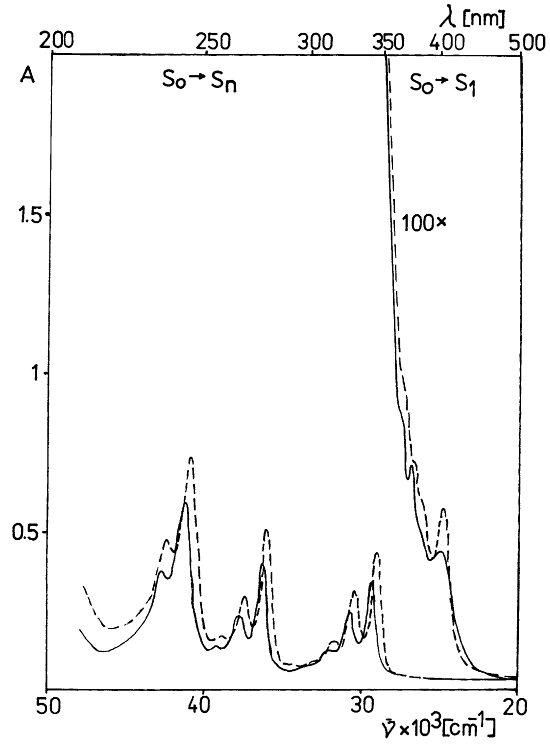


Fig. 2. Absorption spectra of probe IIId in methanol (—) and cyclohexane (– – –) at $c = 10^{-5}$ and 10^{-3} mol dm^{-3}, respectively.

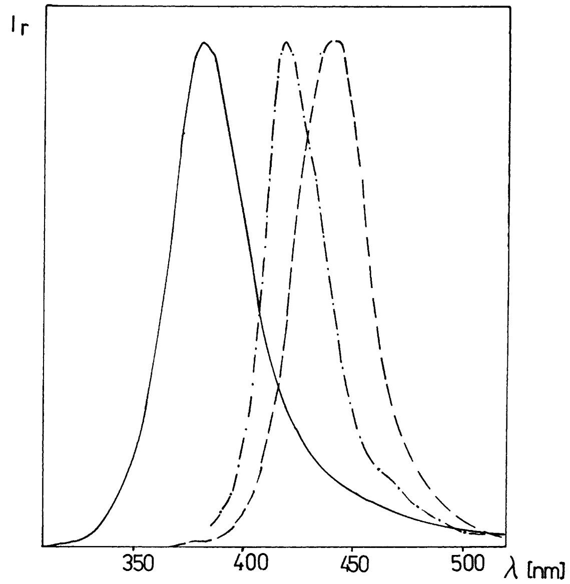


Fig. 3. Emission spectra of derivative Ib in different media: cyclohexane (—) ($c = 10^{-5}$ mol dm^{-3}); PVC (–·–·–) ($c = 2 \times 10^{-3}$ mol kg^{-1}); methanol (– – –) ($c = 10^{-5}$ mol dm^{-3}).

In summary, the absorption spectra of probes in the form of parent amine Ic–IVc as well as amino-oxide Id–IVd exhibit only minor differences when taken in solvents and polymer matrices.

Emission spectra of derivatives of type I differ from spectrum of pyrene. All probes of this type have the same characteristics as unsubstituted Ia. Emission spectra exhibit broad band without any vibrational structure (Fig. 3). In solution going from cyclohexane to methanol, a bathochromic shift is observed (Table 1). This effect is not noticeable in polymer matrices in going from PS to PVC at concentration 0.002 mol kg^{-1}, but it is more pronounced at 0.01 mol kg^{-1}.

Emission spectra of derivatives based on II differ less from the spectrum of pyrene (Fig. 4). The main emission band lies at 377–380 nm and less intense band at 398–420 nm and shoulder at 415–420 nm. Under optimal conditions, additional weak bands are observed at 382 and 388 nm and a shoulder at 394 nm. Vibrational resolution of emission spectra of probes of type II does not depend on solvent polarity and is preserved in all environments. Increasing concentration from 10^{-5} to 10^{-3} mol dm^{-3} in solution and from 0.002 to 0.02 mol kg^{-1} in polymer matrix changes some features of the emission spectra. One example of this effect is shown in Fig. 5 for probe IIc in cyclohexane. The intensity of short wavelength part decreases and that one of the long wavelength at 398 and 417 nm increases. Vibrational structure of IIc is well preserved in all types of media concerning polarity (cyclohexane or iPP and methanol or PVC). Amino-oxide IId exhibits the same spectrum as IIc, but the intensity is lower due to internal quenching by the nitroxyl radical. More polar hydrochloride IIe in polar solvent and polymer matrices exhibits the same spectra as IIc. At higher concentration of IIe, strong excimer emission is observed in solution and non-polar aPP [19]. For IIc and IId, the excimer emission at the same concentration is much weaker.

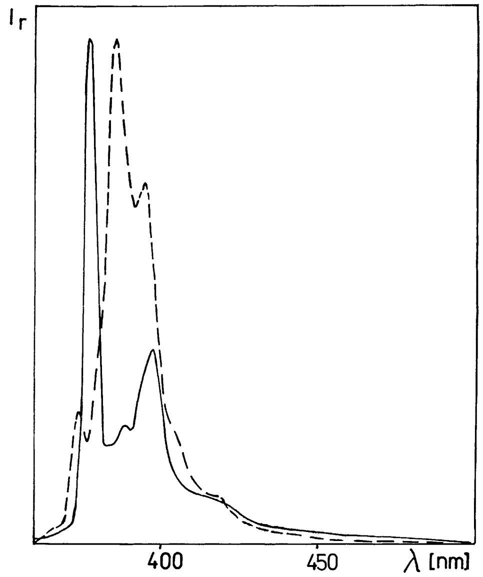


Fig. 4. Comparison of the emission spectra of IId (—) and pyrene (– – –) in deaerated cyclohexane at $c = 10^{-5}$ mol dm^{-3}.

Probe IIIc (parent amine) as well as the oxidised form IIId (amino-oxide or nitroxyl radical) exhibit emission bands of different intensities of respective vibrational bands in four regions. There are four groups of resolved vibrational bands in the range 377–381, 389–392 and 396–400 nm, and as a shoulder at 415–425 nm (Fig. 6). In non-polar cyclohexane and iPP, the most intense band is at 390 nm and others are weaker. In polar media, the most intense bands are at 380

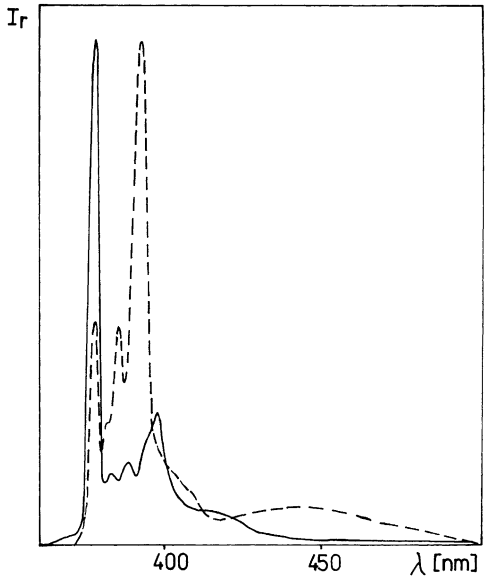


Fig. 5. Emission spectra of probe IIc in dearated cyclohexane at $c = 10^{-5}$ mol dm^{-3} (—) and $c = 10^{-3}$ mol dm^{-3} (– – –).

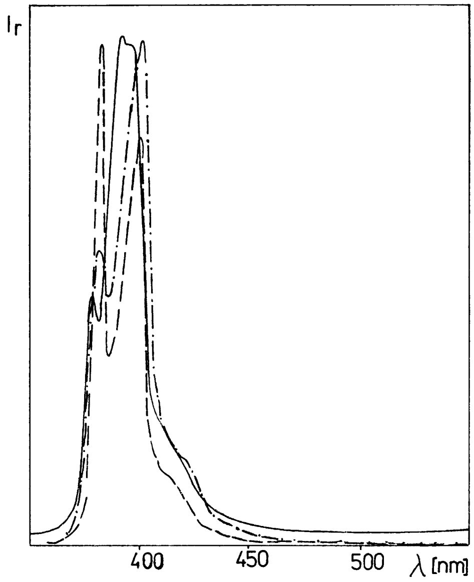


Fig. 6. Emission spectra of IIIc in cyclohexane (—) ($c = 10^{-5}$ mol dm^{-3}), methanol (– – –) ($c = 10^{-5}$ mol dm^{-3}) and polystyrene (–·–·–) ($c = 2 \times 10^{-3}$ mol kg^{-1}).

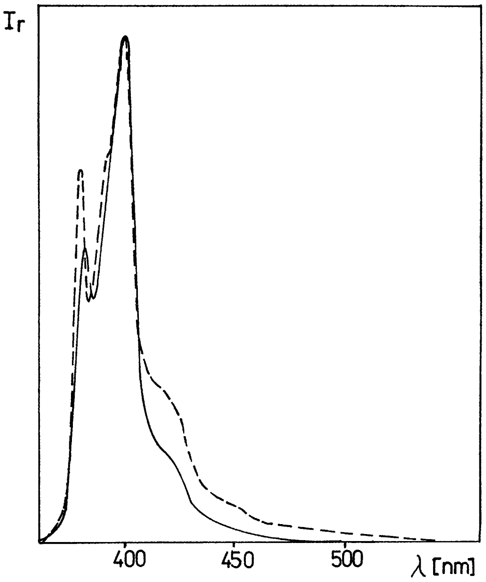


Fig. 8. Emission spectra of IIIc in PS at $c = 2 \times 10^{-3}$ mol kg^{-1} (—) and $c = 2 \times 10^{-2}$ mol kg^{-1} (– – –).

and 400 nm (Table 3). Although, the vibrational structure of emission spectra changes with the polarity of solvent, the correlation of vibrational structure on medium polarity was not established for the type III derivatives. At concentration of 10^{-3} mol dm^{-3} and above, typical excimer band at 470 nm was observed which is higher in methanol than in cyclohexane (Fig. 7). Simultaneously, the rest of the original spectra looses their vibrational structure especially the peak at 380 nm vanishes in methanol. In polymer films, excimer emission of IIIc is not observed even at concentration 0.02 mol kg^{-1}. The long wavelength edge is shifted to red at this concentration (Fig. 8).

Emission spectra of type IV probes are vibrationally well resolved in non-polar cyclohexane with maximum at 387 nm (Fig. 9). Similar emission spectra were observed in iPP. In non-polar media as well as in PMMA, the longest wavelength emission band at 427–430 nm is well resolved, too. Going from non-polar cyclohexane through PMMA to polar methanol, the red shift at lowest wavelength is

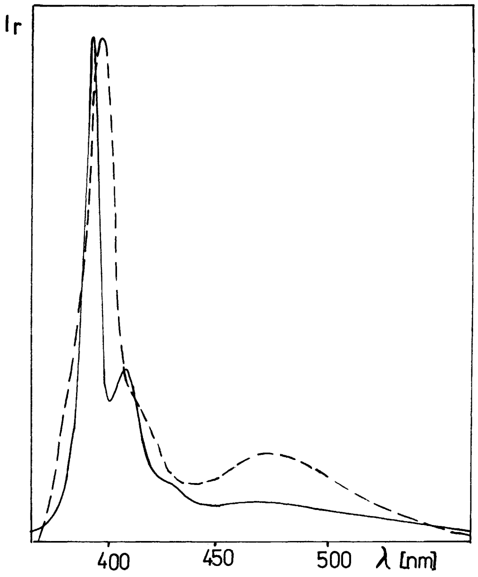


Fig. 7. Emission spectra of IIIc in cyclohexane (—) at $c = 10^{-3}$ mol dm^{-3} and methanol (– – –).

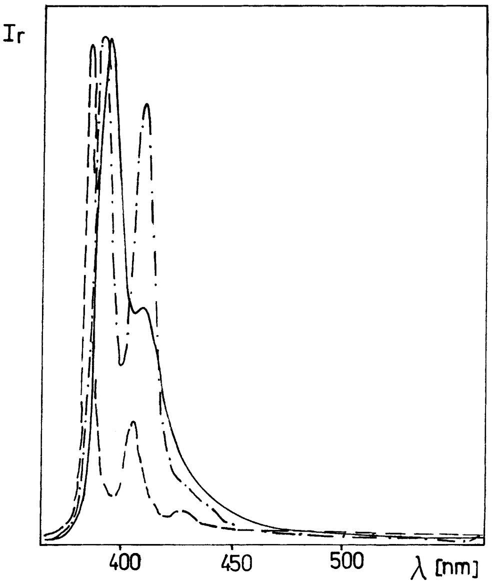


Fig. 9. Emission spectra of IVc in methanol (—) ($c = 10^{-5}$ mol dm^{-3}), cyclohexane (– – –) ($c = 10^{-5}$ mol dm^{-3}) and PMMA (–·–·–) ($c = 2 \times 10^{-3}$ mol kg^{-1}).

clearly demonstrated. In polar media as methanol or PVC, the bands are broader and less resolved.

In fact, the fluorescence spectra of parent amine type of probes Ic–IVc and amino-oxide types Id–IVd are more influenced by medium than absorption spectra. The effect of polarity of medium seems to be most important than other effects.

The lifetime of emission is strongly influenced by the position of carbonyl group in the link of pyrene chromophore with sterically hindered amine. The presence of carbonyl group directly attached to pyrene ring dramatically shortens the lifetime of emission of derivatives of types I and IV. Derivatives of type I exhibit lifetime under 1 ns in methanol and in the range 1–2 ns in polymer matrices (Table 1). The error of fitting of decay to monoexponential function is charged with large error above 5%. Similar effect of carbonyl group was observed for 1-heptanoylpyrene [27]. Probes of type IV exhibit lifetime of emission around 10 ns (Table 4). Decay of emission of IVc is well fitted to monoexponential function. As a result of intramolecular quenching, the lifetime of IVd is shorter and the decay function is not well fitted with monoexponential function. In the case of probes with methylene linkage on pyrene (types II and III), the lifetime is as long as that of alkyl-substituted pyrene in deaerated solutions (Tables 2 and 3). In polymer matrices even in the presence of air, the lifetime is rather long. Monomer emission of IIc and IIIc decays as monoexponential function and it decays faster as pyrene under the same conditions. For probe IIc, lifetime is in range of 100–250 ns and for probe IIIc in range of 150–300 ns. The decay of monomer fluorescence of nitroxyl radicals (IId and IIId) was fitted to biexponential function. The fast component was in the range of 10–85 ns for both probes and the slow component decays roughly as the parent amine.

The probes Id–IVd containing pyrene chromophore and amino-oxide structural unit (paramagnetic centre) exhibit in some extent intramolecular quenching depending on the type of linkage and medium. During 1990s, this intramolecular quenching has been intensively investigated involving naphthalene [14,16], 1,4,5,8-naphthalenediimide [15], 1,8-naphthaleneimide [17], pyrene [19] and fluorescamine [28] as chromophores. The mechanism of intramolecular quenching has not yet been clearly established. Two possible routes are considered namely photophysical one involving new radiationless deactivation route, e.g. internal conversion or energy transfer due to paramagnetic nitroxide channel, which should not be influenced by the medium [14,16,28]. Second possibility is the electron transfer, which is preferred with more polar chromophores and in more polar media [15,17].

The efficiency of intramolecular quenching (Table 5) is quantified based on static and dynamic measurements as well. Results from static measurements represent the ratio of relative quantum yields Φ_{NH}/Φ_{NO} of parent amine versus amino-oxide form of probes. In the case of dynamic measurement, the efficiency is expressed as the ratio of the lifetime of parent amino versus amino-oxide form τ_{NH}/τ_{NO} using the lifetime fitted to a monoexponential for both forms. The efficiency of the intramolecular quenching of type I probe seems to be rather low. The values are slightly above 1 for static and dynamic measurements. The efficiency of the intramolecular quenching process of probes of type I is not influenced by the solvent environment. This process is not very effective. The internal quenching of probes of type II is more efficient. The quenching efficiency according to static and dynamic data are in the interval 1.5–2 for most cases. Like for probes I, there is no influence of the environment on quenching. It means that the rate of the radiationless channel due to the presence of a paramagnetic centre is comparable to that of the radiation path. The independence on solvent environment indicates that the channel is photophysical. The extent of intramolecular quenching of type III probe based on static measurement is higher in non-polar cyclohexane and iPP. In polar methanol and other more polar media, the extent is lower. Dynamic measurements, however, do not show more efficient quenching in non-polar media as

Table 5
Intramolecular quenching of probes of types I–IV in different media

Probe	Medium[a] efficiency[b]	CY	MeOH	iPP	PS	PMMA	PVC
I	Φ_{NH}/Φ_{NO}	1.40	1.29	–	3.05	1.27	1.58
	τ_{NH}/τ_{NO}	–	–	–	1.31	1.53	0.83
II	Φ_{NH}/Φ_{NO}	1.64	1.25	2.40	1.69	1.56	2.54
	τ_{NH}/τ_{NO}	1.69	1.88	1.28	1.04	1.62	1.21
III	Φ_{NH}/Φ_{NO}	13.1	1.9	3.08	1.87	1.08	0.77
	τ_{NH}/τ_{NO}	1.47	1.00	1.16	1.30	1.26	2.04
IV	Φ_{NH}/Φ_{NO}	10.9	14.9	1.87	12.3	6.30	5.30
	Φ_{NH}/Φ_{NO}[c]	–	–	12.1	30.5	10.9	12.8
	τ_{NH}/τ_{NO}	14.6	1.96	1.20	1.49	2.00	1.54

[a] CY: cyclohexane; MeOH: methanol; iPP: isotactic polypropylene; PS: polystyrene; PMMA: poly(methyl methacrylate); PVC: poly(vinyl chloride).

[b] Measurement of Φ at 10^{-5} mol dm^{-3} in solution and at 0.002 mol kg^{-1} in film relative to anthracene; measurement of τ at 1×10^{-4} mol dm^{-3} in solution and 0.002 mol kg^{-1} in film; decay curve of fluorescence was fitted to monoexponential.

[c] Measurement of Φ at.0.02 mol kg^{-1}.

expected from static measurements. They agree quite well with the static data for polar media except of PVC where larger value is observed. For type IV probes, the static values of intramolecular quenching are rather high around 10 units except of iPP at lower concentration. Since the static data at higher concentration are higher, one can assume that intermolecular quenching plays some role as well. The dynamic data based on lifetime are substantially lower which might be due to the fact that lifetime of IVc were not properly evaluated. The efficiency of internal quenching of probes with shorter linkage types III and IV seems to be more sensitive to the environment. Therefore, electron transfer as quenching mechanism might be assumed. In this case, however, more effective quenching would be expected in polar than in non-polar media [15]. Since the mechanism of intramolecular quenching depends on the quencher–quenchee couple, some intramolecular electron transfer even in non-polar environment cannot be completely excluded. Recently, the "inverted solvent effect" has been observed for intermolecular quenching of singlet state of azo alkanes by aromatic amines [29]. It means that higher quenching rate constant for this system has been observed in non-polar than in polar solvents at quenching involving electron transfer. At present, based on the experimental data, it is difficult to conclude that the inverted solvent effect is observed in intramolecular quenching of IIId and IVd. Our data indicate that the efficiency of intramolecular quenching of probes Id and IId in solvent and polymer matrices is comparable. For IIId and Ivd, it is higher in solvents than in polymer matrices. This might suggest that the environment plays some role in intramolecular quenching.

The quantitative data of efficiency of internal quenching determined by static as well as dynamic measurements are charged with rather high error caused by several reasons. Expressed as ratio of Φ_{NH}/I_{NO} and τ_{NH}/τ_{NO}, the efficiency is sensitive on the rather small changes of denominator. These data are obtained by measuring relative quantum yield Φ and lifetime τ of oxidised species, which inherently are prone to larger variations. This might be amplified by measurement in polymer film due to problems with their homogeneity. Since determination of efficiency is the single point measurement and large error is involved in determination, only the qualitative conclusions in this respect are fully justified.

4. Conclusion

In conclusion, the probes based on pyrene linked with sterically hindered amine exhibit interesting spectral properties which show a dependence on the environment. Efficiency of intramolecular quenching depends on the length and type of link between pyrene and sterically hindered amine.

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