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Spectral characteristics of multifunctional probes based on pyrene in solution and in polymer matrices

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Abstract

The spectral properties of multifunctional probes derived from 4-(1-pyrene)butyric acid and 2,2,6,6-tetramethyl-4-hydroxypiperidine in solution and in polymer matrices were investigated. In the absorption spectra, the well-resolved absorption of pyrene dominates and is little influenced by the medium. The absorption of the hydrochloride derived from the amine in non-polar matrices is rather diffuse. All the fluorescence probes with different functional groups at the sterically hindered centre yield well-resolved emission spectra, which are the same in solution and in polymer matrices at low concentration. The main features of the emission spectra are not influenced by the polarity of the medium. A red-shifted excimer emission is observed for the hydrochloride at concentrations in solution (10^{-3} mol dm^{-3}) and in solid matrices (0.1 mol kg^{-1}) at which the parent probe yields the monomer emission only, indicating the formation of ground state aggregates. Steady state and lifetime measurements indicate that the emission of the *N*-oxyl-type probe is quenched by about 50% irrespective of the medium. This new radiationless channel in the *N*-oxyl-type probe is comparable with the rate of the radiation channel. © 1997 Elsevier Science S.A.

Keywords: Multifunctional probes; Polymer matrix; Pyrene; Solution; Spectral characteristics

1. Introduction

Fluorescence probes of different types are used to monitor the photophysical and photochemical processes in various environments, e.g. solutions [1], micelles [2], polymer systems [3] and biosystems [4,5]. All parameters which depend on the environment can be used for this purpose. The application of fluorescence has several advantages due to its high sensitivity and pronounced influence of the environment on suitably selected chromophores. Pyrene has been widely used as a probe [6]. Certain derivatives of pyrene may offer additional functions. The attachment of a sterically hindered reaction centre of amine type to pyrene results in a variation in the intensity due to intramolecular quenching after oxidation of amine to *N*-oxyl. Transformation of the sterically hindered amine to hydrochloride results in an increased solubility in polar solvents.

Recently, we have described the application of this probe for the characterization of premicellar aggregates of surfactants and polyelectrolytes [7]. In this paper, the oxidation of sterically hindered amine is employed to prepare a modified probe which exhibits intramolecular quenching. The mechanisms of intramolecular and intermolecular quenching of the excited states of aromatic hydrocarbons and paramagnetic *N*-oxyls have not been established unequivocally. The following mechanisms are considered:

1. a catalytic increase in intersystem crossing as a result of spin–orbital interaction in the presence of a paramagnetic centre [8,9];
2. a catalytic increase in intersystem conversion [8,9];
3. the transfer of electronic energy by resonance or exchange [10];
4. the transfer of electrons and the formation of cation or anion radicals [11].

We focus our attention on the spectral characteristics of the derivatives of pyrene in different environments aiming to obtain further data on their application as probes.

2. Experimental details

The structure of the fluorescence probes used in this paper is shown in Scheme 1.

The 2,2,6,6-tetramethyl-4-hydroxypiperidinium ester of 4-(1-pyrene)butyric acid (1PyBuATMP) was prepared by re-esterification of the methyl ester of 4-(1-pyrene)butyric acid

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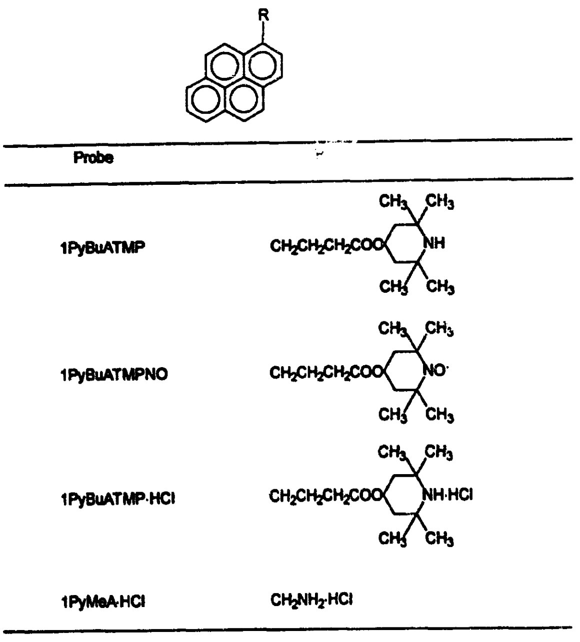

Scheme 1.

with 2,2,6,6-tetramethyl-4-hydroxypiperidine referred to in Ref. [7].

Chloride 2,2,6,6-tetramethyl-4-hydroxypiperidinium 4-(1-pyrene)butyrate (1PyBuATMP.HCl) was the same as that prepared previously (m.p., 220–230 °C) [7].

1-Oxo-2,2,6,6-tetramethylpiperidine 4-(1-pyrene)butyrate (1PyBuATMPNO) was prepared by oxidation. To a diethylether solution of 0.5 g (1.17 mmol) of 1PyBuATMP, 3-chloroperbenzoic acid (0.5 g, 2.93 mmol) was added with stirring and cooling. The mixture was stirred for 1 h at 0 °C and for another 1 h at laboratory temperature. The reaction mixture was washed with dilute sodium carbonate and with water. After drying and solvent removal, the crude product was purified by chromatography (silica gel, chloroform). The product was crystallized from *n*-hexane (m.p., 110–112 °C); yield, 0.3 g (57%).

4-(1-Pyrene)butyric acid (1PyBuA) and 1-pyrenemethylammonium chloride (1PyMeA.HCl) were the commercial products (Aldrich-Chemie, Steinheim, Germany).

Sodium dodecylsulphate (SDS; Merck, Darmstadt, Germany) was used without further purification.

Anthracene was zonally refined (Lachema n.e., Brno, Czech Republic). Quinine sulphate was an analytical reagent.

The solvents cyclohexane (Merck, Darmstadt, Germany), ethanol and methanol were of UV spectroscopy grade. Chloroform and tetrahydrofuran (Lachema n.e., Brno, Czech Republic) were analytical reagents.

Polymer films doped with fluorescence probes were prepared by casting from solution. Films of atactic polypropylene (aPP) (Slovnaft, Bratislava), polystyrene (PS) (Chemische Werke Huels, Germany) and poly(methyl methacrylate) (PMMA) (Diacon, ICI, UK) were prepared by casting 0.02–2 mg of probe in 1 ml of chloroform solution of the polymer (5 g per 100 ml) on a quartz or glass plate (28 mm × 35 mm). The solvent was evaporated slowly. Films of poly(vinylchloride) (PVC) (Neralit, Spolana Neratovice s.e., Czech Republic) were prepared by casting tetrahydrofuran solution (5 g per 100 ml) similarly. The concentration of the probe was in the range 0.002–0.2 mol kg^{-1}.

The absorption spectra were recorded on a SPECORD UV–visible M-40 spectrometer (C. Zeiss, Jena, Germany) in non-polar cyclohexane and polar methanol.

The emission spectra were recorded on a Perkin–Elmer MPF-4 spectrofluorometer (Perkin–Elmer, Norfolk, CT, USA), which was connected through an interface and A/D converter to a microcomputer [12] for data collection, processing and plotting on an XY 4110 plotter (Laboratorní přístroje n.e., Prague, Czech Republic). Solution emission was measured in a 1 cm cuvette in a right angle arrangement. The quantum yields were determined relative to quinine sulphate in 0.1 N sulphuric acid and to anthracene in cyclohexane or methanol. The emission of polymer films was measured in the front face arrangement using a solid sample holder. The quantum yield of doped polymer films was determined using anthracene as a standard which fulfils the following requirements:

1. good solubility in solvents of different polarity and good compatibility with polymer matrices;
2. absorption and emission in the same region as the probes under study;
3. availability in high purity;
4. small or no influence of the spectral properties by the medium.

The quantum yields in solution and in the films were determined according to the relation [13]

$$\phi=\phi_{\mathrm{F}}^{\mathrm{S}}\frac{\int_0^\infty I_{\mathrm{F}}(\tilde{\nu})\mathrm{d}\tilde{\nu}}{\int_0^\infty I_{\mathrm{F}}^{\mathrm{S}}(\tilde{\nu})\mathrm{d}\tilde{\nu}}\left(\frac{1-10^{-A^{\mathrm{S}}}}{1-10^{-A}}\right)\left(\frac{n}{n^{\mathrm{S}}}\right)^2\left(\frac{2-r^{\mathrm{S}}}{2-r}\right)$$

where $\phi_{\mathrm{F}}^{\mathrm{S}}$ is the quantum yield of the standard, $\int_0^\infty I_{\mathrm{F}}(\tilde{\nu})\mathrm{d}\tilde{\nu}$ and $\int_0^\infty I_{\mathrm{F}}^{\mathrm{S}}(\tilde{\nu})\mathrm{d}\tilde{\nu}$ are the areas under the fluorescence curves of the probe and standard respectively, A and A^{S} are the absorptions of the probe and standard respectively and n and n^{S} are the refractive indices and r and r^{S} are the emission anisotropies on excitation by unpolarized light of the probe and standard respectively. No correction was made to the emission anisotropy due to excitation by unpolarized light.

The fluorescence lifetime measurements were performed on a LIF 200 (Lasertechnik Ltd., Berlin, Germany) which operates as a stroboscope. The output signal was digitized and transferred to a microcomputer [14]. Since the fluorescence lifetimes of pyrene and its derivatives are longer than 0.5 ns, which is the half-width of the nitrogen laser, a simple linear least square without deconvolution was applied for the fitting of the decay curve to monoexponential and biexponential functions [15]. The standard deviation $G^{1/2}=\Sigma[(I_{\mathrm{exp}}-I_{\mathrm{calc}})^2/n]^{1/2}$, where I_{exp} and I_{calc} are the experimental and calculated emission intensities respectively, was used to determine whether the decay was monoexponential. It is assumed that the decay curve satisfies a monoexponential function if $G^{1/2}$ is less than 5%.

Steady state and time-resolved measurements were performed on deaerated solutions by passing a stream of argon for 10 min. All measurements on polymer films were performed in the presence of air.

^{1}H NMR spectra were measured on a 300 MHz AM-300 instrument (Bruker, Germany).

3. Results and discussion

The absorption spectra of pyrene-based probes are vibrationally well resolved similar to parent pyrene. The absorption spectrum of the probe with a sterically hindered amine centre (1PyBuATMP) shows no influence of the medium (Table 1). On going from non-polar cyclohexane to polar methanol, a small hypsochromic shift is observed. In micellar solutions of SDS, the absorption spectra of these probes are more similar to those in cyclohexane than in methanol. The opposite effect is observed on going from a non-polar polymer matrix such as aPP to polar PVC. Although there is some variation in the extinction coefficients, especially in polymer matrices, the main features of the absorption spectrum of unsubstituted pyrene are well preserved for all probes under study in all environments. The polar probe 1PyBuATMP.HCl exhibits a rather diffuse absorption spectrum in non-polar aPP (Fig. 1). On the other hand, the absorption of this probe is vibrationally well resolved in polar solvents such as methanol or water.

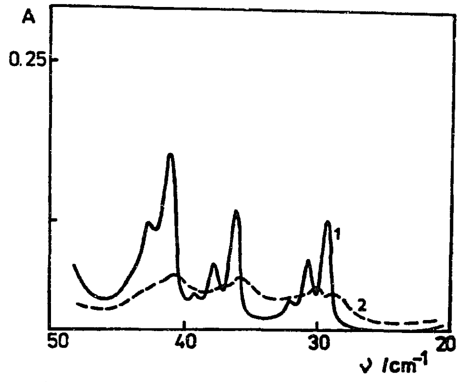

Fig. 1. Absorption spectra of probes in aPP film (thickness, 0.005 cm): 1, 1PyBuATMP; 2, 1PyBuATMP.HCl.

The emission spectra of the probes based on 4-(1-pyrene)butyric acid and 2,2,6,6-tetramethylpiperidine exhibit the same character as the parent acid [16]. The emission spectra of the parent amine and the oxidized and neutralized derivatives differ from that of unsubstituted pyrene. The emission spectra are dominated by a narrow first emission band at 377–380 nm, a less intense band at 398–400 nm (about 30% of the intensity of the first band) and a weak band at 415–420 nm (about one-tenth of the intensity of the first band). Under optimal conditions, bands at 382 and 388 nm and a shoulder at 394 nm are also observed. The vibrational resolution of the emission of these pyrene derivatives is not dependent on the polarity of the solvent, in comparison with unsubstituted pyrene which is the base for a polarity scale [17]. With increasing concentration in the range 10^{-5}–10^{-3} mol dm^{-3} in solvents and 0.002–0.2 mol kg^{-1} in polymer matrices, the shapes of the spectra change. The intensity of the first band decreases and the intensities of the bands at 398 and 417 nm increase. The red-shifted excimer emission in this concentration range is observed only under special conditions.

Table 1
Absorption spectra of the probe 1PyBuATMP in different surroundings

Solvent	λ (nm) (log ϵ, dm^3 mol^{-1} cm^{-1})
Cyclohexane	235 (4.67), 244 (4.90), 266 (4.45), 277 (4.74), 327 m(4.24), 343 (4.41)
Methanol	243 (4.88), 265 (4.42), 276 (4.70), 326 (4.460), 341 (4.63)
0.1 M SDS	267 (4.13), 278 (4.40), 329 (4.16), 345 (4.33)
aPP	245 (4.81), 266 (4.38), 277 (4.64), 328 (4.40), 344 (4.61)
PS	316 (3.99), 331 (4.30), 348 (4.44)
PMMA	244 (4.50), 267 (4.19), 277 (4.47), 329 (4.24), 345 (4.36)
PVC	247 (4.53), 269 (4.13), 279 (4.40), 332 (4.20), 348 (4.29)

The main features of the emission spectrum of the parent amine (1PyBuATMP) at low concentration in solution (10^{-5} mol dm^{-3}) and in polymer matrices (10^{-3} mol kg^{-1}) are well preserved in all surroundings, including non-polar cyclohexane, aPP, polar methanol and PVC (Table 2). In polymer matrices, the intensity of the band at 399 nm is stronger than that in solvents. A similar emission spectrum is observed for the probe 1PyBuATMP.HCl in polar solvents and in polymer matrices. The oxidized probe 1PyBuATMPNO exhibits the same spectrum as the parent amine, but the intensity is lower. The ratio of the emission intensities of the parent amine and oxidized amine is a measure of the extent of intramolecular quenching.

The quantum yield of emission for probe 1PyBuATMP exhibits a dependence on the surroundings (Table 2) which is rather surprising. The same effect was also observed for oxidized and neutralized probes. Since two standards were used, the quantum yields of anthracene in cyclohexane ($\phi = 0.26$) and in methanol ($\phi = 0.21$) were determined taking the quantum yield for quinine sulphate in 0.1 N sulphuric acid as $\phi = 0.55$ [12]. The quantum yield in a non-polar polymer matrix was determined relative to anthracene in cyclohexane, whereas that in a polar polymer matrix was determined relative to anthracene in methanol. Although the quantum yields of emission of the probes doped in polymer films exhibit a higher error, their values approach that of pyrene in cyclohexane (0.56) or in ethanol (0.53) on 313 nm excitation [18].

Table 2
Emission spectra of 1PyBuATMP in different environments

Solvent	c^{a} (mol dm^{-3})	λ_{exc}^{b} (nm)	λ_{em} (nm) (I_r)^{c}	ϕ^{d}	I_{NH}/I_{NO}^{e}
Cyclohexane	10^{-5}	342	378 (1.00), 398 (0.25)	0.046	1.64
Methanol	10^{-5}	340	378 (1.00), 398 (0.26)	0.084	1.25
0.1 M SDS	10^{-5}	340	378 (1.00), 398 (0.27)	0.098	1.69
aPP	0.004	342	378 (1.00), 398 (0.28)	0.360	2.40
PS	0.002	347	380 (1.00), 399 (0.67), 418 (0.11)	0.224	1.69
PMMA	0.002	345	379 (1.00), 398 (0.47), 417 (0.11)	0.252	1.56
PVC	0.002	347	380 (1.00), 399 (0.51)	0.672	2.54

[a] Concentration in polymer film (mol kg^{-1}).
[b] Wavelength of excitation radiation.
[c] Wavelength of the maximum of the emission band (relative intensity).
[d] Quantum yield.
[e] Ratio of intensity of parent amine to oxidized amine based on steady state data.

In the past, Birks et al. [19] found that the deactivation process in photoexcited pyrene was influenced by the surroundings. Recently, the change in intensity of the monomer fluorescence of pyrenemethylpivalate was employed to monitor the course of radical copolymerization [20]. This is possible when the fluorescence intensity is strongly dependent on the rigidity of the medium. The change in the fluorescence intensity due to the change in rigidity was not quantified. The low quantum yields of monomer fluorescence of the probes under study in solution may be caused by the following:

1. oxygen quenching, because degassing with a stream of argon for 10 min is not sufficient;
2. different excitation (313 nm in Ref. [18] compared with 345 nm);
3. a novel radiationless channel, caused by substitution on pyrene, which is operative in solution and partially or fully hindered in a polymer matrix.

The fluorescence lifetimes in solution and in polymer films were determined under the same conditions as the quantum yields. The pertinent values are given in Table 3 for probe 1PyBuATMP. The lifetimes in solution were determined under deaerated conditions, whereas those in the films were determined in the presence of air. The oxygen concentration in aerated solvents and polymers is about the same. The fluorescence lifetimes are longer in deaerated solutions than in films in the presence of air. Consequently, the difference in the quantum yields is not caused by oxygen quenching which is more effective in solution than in polymer matrices. Therefore the dependence of the quantum yield on the surroundings is a genuine effect for probes derived from 4(1-pyrene)butyric acid due to mobility restriction of the substituent on the pyrene chromophore in the polymer matrix.

With increasing concentration in solution, excimer emission is observed for probe 1PyBuATMP.HCl in methanol (Fig. 2). At a concentration of 10^{-3} mol dm^{-3}, the other non-ionic probes exhibit no emission in the excimer region. Only an increase in intensity of the 398 nm band is observed. Moreover, the probe 1PyMeA.HCl under these conditions does not yield excimer emission. Under these conditions, excimer formation occurs as a result of hydrophobic interactions for ionic derivatives. At the same time, a certain distance between the chromophore and ionic centre and flexibility of their connection are required. Based on depolarization measurements, it was found that ionized 4-(1-

Table 3
Lifetime of the emission of 1PyBuATMP in various surroundings

Solvent	c^{a} (mol dm^{-3})	I_0^{b}	τ^{c} (ns)	$k\times10^{6d}$ (s^{-1})	$G^{1/2e}$	r^{f}	I_{NH}/I_{NO}^{g}
Cyclohexane	0.0001	109.25	235.9	3.94	1.65	0.9994	1.69
Methanol	0.0001	111.96	248.9	4.02	2.31	0.9989	1.88
0.1 M SDS	0.0001	82.02	189.3	5.28	3.05	0.9945	2.04
aPP	0.004	97.06	208.0	4.81	0.93	0.9996	1.28
PS	0.002	85.28	159.3	6.28	3.28	0.9973	1.04
PMMA	0.002	84.17	157.0	6.37	4.02	0.9963	1.62
PVC	0.002	89.23	100.5	9.95	2.33	0.9985	1.21

[a] Concentration of probe in polymer film (mol kg^{-1}).
[b] Calculated intensity based on least-squares parameters.
[c] Lifetime of fluorescence.
[d] Rate constant of fluorescence.
[e] Standard deviation.
[f] Correlation coefficient of dependence log I on t.
[g] Ratio of lifetime of fluorescence of parent amine to oxidized amine.

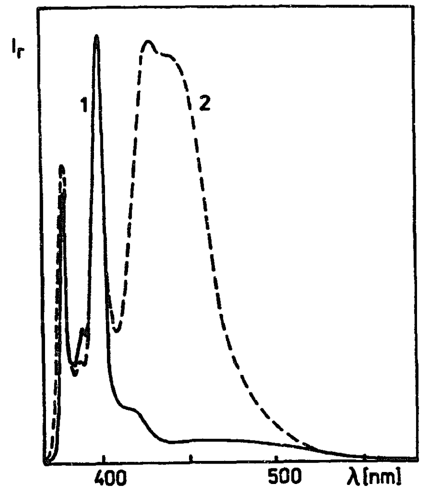

Fig. 2. Emission spectra of 1PyBuATMP.HCl in methanol at concentrations: 1, 10^{-5} mol dm^{-3}; 2, 10^{-3} mol dm^{-3}.

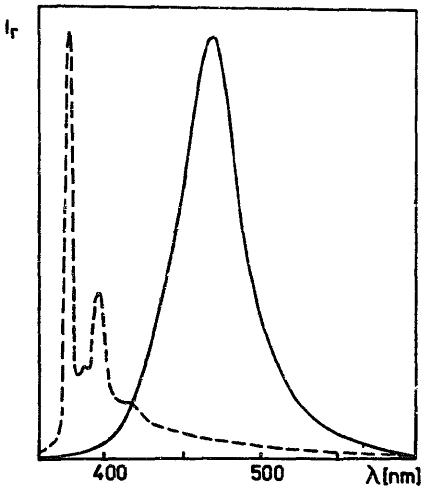

Fig. 3. Emission spectra of 1PyBuATMP.HCl in aPP at concentrations: 1, 0.002 mol kg^{-1}; 2, 0.2 mol kg^{-1}.

pyrene)butyric acid in glycerol forms bimolecular ground state associates [21]. A similar situation must exist in less viscous methanol because the diffusion-controlled (dynamic) formation of excimers is negligible at this concentration.

It is well established that excimer emission is not observed in glassy polymers, such as PS and PMMA, at concentrations below 0.1 mol kg^{-1} [22,23]. All the probes under investigation, at 0.1 mol kg^{-1} in glassy polymer matrices (PS, PMMA and PVC), exhibit a slightly red-shifted emission in the monomer region and a weak emission in the excimer region. This is also the case for non-ionic probes in aPP. On the other hand, exclusive excimer emission is observed for 1PyBuATMP.HCl in aPP (Fig. 3). The parent amine and *N*-oxyl derivative, even at 0.2 mol kg^{-1}, yield monomer fluorescence with a more intense 398 nm band. Again, the ionic probe 1PyMeA.HCl does not exhibit any emission in the excimer region even at this high concentration. The hydrophobic interaction of pyrene chromophores and ionic repulsion, which influence the excimer formation of the ionic probe 1PyBuATMP.HCl in methanol, probably play a role in the non-polar aPP matrix, but the importance of these factors may be different in aPP.

The monomer emission of the parent amine 1PyBuATMP (Table 3) at low concentration in solution (10^{-4} mol dm^{-3}) and in films (0.002 mol kg^{-1}) decays monoexponentially. The standard deviation $G^{1/2}$ is better than 1%. The initial intensity I_0 of the decay curve was normalized to 100. Therefore the deviations from the value of 100 for I_0, calculated using least-squares parameters, indicate that another process is competing with fluorescence decay at the beginning. In solution, higher values of I_0 (10% higher) are calculated, which are difficult to explain. In polymer matrices, the best fit to a monoexponential decay with I_0 near to 100 is observed for aPP. For the other polymer matrices, I_0 values, lower by 10% or more, are calculated based on fitting parameters. This decrease in I_0 is due to a fast process which may be related to the presence of oxygen. The excited pyrene molecules accessible by oxygen during its lifetime are quenched; this is more rapid than the fluorescence decay. The concentration of oxygen in the polymer film lies in the range 1.6×10^{-3} mol dm^{-3} for PS to 2.9×10^{-5} mol dm^{-3} for PMMA. Although there is a large difference in oxygen content in PS and PMMA matrices, the deviation from I_0 is the same. Therefore the fast process at the beginning in the polymer matrix is more complex.

The lifetimes of monomer fluorescence of the parent probe (Table 3) are shorter than the lifetimes of pyrene under similar conditions. For instance, in cyclohexane $\tau=368$ ns and in aPP $\tau=333$ ns, which agree well with $\tau=330$ ns for pyrene in 3-methylpentane and polyethylene [24].

The lifetimes of monomer fluorescence of 1PyBuATMP.HCl are 194 ns in methanol and 167 ns in water, which are slightly shorter than that of the parent probe in methanol. The lifetime in aerated water was previously reported to be 130 ns [7].

The decay of the monomer fluorescence of 1PyBuATMPNO can be fitted to a monoexponential function with $G^{1/2}$ greater than 5%. The decay can be fitted better to a biexponential function, where the fast component (30%–50%) lies in the range 20–100 ns and the slow component decays with a rate typical of the parent probe at low concentration. The mean lifetime based on fitting to a biexponential function approaches the lifetime based on monoexponential fitting. The ratio of the lifetimes of monomer fluorescence of the parent and oxidized probes (τ_{NH}/τ_{NO}), similar to I_{NH}/I_{NO}, indicates the extent of intramolecular quenching of the pyrene emission by the N–O$^{\cdot}$ radical centre. The scatter of the data in different environments is rather high, but at least two conclusions can be drawn:

1. the value of both ratios is about two; this means that the rate of the new radiationless channel due to the presence of the paramagnetic centre is as fast as the radiation channel;
2. the value of both ratios does not depend on the surroundings; this indicates that this channel is photophysical.

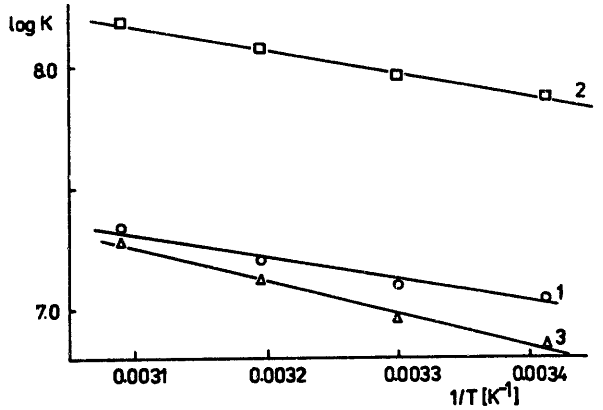

Fig. 4. Arrhenius plot of the deactivation rate vs. $1/T$ for: 1, k based on monoexponential fitting; 2, k_1 based on biexponential fitting; 3, k_2 based on biexponential fitting.

The lifetime of 1PyBuATMP is strongly influenced by the temperature and decreases with increasing temperature. This means that the total deactivation rate increases due to the temperature-dependent part. The dependence of the total deactivation rate on $1/T$ is linear in the temperature range 20–50 °C (Fig. 4). The calculated activation energy for the rate constant k based on monoexponential fitting is 17 kJ mol^{-1}. In the case of biexponential fitting of the decay curve, the activation energy for the fast rate k_1 is 26 kJ mol^{-1} and for the slow rate k_2 is 19 kJ mol^{-1}. The second value is similar to the activation energy obtained by monoexponential fitting. The activation energy for the viscosity change in methanol is 11 kJ mol^{-1}. Comparison of these two values shows that the activation energy of intramolecular quenching is about twofold higher than the activation energy of the viscosity change. The flexibility of the methylene chain connecting the pyrene chromophore and paramagnetic centre hinders intramolecular quenching more than intermolecular friction.

In polymer films in the front face arrangement, it is possible to determine the decay curves of emission with increasing concentration of the probe. At a concentration of 0.2 mol kg^{-1} of 1PyBuATMP.HCl, the lifetime of the red-shifted excimer emission is 53 ns. The decay is monoexponential. On the other hand, the lifetime of the monomer fluorescence of the parent amine at the same concentration decreases from 205 to 159 ns. In all polymer matrices at concentrations around 0.1 mol kg^{-1}, shortening of the monomer fluorescence lifetime is observed. The most pronounced decrease is observed for a PMMA matrix. The decrease in the lifetime of the probes at higher concentration indicates some extent of self-quenching. Even the polymer films at 0.1 mol kg^{-1} are optically clear, and weak or negligible emission is observed in the excimer region; the shortening of the lifetimes indicates some degree of aggregation.

The probe 1PyMeA.HCl, which in deaerated solution exhibits the same lifetime as 1PyBuATMP.HCl (methanol, 209 ns; water, 186 ns), exhibits a distinctly shorter lifetime in polymer matrices (aPP, 36 ns; PS, 135 ns; PMMA, 100 ns; PVC, 90 ns) at 0.002 mol kg^{-1}. Excimer emission is not observed at higher concentration, but the lifetime is even shorter.

In conclusion, we can state that the transformation of the reaction centre of the probe well separated from the reporting chromophore may influence the spectral behaviour.

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