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Spectral characteristics and photochemical stability of fluorescence probes based on 1,8-naphthaleneimide in solution and in polymer matrix

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Abstract

Fluorescence probes of type *N*-(1′-*R*-2′,2′,6′,6′-tetramethyl-4′-piperidinyl)-1,8-naphthaleneimide exhibit spectral properties which are influenced by environment and substitution (*R*) on sterically hindered nitrogen of piperidine moiety. Absorption spectra of parent amine and its N substituted derivatives show the longest wavelength band around 340 nm ($\log\varepsilon \sim 4.0$) which is well resolved in cyclohexane. In polar methanol it is only slightly blue shifted. Substitution on sterically hindered nitrogen does not influence the absorption spectra in near UV region. Fluorescence spectra of the probes have maximum around 385 nm in methanol and comparable intensity as anthracene. In nonpolar cyclohexane the fluorescence intensity is low (more than 100×). In nonpolar isotactic polypropylene matrix the red shifted excimer like emission in the range 440–470 nm was observed. The *N*-oxy and *N*-hydroxy derivatives under the same conditions do not yield the excimer emission. In other polymer matrices as polystyrene, poly(methyl methacrylate) and polyvinylchloride similar emission as in methanol was observed, the emission in latter matrix being the most intense. The fluorescence lifetime in polar solvent and matrices is less then 1 ns and deviates slightly from monoexponential. In nonpolar iPP, the fluorescence lives longer around 5 ns and its decay is more complex. Intermolecular quenching of the probes by 1-oxy-2,2,6,6-tetramethyl-4-hydroxypiperidine in methanol occurs at the rate which is above the diffusion controlled limit what might indicate the involvement of the polar medium in the process. Intramolecular quenching, expressed as the ratio I_{NH}/I_{NO} for parent and oxidized amine respectively, strongly depends on the medium as well. In polar methanol this ratio is about 30 while in polymer matrices 2–4 only. Photolysis of probes doped in polymer matrices with radiation above 300 nm revealed that the parent amine is about 3× more stable as 1,8-naphthoic anhydride or *N*-octadecyl-1,8-naphthaleneimide. © 1998 Elsevier Science S.A.

Keywords: Flourescence probes; Polymer matrix; Spectral property; 1,8-Naphthaleneimide derivatives

1. Introduction

Multifunctional fluorescence probes of different structure are used to monitor photophysical and photochemical processes in different environments. The ultimate goal of these studies is to employ them for construction of various sensors [1,2]. Preferably, those parameters which exhibit strong dependence on medium are exploited in sensor technology. The advantages of parameters connected with fluorescence are the high sensitivity, simple detection, easy quantitative evaluation for selected chromophores and distinct medium effect. Simple chromophores as aromatic hydrocarbons or several dyes are not suitable for monitoring several parameters. For that, usually more complex molecules containing different structural units—modules—are needed.

Recently, we have spectrally characterized probes composed from 1-naphthoic, 1-naphthylacetic [3], 4-(1-pyrene)butyric acids [4] and 2,2,6,6-tetramethyl-4-hydroxypiperidine in solutions and in polymer matrices. In order to extent the range of application of the probes, a simple chromophore as 1,8-naphthaleneimide seems to be suitable.

The derivatives of naphtaleneimide substituted in different positions by electron-donating and accepting substituents exhibit interesting spectral properties and undergo photochemical reaction yielding interesting products [5]. Several derivatives are potential dyes for polymers [6] or for applications in lasers [7] and exhibit biological activity namely toxicity towards selected (tumor) cells [8,9].

The photophysical and photochemical processes of naphthaleneimides strongly depend on the position of dicarboxyimide group on the naphthalene ring and on the solvent. Comparison of photophysical properties of unsubstituted and *N*-methyl of 1,2-, 2,3-, and 1,8-naphthaleneimide revealed that the rate of intersystem crossing is three order of magnitude higher for 1,8- than for 1,2-derivative. At the same time, the quantum yield of fluorescence decreased from 0.77 for

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1,2- to 0.03 for 1,8-derivative. This is due to the different energy gap between $^1(\pi\pi^*)$ and $^3(n\pi^*)$ states which is for 1,2-naphthaleneimide 9 kcal/mol and for 1,8-naphthaleneimide 2 kcal/mol, only [10,11]. The protic solvents increase this gap [10]. *N*-Phenyl-1,8-naphthaleneimide exhibits weak fluorescence and low quantum yield of intersystem crossing. Substitution in para position on phenyl ring with electron donating substituent causes the red shift within 70–200 nm of fluorescence and an increase in intersystem crossing. If position 4 of naphthalene ring is substituted with methoxy group, the fluorescence increases substantially and its life time extends to 10 ns [12].

Since the lowest excited singlet state of 1,8-naphthaleneimide is $\pi\pi^*$ and lives less than 1 ns, the majority of photochemical reactions of aromatic imides occur from triplet state. The laser flash photolysis showed that the triplet state of 1,8-naphtaleneimide does not abstract hydrogen from protic solvents. The reaction with electron-donating compounds occurs at the diffusion controlled limit [11].

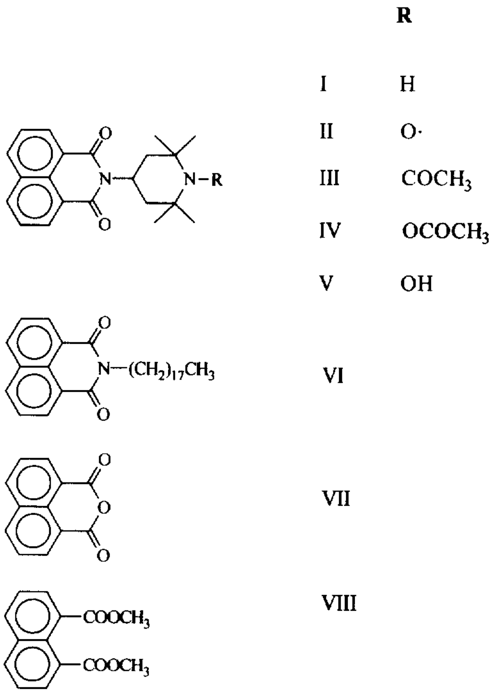
Unsaturated acrylates of 4-amino-1,8-naphthaleneimides yield the same intense fluorescence at 530 nm as free and as well as copolymerized with styrene and methyl methacrylate. Kinetics of radical copolymerization is not influenced by this type of chromophore [13].

Study of absorption steady-state and time-resolved fluorescence spectra of adducts of naphthalene chromophore/nitroxyl radical leads to conclusion that the intramolecular quenching involves the opening of the preexisting radiationless channel in the luminophore [14]. On the other hand, the efficient electron transfer taking place after photoinitiation was clearly demonstrated in the simple systems containing 1,4,5,8-naphthalenediimide [15] and in the larger rod-like complex molecules containing 4-amino-1,8-naphthaleneimide as well [16]. Quenching of poly(allyl amine) modified with 1,8-naphthoic anhydride indicated the involvement of electron transfer as well. In polar solution, this polymer exhibited excimer emission even at low degree of imidization due to strong intramacromolecular interaction [17].

Although the 1,8-napthaleneimide exhibits rather complex behaviour after photoinitiation, it is worth to apply it in a more complex molecules suitable as modules for sensors. The aim of this paper is to investigate this type of molecules as probes in different environments stressing the importance of polymer matrices. In any meaningful application the embedding in solid (polymer) matrix will be the most important.

2. Experimental

The structures of fluorescence probes used in this paper are shown on Scheme 1. Their synthesis, and characterization has been described elsewhere [18]. The following derivatives were investigated: *N*-(2′,2′,6′,6′-tetramethyl-4′-piperidinyl)-1,8-naphthaleneimide (I) m.t.:168–170°C, *N*-(1′-oxo-2′,2′,6′,6′-tetramethyl-4′-piperidinyl)-1,8-naphthaleneimide (II) m.t.:227–229°C, *N*-(1′-acetyl-2′,2′,6′,6′-tetramethyl-4′-piperidinyl)-1,8-naphthaleneimide (III) m.t.:200–201°C, *N*-(1′-acetyloxy-2′,2′,6′,6′-tetramethyl-4′-piperidinyl)-1,8-naphthaleneimide (IV) m.t.:186–188°C, *N*-(1′-hydroxy-2′,2′,6′,6′-tetramethyl-4′-piperidinyl)-1,8-naphthaleneimide (V) m.t.:224–228°C, *N*-octadecyl-1,8-naphthaleneimide (VI) m.t.:48–50°C, and dimethylester of 1,8-naphthalenedicarboxylic acid (VIII) m.t.:91–93°C Ref. [19] 102–104°C. Anhydride of 1,8-naphthalenedicarboxylic acid (VII) is a commercial product (Aldrich, Steinheim, Germany).



Scheme 1.

Anthracene was zonally refined (Lachema n.e., Brno, CR). Quinine sulfate was an analytical reagent.

Solvents cyclohexane (Merck, Darmstad, Germany) ethanol and methanol were for UV spectroscopy. Chloroform, tetrahydrofurane (Lachema n.e., Brno, CR) were analytical reagents.

Polymer films doped with fluorescence probes were prepared by casting from solution. Films of polystyrene (PS) (Chemische Werke Huels, Germany), 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) on a quartz or glass plate (28×35 mm). The solvent was evaporated slowly. Films of poly(vinylchloride) (PVC) (Neralit, Spolana Neratovice s.e., CR) were prepared similarly by casting tetrahydrofurane solution (5 g/100 ml) similarly. Concentration of the probe was in the range 0.002–0.01 mol kg^{-1}. Films of isotactic polypropylene (iPP) (Daplen, PCD Linz, Austria) were prepared by impregnation of 25 g of unstabilized powder with 10 ml of dichloromethane solution of the probes for 18 h.

After evaporation of the solvent under reduced pressure, the mixture was homogenized in the mixing chamber of Brabender Plastograph for 5 min at 190°C under air. Films of thickness 0.09–0.11 mm were prepared by hot pressing at 200°C for 1 min in electrically heated laboratory press Fontune (Netherlands). Concentration of the probe was 5.95×10^{-3} mol/kg.

Absorption spectra were taken on a SPECORD UV–VIS and M-40 (C. Zeiss, Jena, Germany) in nonpolar cyclohexan and polar methanol.

Emission spectra were recorded on spectrofluorimeter Perkin–Elmer MPF-4 (Perkin-Elmer, Norfolk, CT, USA) which was connected through interface and A/D convertor to microcomputer [20] for data collection, processing and plotting on an XY 4110 plotter (Laboratorní přístroje n.e., Prague, CR). Emission of solution was measured in 1 cm cuvette in the right angle arrangement. The quantum yields were determined relative to quinine sulfate in 0.1 N sulfuric acid and to anthracene in cyclohexane or methanol. Emission of polymer films was measured in front face arrangement on the solid sample holder. The quantum yield of doped polymer films was determined using anthracene as 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 film were determined according to relation [21].

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

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

The fluorescence lifetime measurements were performed on a LIF 200 (Lasertechnik, Berlin, Germany) which operates as a stroboscope. The output signal was digitized and transferred to the microcomputer [22]. The fluorescence decay curves were evaluated by simple phase plane method [23]. The standard deviation $G^{1/2}=\sum((I_{\exp}-I_{\mathrm{calc}})^2/n)^{1/2}$, where $I_{\exp}$ and I_{calc} are intensity of emission experimental and calculated, respectively, is used to judge if the decay is monoexponential. It is assumed that the decay curve satisfies the monoexponential if $G^{1/2}$ is lower than 5%.

The steady state and time resolved measurements were performed in aerated solutions. All measurements on polymer films were done in the presence of air.

Photolysis was performed on a merry go round type of set up. Medium pressure mercury arc with luminophore envelope (125 RVL, Tesla Holešovice, Prague, CR) was used as the source of radiation. The temperature of photolysis was 30°C. Films were fixed in holders made from aluminium foil. The course of photolysis was monitored by UV absorption spectrometry.

3. Results and discussion

Generally at the analysis of the influence of the medium on spectral properties of the doped molecule in the polymer matrix, it is assumed that the solvation power of the polymer matrix is similar to the low molecular solvent provided that the same structural unit are involved. Only in a few cases, it has been clearly demonstrated until now that, although the solvating power of the structural units of low molecular solvent and polymer is the same, there is a difference in the solvation power of polymer matrix due to connectivity. In other words, the mobility of low molecular solvent molecules is high and therefore the solvation is not restricted if other factors are similar but the solvation power of polymer matrix is restricted due to lower mobility of the polymer chain.

It can be expected that this effect plays no role in absorption spectra but it might be demonstrated in the emission spectra because of their higher sensitivity on the medium.

Absorption spectra of N′ substituted 2′,2′,6′,6′-tetramethyl-4′-piperidinyl derivatives of 1,8-naphthaleneimide I–V are rather the same in solvents and in polymer matrices. Derivative I exhibits both in polar methanol and non-polar cyclohexane intense band at 235 nm (logε 4.3) and less intense band at 340 nm (logε 4.0) whose position is nearly solvent independent (Fig. 1). In nonpolar cyclohexane the

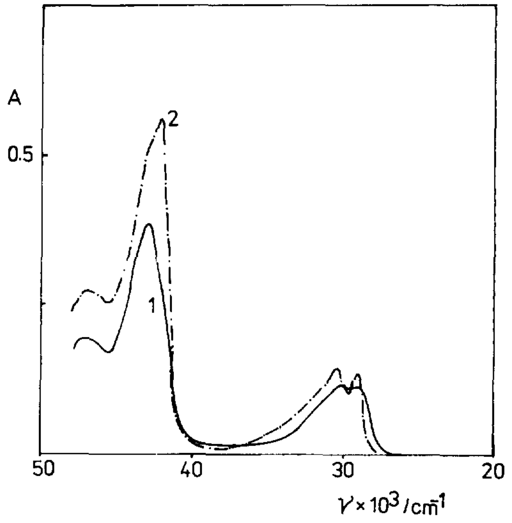


Fig. 1. Absorption spectrum of parent amine I (concentration 10^{-5} mol dm^{-3}) in (1) methanol, and in (2) cyclohexane (10× diluted saturated solution).

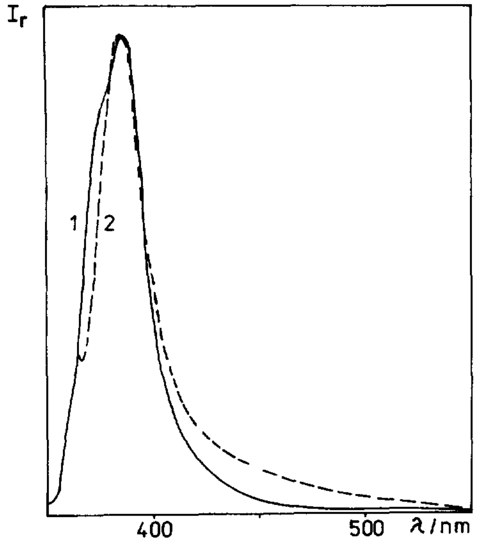


Fig. 2. Emission spectrum of parent amine I in (1) methanol, and (2) cyclohexane.

long wavelength band is resolved into two bands while in polar methanol there is only one broader band with a shoulder. These main features are preserved in all polymer matrices. In iPP matrix the resolution of the long wavelength band into two bands is even better than in cyclohexane. The absorption spectra of derivatives II–V exhibit the same features as I. The distinct difference is observed for derivatives 1,8-naphthalic anhydride (VII) and dimethylester of 1,8-naphthalenedicarboxylic acid (VIII). For VII the longest wavelength band is at 296 nm in methanol but in some matrices the band at 340 nm is preserved. For VIII the longest wavelength is around 295 nm in all media. Therefore, the longest wavelength band is evidently connected with the 1,8-naphthaleneimide chromophore.

The fluorescence spectrum of derivative I exhibits the broad emission band at 385 nm with shoulder at the short wavelength side (Fig. 2) in methanol. The relative quantum yield is about half that of anthracene (Table 1). On the other hand, the fluorescence of I is rather weak in cyclohexane (about 50×) but the band is more symmetrical without shoulder at short wavelength part. In polymer matrices as PS, PMMA and PVC, the fluorescence spectrum is the same as in methanol being rather broad in PS (Fig. 3). In more polar matrices as PMMA and PVC, there is well resolved band at 363 nm. Taking 0,0 absorption band at 345 and 0,0 emission band at 362 nm, then the Stokes shift is about 1400 cm^{-1} what indicates that the geometry of the ground and excited state is quite similar. The relative quantum yield to anthracene is in nonpolar PS substantially higher than in cyclohexane. In polar PMMA, it is lower than anthracene but in PVC it is even higher, what clearly indicates that there are no structural changes in going from excited state to ground state.

The derivative I exhibits red-shifted excimer like emission at 445 nm in non-polar iPP (Fig. 3) which is more intense as in cyclohexane (about 10×). The red-shifted emission was observed for III at 443 nm, IV at 447 nm, VI at 438 nm, VIII at 457 nm. This emission originates from an aggregate (dimer) in ground state which is formed as a result of polar interaction of the probes in non-polar iPP in course of the preparation of films at the concentration 5×10^{-3} mol/kg. At this concentration, the probe I is insoluble in cyclohexane, therefore, the comparison is not possible. The excimer like emission is about five time less intense as antracene in PS. The most intense emission is that of anhydride (VII). It is rather surprising that this excimer like emission is not observed for derivatives II (Fig. 4) and V which are in fact oxidized derivatives of I. The reasons why the oxidized sterically hindered amine prevents aggregation or prefers

Table 1
Spectral characteristics of probe I

Medium [a]	λ_{abs} [b], nm	$\log\varepsilon$ [c], $dm^3\ mol^{-1}\ cm^{-1}$	$\lambda_{em}(I_r)$ [d], nm	$\phi_r(A)$ [e]	τ [f] ns	$G^{1/2}$, [g]
MeOH	334	4.06	388(1.00)	0.55	0.6	1.4
Cy	339		383(1.00)	0.02		
iPP	345	3.88	380(0.07), 427(0.91), 444(1.00)	0.22	2.8 [h]	7.8
PS	337	4.06	388(1.00)	0.16	0.9	6.9
PMMA	334	4.18	366(0.47), 381(1.00)	0.49	0.6	3.5
PVC	337	3.96	367(0.30), 387(1.00)	1.63	1.0	4.6

[a] MeOH: methanol, Cy: cyclohexane, iPP: isotactic polypropylene, PS: polystyrene, PMMA: polymethyl methacrylate, PVC: polyvinyl chloride. Concentration = 10^{-5} mol dm^{-3} in solution and 0.002 mol kg^{-1} in polymer film.

[b] Maximum of the longest wavelength absorption band.

[c] Molar extinction decadic coefficient.

[d] Maximum of emission (relative intensity), excitation wavelength = 345 nm.

[e] Quantum yield relative to anthracene in the given medium.

[f] Life time of fluorescence determined by phase plane method.

[g] Standard deviation.

[h] Fitting experimental data to biexponential by nonlinear least square regression gives $\tau_1 = 0.22$ ns (17%) and $\tau_2 = 4.35$ ns (83%).

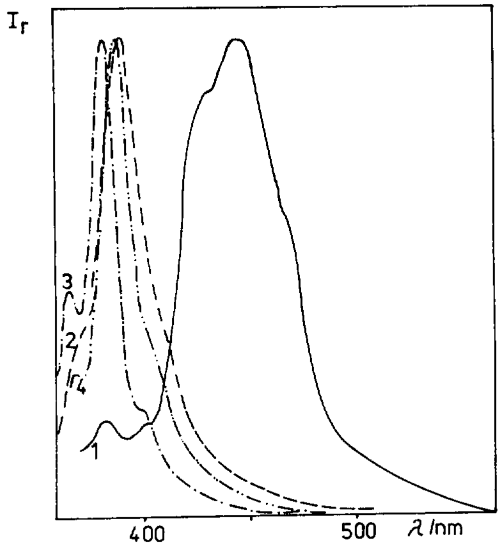


Fig. 3. Emission spectrum of parent amine I in polymer matrices (1) iPP (0.005 mol/kg, 100 μm thickness), (2) PS (0.002 mol/kg, 50 μm), (3) PMMA (0.002 mol/kg, 50 μm), and (4) PVC (0.002 mol/kg, 50 μm).

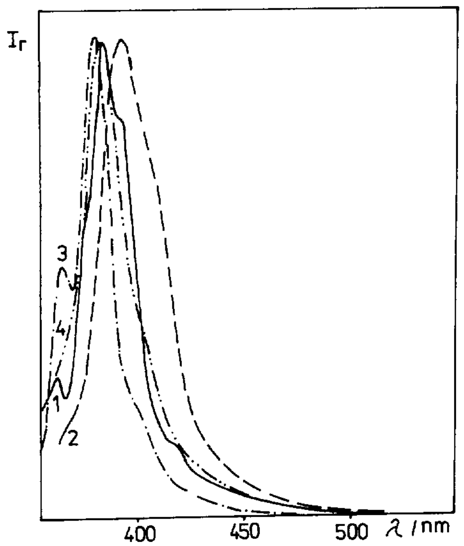


Fig. 4. Emission spectrum of oxidized amine II in polymer matrices (1) iPP (0.005 mol/kg, 100 μm thickness), (2) PS (0.002 mol/kg, 50 μm), (3) PMMA (0.002 mol/kg, 50 μm), and (4) PVC (0.002 mol/kg, 50 μm).

monomer instead excimer emission are not clear at all. The monomer emission of II and V, (V is easily transformed to II), is less intense in all media but it is more intense as parent amine I in cyclohexane.

The decay of fluorescence of I fits monoexponential very well in methanol and the life time is 0.6 ns (Table 1). For other derivatives, the life times are: III 0.5 ns, IV 0.6 ns, VI 0.4 ns and VII 1.4 ns. The standard deviation $G^{1/2}$ lies in the range 1–3%. Derivative II yields weak but measurable signal with life time 0.6 ns which decays non-monoexponentially. The life times of 1,8-naphthaleneimide derivatives was not determined in cyclohexane since the signals was weak for LIF 200 set up. In all polymer matrices, the life times were longer than in methanol (for all derivatives about 1 ns). In PS, they were slightly longer and in iPP they were substantially longer. The decay of fluorescence of all derivatives deviates from monoexponential in polymer matrices but the most in iPP. The life times evaluated by the simple phase plane method are longer about 3–8 ns with large fraction which lives longer than 10 ns.

The absorption and emission spectra of derivatives I–VI agree well with those of 1,8-naphthaleneimide and its *N*-methyl derivative. The fact, that the quantum yield and lifetime and increased in going from non-polar cyclohexane to polar methanol, can be rationalized in a similar manner as in [10]. The hydroxylated solvent interacts with n orbitals of dicarboxyimide carbonyl group. As a result the energy level of the n,π^* second triplet excited state will increase and the gap between this state and the nearby lowest excited π,π^* will increase as well. Consequently, the mixing will decrease and the singlet excited state will have more π,π^* character and the extent of radiation deactivation path will increase.

The singlet excimer emission at 465 nm was observed for *N*-methyl-1,8-naphthaleneimide at 465 nm as a result of triplet annihilation after laser excitation in polar acetonitrile [10]. On the other hand, the excimer fluorescence at 500 nm of 1,8-naphthaleneimide bound or macromolecule was observed even at low loading in ethanol/water solution due to intramacromolecular chromophore–chromophore interaction in ground state [17]. Although the red-shifted emission of derivatives I, III, IV, VI, and VII in iPP has maximum at 450 nm and is based on different processes, the main features of excimer emission are preserved.

Another route of excited state deactivation has been recently proposed for 4-amino-1,8-naphthaleneimide through the distribution of excitation energy on the stretching vibrations of water clusters [24]. This effect, however, does not operate in the environments under study.

The probes under study exhibit two functional centres: namely 1,8-naphthaleneimide chromophore and sterically hindered amine which might be oxidized, substituted or protonized. The presence of free radical reaction centre brings about intramolecular quenching. The extent of this quenching can be expressed as ratio of fluorescence intensity of parent amine I and oxidized derivative II I_{NH}/I_{NO}. Data in Table 2 indicate that this values strongly depend on the environment. In polar methanol, this value is high about 30. On the other hand, in non-polar cyclohexane it is about 1. It means the intramolecular quenching does not occur at all. In polymer matrices where monomer fluorescence is observed this value is about 1 for PS and in more polar PMMA and PVC it is about 3. The intramolecular quenching is observed in iPP, as well. In this case, the different states are involved in emission of derivatives I and II. Consequently, these data cannot be compared. At intramolecular quenching, the electron from radical centre at *N*-oxyl is transferred on 1,8-naphthaleneimide chromophore. This transfer must occur at certain limited distance determined by the structure of derivative II. Probably, the near approach of these parts of molecule as needed for collisional transfer is not possible. If this process occurs,

Table 2
Spectral characteristics of probe II [a]

Medium	λ_{abs} [b], nm	logε, $dm^3\ mol^{-1}\ cm^{-1}$	$\lambda_{em}(I_r)$, nm	ϕ_f(A)	I_{NH}/I_{NO} [b]
MeOH	334	4.05	387(1.00)	0.02	27.5
Cy	346	4.08	376(1.00)	0.02	1.0
iPP	347	4.17	364(0.29), 387(1.00)	0.05	4.4
PS	336	4.08	393(1.00)	0.17	1.0
PMMA	334	4.10	365(0.53), 382(1.00)	0.18	2.7
PVC	336	4.00	384(1.00)	0.42	3.9

[a] Meaning of the symbols is the same as in .

[b] Ratio of the integral intensity of the parent amine I and oxidized derivative II.

Table 3
Spectral parameters of some 1,8-naphthaleneimide derivatives and 1,8-naphthaleneanhydride [a]

Comp.	λ_{abs}, nm	logε, $dm^3\ mol^{-1}\ cm^{-1}$	λ_{em}, nm	ϕ_f(A)	τ, ns	$G^{1/2}$	K_{SV}, $dm^3\ mol^{-1}$	$k_q \times 10^{10}$, $dm^3\ mol^{-1}\ s^{-1}$
I	334	4.063	388	0.55	0.6	1.4	70	11.7
III	334	4.033	387	0.19	0.5	4.8	102	20.4
IV	334	4.19	386	0.17	0.6	1.1	70	11.7
VI	334	4.08	386	0.25	0.4	0.8	47	11.8
VII	296	3.904	381	0.39	1.4	1.6	102	7.3
VIII	296	3.939	372	0.03	2.4 [b]	1.9 [b]	37	1.5

[a] Meaning of the symbols the same as in .

[b] The intensity of fluorescence VIII was weak for determination of lifetime. The data are for 2,2,6,6-tetramethyl-4-piperidinyl-1-naftoate.

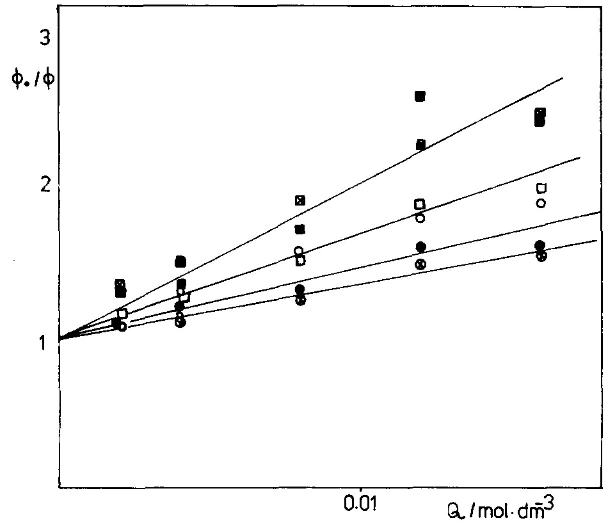


Fig. 5. Stern–Volmer dependence of quenching emission of 1,8-naphthalimide derivatives: I (○), III (⊠), IV (□), VI (●) VII (■) VIII (⊗) with 1-oxy-2,2,6,6-tetramethyl-4-hydroxypiperidine in methanol.

it must be mediated through the surrounding. Clearly, the more polar surrounding favours this process in solutions. In polymer matrices, the solvation by macromolecular chains competes with aggregation of doped molecules and some electron transfer is observed even in nonpolar matrix as iPP.

Intermolecular quenching of fluorescence of derivatives I, III, IV, VI and VII by 1-oxo-2,2,6,6-tetramethyl-4-hydroxypiperidine obeys the Stern–Volmer kinetics (Fig. 5). The values of K_{SV} are about 100 $dm^3\ mol^{-1}$ and especially for derivative VII they are loaded with considerable error. Using life time of fluorescence lower than 1 ns, the rate constant of bimolecular quenching is by an order of magnitude higher than the diffusion controlled bimolecular rate (Table 3). For dimethylester VIII only, the value of k_q is in generally accepted range. Although the value K_{SV} and τ are loaded with error, the higher values of k_q indicate that quenching of 1,8-naphthaleneimide is due to electron transfer from free radical centre to chromophore supported by polar surrounding [15]. The opening of the new radiationless channel plays a less important role in this case [14].

Derivative I is photochemically active in a relatively inert matrix even if it contains structural unit typical for light sta-

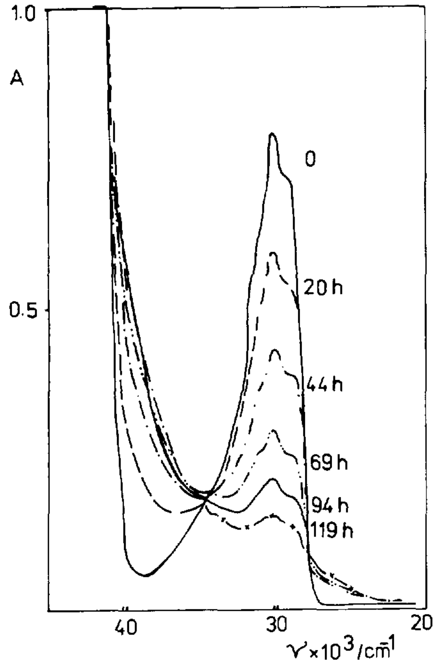


Fig. 6. Photolysis of I in PMMA film with radiation λ > 300 nm.

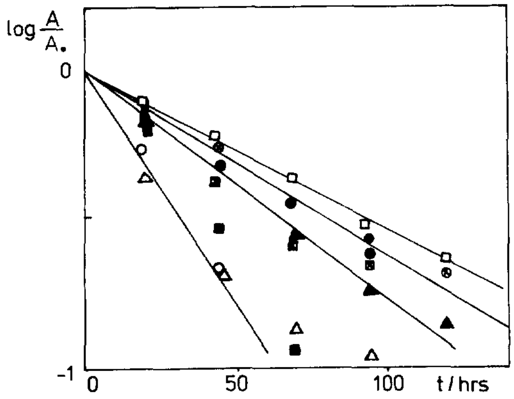


Fig. 7. Kinetics of photolysis of derivatives of 1,8-naphthaleneimide in PMMA film: I (H), II (●), III (△) IV (□), V (▲), VI (○), VII (■), VIII (⊠).

bilizer (Fig. 6). The longest absorption wavelength band disappears under irradiation with λ > 300 nm irreversibly. There is some indication of isosbestic point what indicates that this photobleaching occurs as simple A to B transformation. This is similar for all derivatives I–VII. Formal kinetic analysis shows that photolysis occurs as the reaction of first order (Fig. 7). Although there is a difference in the rate of photolysis under equal conditions, no pronounced stabilizing effect of parent sterically hindered amine or its oxidized form is observed. The most stable derivative is IV and less one is III. The rate of photobleaching of the III is 3 × higher.

4. Conclusion

The probes based on 1,8-naphthaleneimide exhibit rather complex spectral behaviour. The strong medium effect on emission and intra- as well as intermolecular quenching is clearly demonstrated. In any application of these probes, the limited photochemical stability must be taken into account.

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