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Dedicated to the 80th Birthday of Dr. Otto Vogl, Herman F. Mark Professor Emeritus

Medium Effect of Polymer Matrices on Spectral Properties of 4-Aminophthalimide and 4-Dimethylaminophthalimide

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Absorption and fluorescence spectra of 4-aminophthalimide (API) and 4-dimethylaminophthalimide (DAPI) were taken in solution of chloroform, methanol and water and polymer matrices as polystyrene (PS), poly(methyl methacrylate), (PMMA), polyvinylchloride (PVC) and polyvinylalcohol (PVA). The absorption spectra were dependent on the medium slightly; the longest wavelength band being around 350 nm for API and 390 nm for DAPI. Contrary to it, fluorescence of both probes is strongly influenced by polarity of the medium. The fluorescence in polar methanol or water is strongly bathochromically shifted from around 410 nm in cyclohexane up to 550 nm for API and 570 nm for DAPI in water. The quantum yield of fluorescence in polar solvents is low and it exhibits a short lifetime (under 1 ns for both API and DAPI). In polar solvents, both probes exhibit a large Stoke's shift up to 8,000 cm^{-1}. In polymer matrices both probes exhibit intense fluorescence as compare to anthracene with a lifetime longer than 10 ns and with a Stokes shift around 4,000 cm^{-1}. The less polar polymer matrix is polystyrene. In contrast, no strong medium effect is observed in polar PVA as compared with polar solvents. The reasons for different behavior of molecular probes in polar solvents of low viscosity and in polymer matrices are discussed.

Keywords: fluorescence; probes; 4-aminophthalimide; 4-dimethylaminophthalimide; medium effect; quenching; N-oxyls

1 Introduction

The simple or more complex molecules are exploited as reporters of the local environment in solvent mixtures or polymer matrices, as well as in micro-heterogeneous systems such as micelles, cyclodextrins and membranes. The necessary precondition for such application is that some properties are strongly medium dependent. This dependence is known as solvatochromism when considering spectral effects (1) or more generally, perichromism. Many factors influence the spectral behavior of the dissolved molecules such as solvents polarity, its temperature, hydrogen donor or acceptor capacity.

Considerable effort is devoted to the search of simple molecules responding to the environment with the goal of exploiting them in a more complex molecular assembly as probes, sensors, molecular switches or nano-machines. Such simple molecule responding on the environment seems to be 4-aminophthalimide (API) or its 4-dimethylamino derivative (DAPI) exhibiting an exceptionally strong solvent effect. Considerable attention was devoted to API since the early sixties (2) which continued with the advent of time resolved measurements (3–5). The interest in the spectral and photophysical properties API and to a lesser extent, DAPI was intense and is still actual up to now. There are several reasons for this interest, for instance, in non-protic solvents, the dipole moment of the first excited state of API increases to the 7 D from the ground state dipole moment of 3.5 D. In protic solvents such alcohols or water, hydrogen bonding results in a further increase in a dipole moment to about 18 D corresponding to nearly total charge transfer (CT) from aromatic ring to the acceptor imide system. Quenching of fluorescence in CT state is due to protonation (6). The fluorescence maximum of API shifts of more than 100 nm in going from non-polar solvents to polar water and the fluorescence quantum yield decreases by a factor of more than 70 for the same solvent change. Photophysical behavior of API and DAPI was compared in a series of solvents. This

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comparison revealed that they behave quite differently despite their structural similarity. The efficient radiationless decay of DAPI is due to a non-emitting twisted state (7).

Taking advantage of this polarity sensitive fluorescence, API or its derivatives was used to in the study of cyclodextrin interior (8, 9) and micelle water interface (10–12). The fluorescence response of series of N-alkyl-4-aminophthalimide allows us to monitor the changes in micro-environment of fluorophore resulting from aggregation in water. A new fluorescence is observed for the derivatives with longer alkyl chain which is unambiguously due to the aggregates of the molecules in aqueous media (13). A remarkable sensitivity of the fluorescence properties to the polarity of the media was observed for 11-(4-N,N-dimethylaminophthalimido)undecanoic acid which is probably due to a low lying nonfluorescent twisted intramolecular charge transfer state (TICT) (14).

The advent of time resolved measurement in picosecond time domain allows us to follow the salvation dynamics in solvents, solvent mixtures, in cyclodextrin nanocavity and inside micellar systems (15–25). The API is mainly used as an indicator at the time resolved emission spectroscopy in picosecond time domain. In spite of the considerable effort devoted to the system API–solvent, there are differences in interpretation of the large effect of the medium on the maximum, quantum yield and lifetime of fluorescence. The three main reasons given for this effect are namely: a) an increase in dipole moment of S_1 relative to S_0; b) the formation of much stronger hydrogen bond in the S-1-ICT state than in the S_0 state; and c) formation of emitting enol form of API as the result of proton transfer from imino or amino groups to the carbonyl group of API with involvement of one or two protic solvent molecules (25). On the basis of time resolved spectra, the emission was assigned to S-1-ICT state, but also exciplex formation between 4-aminophthalimide and water. In strong protic solvents, the excitation of ground state complex and its deactivation is involved as well (25).

Recently, time resolved measurements has been performed on poly(vinyl alcohol, PVA) and poly(vinyl acetate) PVAc doped with API and PRODAN (6-propionyl-2-dimethylaminonaphthalene) in order to monitor relaxation of these matrices. These data show the both API and PRODAN are suitable probes to sense the microheterogeneity and relaxation in polymer matrices. The difference in the behavior of the two probes originates in their location in the polymer matrix. The API is located in more polar environments of PVA (26).

The goal of this study is to compare the spectral properties of 4-aminophthalimide with 4-dimethylaminophthalimide under the same conditions in solvents and in polymer matrices. Although greater attention was paid to 4-aminophthalimide than to the 4-dimethylamino- derivatives, we compare spectral properties of both chromophores. We plan to use both chromopores as the structural unit in a more complex probe to test the polymer environment.

2 Experimental

2.1 General Methods

Commercial reagents were obtained from Sigma-Aldrich and used without further purification. Analytical TLC was performed on commercial Merck plates coated with silica gel 60 F_{254} (0.20 mm).

For flash chromatography Merck Silica gel 60 (0.0603–0.200 mm) was employed.

Anthracene and phthalic anhydride was zonally refined (Lachema n.e., Brno, CR). Solvents methanol was for UV spectroscopy. Chloroform, tetrahydrofuran (Slavus, SR) were analytical reagents. Quenchers: 1-oxo-2,2,6,6-tetramethylpiperidine (TEMPO) was received from Aldrich and 1-oxo-2,2,6,6-tetramethyl-4-hydroxypiperidine (TEMPOL) was the same as previously stated (27).

Polymer films doped with API and DAPI were prepared by casting from solution. Films of polystyrene (PS) (Chemische Werke Huels, F.R.G.), poly(methyl methacrylate) (PMMA) (Diacon, ICI, England) were prepared by casting a 1 ml chloroform solution of polymer (5 g/100 ml) containing the respective amount of probe on a glass plate (28 × 35 mm). The solvent was evaporated slowly. Films of poly(vinylchloride) (PVC) (Neralit, Spolana Neratovice s.e., CR) were prepared in a similar way by casting a tetrahydrofuran solution (5 g/100 ml). Films of polyvinylalcohol (PVA) (Mowiol 18/88, Hoechst, FRG) were cast from water solutions on quartz plates (28 × 35 mm). The final concentration of the probe in film was $0.002\ \mathrm{mol \cdot kg^{-1}}$ and the thickness was about 50 μm.

^{1}H-NMR spectra were recorded in solution with a Bruker AC-300P (300.1 MHz) spectrometer, with the TMS proton signal as an internal standard.

The ^{13}C-NMR spectra were recorded at 75.5 MHz on a Bruker AC-300P with solvent carbon signals as internal standard.

Elemental analyses were performed with a FISONS Instruments EA 1108.

UV-Vis absorption spectra were taken on a UV 1650PC spectrometer (Shimadzu, Japan).

Emission spectra were recorded on a Perkin-Elmer MPF-4 spectrofluorimeter (Perkin-Elmer, Norfolk, Conn., USA), which was connected through interface and A/D convertor to a ISA slot of PC using a homemade program for data collection. Program Origin 6.1 (Microsoft) was used for data plotting. Fluorescence of solution was measured in a 1 cm cuvette in the right angle arrangement. The quantum yield was determined relative to anthracene in cyclohexane, chloroform or methanol. Fluorescence of polymer films was taken in front face arrangement on the solid sample holder. The relative quantum yield of doped polymer films was determined using anthracene as the standard, assuming a small effect of the medium. The relative quantum yields in solution and in film were corrected on different absorption at the wavelength of excitation (28).

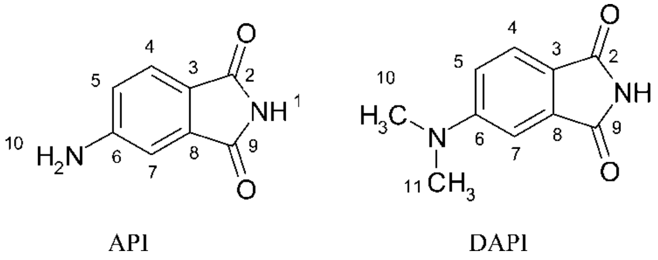
The fluorescence lifetime measurements were performed on a LIF 200 (Lasertechnik Ltd., Berlin, F.R.G.), which operates as a stroboscope. The excitation source is a nitrogen laser emitting at 337 nm and the emission is selected by cut-off filter. The output signal of Box-car Integrator was digitized and transferred to the PC using home made program. The fluorescence decay curves were evaluated by simple phase plane method (29) using program of J. Snyder based on (30). The standard deviation $G^{1/2} = \Sigma((I_{exp}\text{-}I_{calc})^2/n)^{1/2}$, where I_{exp} and I_{calc} are intensity of emission experimental and calculated respectively, is used to judge if the decay is mono-exponential. It is assumed that the decay curve satisfies the monoexponential when $G^{1/2}$ 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.

2.2 *Synthesis of Probes*

The structures of the molecular probes under investigation are given on Scheme 1.

4-Aminophthalimide (API) was synthesized according to the literature (31) in two step reactions. The first step involved nitration of the phthalimide. Fuming H_2SO_4 (20 ml, 20% SO_3) was mixed with fuming HNO_3 (5 ml), followed by adding phthalimide (4.00 g, 27.2 mmol) in a portion over 15 min. intervals with stirring. The temperature was raised slowly to 40–50°C and kept at that range for 40 min. Then, the mixture was cooled to 0°C and slowly poured onto ice with stirring, followed by filtration to present the crude product. The crude product was washed with water and purified by re-crystallization with ethanol to afford 4-nitrophthalimide. The second step involved reduction of this compound. Tin chloride (8.4 g, 4.3 mmol) was mixed with HCl (saturated solution, 45 ml) and 15 ml of water to prepare the $SnCl_2$ solution. To this solution 4-nitrophthalimide (2.00 g, 10.4 mmol) was added slowly with stirring. The mixture was kept at 50°C for 2 h until TLC showed completion of reaction. The mixture was cooled to 0°C, followed by filtration to provide the crude product, which was washed by hot water to afford 4-aminophthalimide.



API DAPI

Sch. 1. The fluorescence probes 4-aminophthalimide (API) and 4-dimethylaminophthalimide (DAPI).

Yield: 1.25 g (74%)
TLC: R_f (isohexane: ethylacetate = 1:1) = 0.22
Melting point: 286–288°C
^{1}H-NMR (DMSO): δ(ppm) = 10.71 (s, 1H, **1**), 7.43 (d,1H, $J = 8.1$ Hz, **4**), 6.88 (d,1H, $J = 1.8$ Hz, **7**), 6.80 (dd, $J = 8.1$ Hz, $J = 1.8$ Hz, **5**), 5.47 (s,2H, **10**).
^{13}C-NMR (DMSO): δ(ppm) = 169.7, 169.3 (**2**, **9**), 154.6 (**6**), 135.4, 125.6 (**3**, **8**), 118.0 (**4**), 116.9 (**5**), 106.7 (**7**).
GC MS (70ev), m/z (%): 162(100%), 119 (24.5%), 91 (36.3%), 63 (9.8%), 41 (4.9%)
C8H6N2O2 (162.15). Calcd.: C, 59.26%; H, 3.73%; N, 17.28%. Found: C, 58.92%; H, 3.85%; N, 16.95%.

4-Dimethylaminophthalimide (DAPI) was prepared according to the literature (31) by refluxing 4-aminophthalimide with acid-free dimethylsulfate at 130°C for 1–2 h. After 15 min. of cooling, the reaction mixture was added to water and filtered. The solid thus obtained was purified by column chromatography using silica gel column and eluted with ethylacetate and pentane mixture.
Yield: 0.65 g (44.5%)
TLC: R_f (isohexane:ethylacetate = 1:1) = 0.51
Melting point: 210–212°C
^{1}H-NMR (DMSO): δ(ppm) = 7.66 (d,1H, $J = 8.7$ Hz, **4**), 7.31(s, 1H, **1**), 7.065 (d,1H, $J = 2.4$ Hz, **7**), 6.83 (dd, $J = 8{,}1$ Hz, $J = 2.4$ Hz, **5**), 3.13 (s, 6H, **10**, **11**).
^{13}C-NMR (DMSO): δ(ppm) = 169.8, 169.2 (**3**, **8**), 154.2 (**6**), 135.1, 124.2 (**3**, **8**), 117.6 (**4**), 114.9 (**5**), 104.7 (**7**), 39.90 (**10**, **11**).
GC MS (70ev), m/z (%): 189 (100%), 173(3.9%), 146 (3.4%), 119 (9.2%), 103 (4.9%), 75 (4.8%), 69 (4.8%), 63 (4.8%)
$C_{10}H_{10}N_2O_2$ (190.20) Calcd.: C, 63.15%; H, 5.30%; N, 14.73%. Found: C, 62.98%; H, 5.54%; N, 14.56%.

3 Results and Discussion

The simple molecular fluorescence probes of a substituted phthalimide API type exhibit three absorption bands around 250, 300, and 350 nm. The substitution with dimethylamino group, as in DAPI, shifts absorption about 10–20 nm to the longer wavelength. The exact position depends on the medium as is seen on Figures 1 and 2 for solvents and Figures 3 and 4 for polymer matrices. The absorption spectra of DAPI seem to be less sensitive on the medium as compared to API in the solvents and matrices under investigation. The longest wavelength absorption bands of API and DAPI in various media are given in Tables 1 and 2. This is rather broad band without any sign of vibrational resolution. It has medium strong intensity around 5000 $\text{mol}^{-1}\,\text{cm}^{-1}$. Basically, the same features are observed for absorption spectra of API and DAPI in polymer matrices as well.

Unsubstituted parent structures as phthalanhydride and phthalimide exhibit no absorption above 300 nm. Absorption

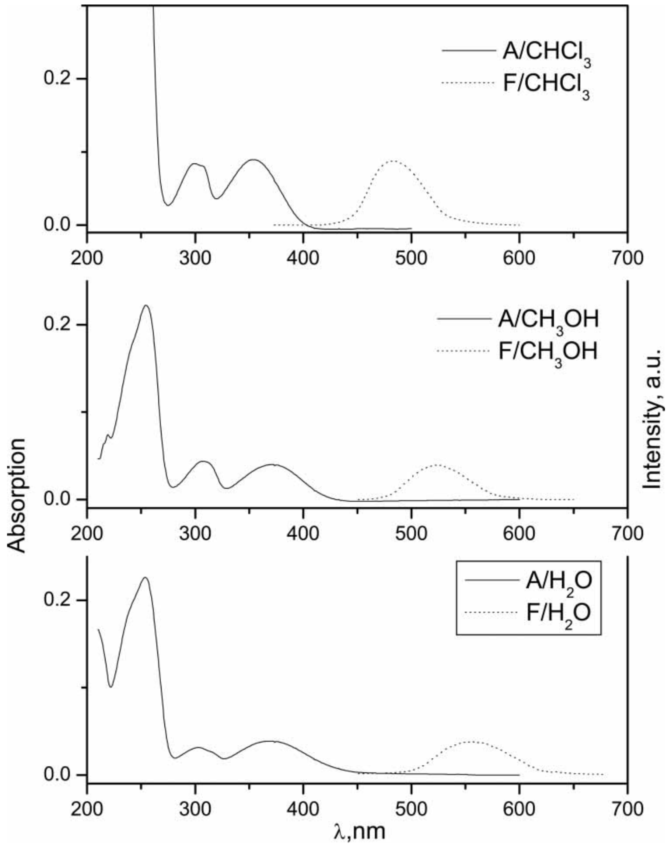


Fig. 1. Absorption (A) and fluorescence (F) spectra of 4-aminophthalimide (API) in water, methanol (10^{-5} moldm^{-3}) and chloroform (4×10^{-5} moldm^{-3}).

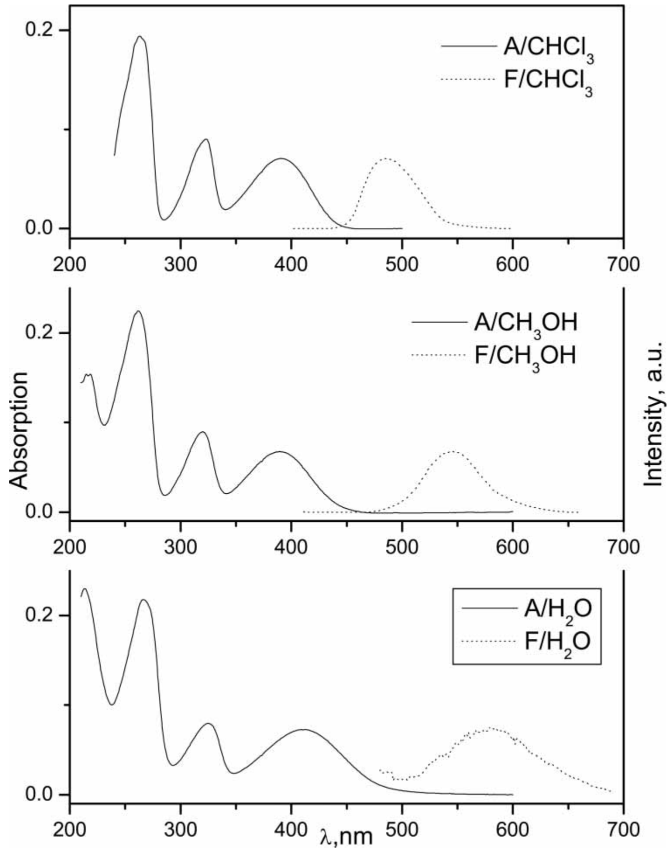


Fig. 2. Absorption (A) and fluorescence (F) of 4-dimethylaminophthalimide (DAPI) in $^{-1}$ methanol and chloroform (10^{-5} moldm^{-3}).

above 300 nm is due to strong donor-acceptor interaction of electron rich 4-aminoamino respective 4-dimethylamino substituent with an electron deficient phthalanhydride or phthalimide part.

The fluorescence of both probes is more sensitive on the medium as absorption. Limited spectral data might be obtained with API in non-polar cyclohexane because of a solubility problem. In this study, the fluorescence maximum was observed at the shortest wavelength in polystyrene matrix at 423 nm. However, weak fluorescence was observed at 404 nm in a saturated cyclohexane solution. In water (1 vol% of methanol), the maximum of fluorescence was observed at 556 nm. Therefore, the shift is about 150 nm or 6 767 cm^{-1}. Similarly, the fluorescence maximum of DAPI shifts from 416 nm in cyclohexane to 583 nm in water with 1 vol% methanol which is about 170 nm or 6 886 cm^{-1}. There is a considerable change in the Stoke's shift in going from cyclohexane to water for API 3 660 and 9 110 cm^{-1} and for DAPI 3 280 and 7 130 cm^{-1}, respectively.

The spectral data in the solvents and polymer matrices where API and DAPI are well soluble are summarized in Tables 1 and 2. The fluorescence band in all media is broad without any structure and has a similar feature in solution, as well as in polymer matrices. Surprisingly, the fluorescence maximum is at a shorter wavelength as in chloroform, the shortest being in polystyrene matrix.

The relative quantum yield of API and DAPI is lower than anthracene in polar media as methanol and water. The lowest

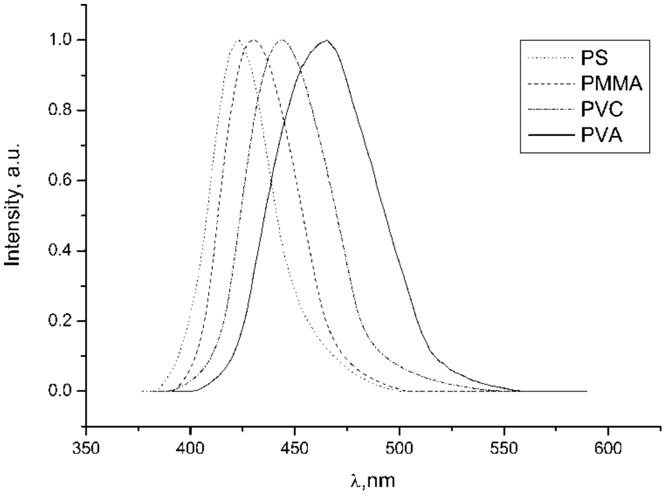


Fig. 3. Normalized fluorescence (F) of 4-aminophthalimide (API) in different polymer matrices (thickness 50 μm) at 0.002 molkg^{-1}.

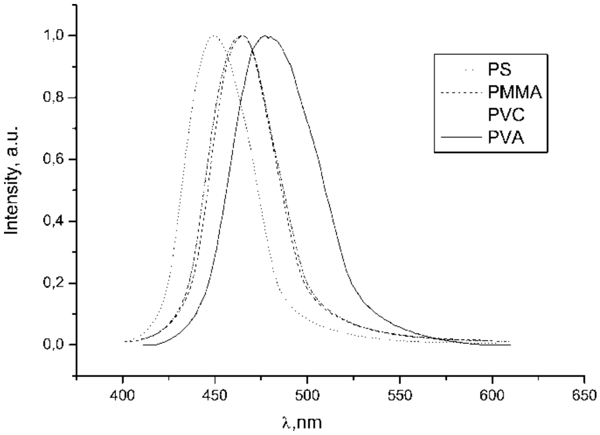


Fig. 4. Normalized fluorescence (F) of 4-dimethylaminophthalimide (DAPI) in different polymer matrices (50 μm) at 0.002 molkg^{-1}.

Φ_r(A) for DAPI is 0,1 in water. On the other hand, in less polar chloroform and polymer matrices, the relative quantum yield of fluorescence is higher than that of anthracence. DAPI especially exhibits strong fluorescence Φ_r(A) being about 11 for PMMA. This fluorescence can be easily observed by the naked eye in polymer films (Tables 1 and 2). The determination of relative quantum yields of fluorescence is charged with high error due to film preparation and problems with reproducible positioning of the doped film in the spectral instruments. Even under these conditions, the decrease in relative quantum yield of fluorescence of DAPI in going from polymer matrix to water is more than 100 times, might be considered as proven.

The lifetime of fluorescence in water is rather short 1.0 ns for API and 0.3 ns for DAPI. These data are on the limits of our setup for determination of lifetime. In less polar chloroform and polymer matrices the lifetimes are longer above 10 ns. The decay of fluorescence fits the mono-exponential and the standard error for lifetime determination is about 5%.

The spectral data on API in solution measured in this study basically agree with the data summarized in (25) based on their own measurements and literature. The position of fluorescence maximum of API in this study in the paper (26) agrees as well. The spectral data (steady state and time resolved) of DAPI are bathochromically shifted 10 up to 20 nm as compared with API, which seems to be quite reasonable.

The fluorescence of API and DAPI is quenched by TEMPO and TEMPOL in methanol (Figure 5). For pair quenchee/quencher API/TEMPO or TEMPOL the quenching constant

Table 1. Spectral properties of 4-aminophthalimide (API) in various media

Medium	λ_{max}^{a} (nm)	logϵ^{b} (mol^{-1}cm^{-1})	λ_{max}^{c} (Nm)	Φ_r^{d}	τ^e (ns)	G$^{1/2,f}$ (%)	$\Delta\nu^g$ (cm^{-1})
H_2O^h	369	3.49	556	0.3	1.0	2.3	9 115
MeOH	371	3.60	522	0.8	5.1	1.4	7 797
$CHCl_3$	352	3.32	483	6.3	13.1	2.9	7 705
PVA	370	3.64	465	7.1	14.8	2.3	5 160
PVC	361	3.61	443	2.6	12.8	7.2	5 127
PMMA	357	3.63	431	7.9	13.5	1.6	4 809
PS	356	3.49	423	1.5	10.8	1.9	4 449

[a] Maximum of the longest wavelength absorption band.
[b] Molar decadic extinction coefficient.
[c] Maximum of the fluorescence band.
[d] Relative quantum yield to anthracene in the respective medium.
[e] Lifetime.
[f] Standard error of life time determination.
[g] Stoke's shift.
[h] 1 vol% of methanol.

Table 2. Spectral properties of 4-dimethylaminophthalimide (DAPI) in various media

Medium	λ_{max}^{a} (nm)	logϵ^{b} (mol^{-1}cm^{-1})	λ_{max}^{c} (nm)	Φ_r^{d}	τ^e (ns)	G$^{1/2,f}$ (%)	$\Delta\nu^g$ (cm^{-1})
H_2O^h	409	3.71	575	0.1	0.3	6.9	7 060
MeOH	389	3.83	545	0.2	0.8	4.1	7 358
$CHCl_3$	390	3.85	483	13.9	12.0	2.1	4 937
PVA	394	3.74	477	4.5	11.6	1.6	4 384
PVC	389	3.73	464	6.8	14.2	2.6	4 122
PMMA	380	3.73	451	11.3	14.7	4.0	4 810
PS	383	3.68	449	8.8	12.9	3.5	3 838

[a] Maximum of the longest wavelength absorption band.
[b] Molar decadic extinction coefficient.
[c] Maximum of the fluorescence band.
[d] Relative quantum yield to anthracene in the respective medium.
[e] Life time.
[f] Standard error of life time determination.
[g] Stoke's shift.
[h] 1 vol% of methanol.

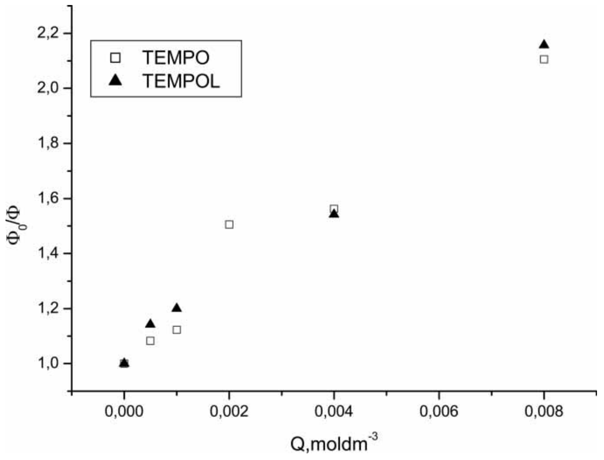


Fig. 5. Stern-Volmer dependence of quenching of fluorescence of 4-aminophthalimide (API) in methanol by TEMPO and TEMPOL.

is 137 dm^3 mol^{-1} and using lifetime 5.1 ns the bimolecular rate constant is 2.7×10^{10} dm^3 mol^{-1} s^{-1}. Since DAPI in methanol lives shorter, about 0.8 ns, the quenching constant is lower about 20 dm^3 mol^{-1}, but the kq equals 2.5×10^{10} dm^3 mol^{-1} s^{-1}. The data summarized in Table 3 indicates that the fluorophores API and DAPI are quenched by N-xyls with the rate constant for diffusion controlled bimolecular rate constant or slightly higher. Therefore, it might be concluded that the ICT singlet state is intermolecularly quenched by N-oxyls.

The medium (solvent) effect on spectral properties of dissolved chromophores is well understood for low viscosity media (1, 32). Less attention was devoted to medium effect on spectral molecules of doped molecules in the of polymer matrices (33), although the polymer environment (support) is very important in many industrial applications such as the textile, automotive, and electronic industry. There are two extreme assumptions for judging the effect of polymer matrix:

1. The polymer matrix is inert even at laboratory temperature so that it has no or a negligible effect on spectral properties.
2. The polymer matrix influences the spectral properties in a similar way as a low viscosity solvent.

The polymer matrix as a medium differs from low molecular solvent in several respects. Even though the chemical structure of monomeric units is the same as that of low molecular solvent, the polymer matrix might exhibit different micro- and macro-viscosity, and micro- and macro-polarity. This difference is due to interconnectivity of monomer units. It means that the assembly of low molar mass molecules of solvent around solute (doped molecule) has different mobility, as compared with polymer as surrounding molecule. The main question is whether or not there is a substantial change in the arrangement of surrounded (macro)-molecules during the lifetime, the excited state at temperatures below or above glass transition. The general answer does not exist until now and depends on the given pair doped chromophore/polymer matrix.

Table 3. Quenching of API and DAPI by N-oxyls in solution

System	K_{SV}[a] (dm^{3}mol^{-1})	r[b]	τ[c] (ns)	k_q[d] $\times 10^{10}$ (dm^{3}mol^{-1}cm^{-1})
API/TEMPO/ $CHCl_3$	991.4	0.986	13.1	7.5
DAPI/TEMPO/ $CHCl_3$	533.4	0.987	12.0	4.4
API/TEMPOL/ $CHCl_3$	1 386.9	0.957	13.1	10.6
DAPI/TEMPOL/ $CHCl_3$	332.1	0.995	12.0	2.8
API/TEMPO/ MeOH	135.4	0.975	5.1	2.6
DAPI/TEMPO/ MeOH	20	0.950	0.8	2.6
API/TEMPOL/ MeOH	138.1	0.997	5.1	2.1
DAPI/TEMPOL/ MeOH	52.5	0.954	0.8	6.7

[a] Stern-Volmer constant.
[b] Correlation coefficient of the Stern-Volmer plot.
[c] Lifetime of fluorescence.
[d] Bimolecular quenching rate constant.

The spectral data of probes API and DAPI in polymer matrix as compared with the polar solvents correspond to the less polar environment. Clearly, the maximum of fluorescence of API and DAPI indicates that the PS matrix is less polar medium as compared with chloroform, PMMA and PVC, but the relative quantum yield of fluorescence is lower in PMMA or PVC. On the other hand, PVA, having a high concentration of hydroxyl groups, is the more polar matrix as PMMA and PVC. Although there is a great possibility to form hydrogen bonds in PVA matrix, this is not sufficient to exhibit such a medium effect as low viscosity protic solvent as methanol or water. Therefore, besides the ability to form a hydrogen bond in the medium, certain flexibility of probe and surroundings molecules must be allowed. This allows us to conclude that in the polymer matrices under glass transition temperature, the spectral data indicate that the surrounding envelope around probes API and DAPI is rather rigid, which results in a high yield of fluorescence and relatively long fluorescence lifetime, even in polar PVA matrix.

4 Conclusions

It was shown that the phthalimide type probes, which are widely used to test solvent polarity and might be used in polymers as well. The phthalimide type probes API and DAPI exhibit strong fluorescence in the tested polymer matrices, even in PVA matrix containing a large concentration of hydroxylic groups. Therefore, the specific species between fluorophore and hydroxyl groups of polar environment as ground state complexes or exciplexes are not involved in deactivation of the S1 state as it is the case of polar water or alcohols. It might be concluded that API or DAPI in polar PVA exhibit behavior as in non-polar medium, preserving more or less ground state solvation even in the excited state.

5 Acknowledgement

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