Photophysical Properties of new Polymerizable 1,8-Naphthalimides and their Copolymers with Methylmethacrylate

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In this paper we discuss the photophysical properties of some 4-nitro- and 4-allylamino-*N*-phenyl-1,8-naphthalimides having different substituents in the phenyl ring, and their copolymers with methylmethacrylate in solid films. The influence of the substituents at the phenyl ring and the environment (methanol or polymer matrix) on the absorption and fluorescence properties is also discussed.

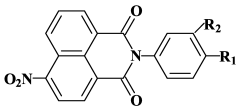
Key words: 1,8-naphthalimide Derivatives; Absorption; Fluorescence; Photophysics.

1. Introduction

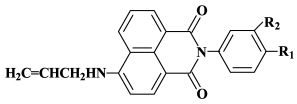
1,8-naphthalimides and their 4-substituted derivatives constitute a versatile class of compounds which have been used in many areas [1 – 9]. The 1,8-naphthalimide derivatives with amino groups at the C-4 position are of bright yellow colour enhanced by the fluorescence emission, while those with alkoxy groups are colourless and emit blue light. The 4-amino- and 4-alkoxy-1,8-naphthalimide derivatives have aroused our interest because of their potential use as polymerizable fluorophores in synthetic polymers. They show an intensive fluorescence and a very good photostability [10 – 13]. Due to the presence of a polymerizable group, the dyes can polymerise with some commercial monomers. The quantum yield of fluorescence, photo-, and termostability of these copolymers is high. Moreover, the fluorescence is intensive when they are dissolved in organic solvents [14 – 23].

Recently it has been shown that 1,8-naphthalimide derivatives can also be appropriate components in "guest-host" liquid crystal systems for electro-optic displays [24 – 28]. In these displays a dichroic dye (guest) is dissolved in a nematic host, which acts as anisotropic matrix. Under electric voltage, the matrix orients the dye molecules, thus causing selective absorption. Some fluorescent copolymers have recently been used as luminophores in liquid crystal systems [14, 27, 28].

In this paper the photophysical properties of some new 4-nitro- and 4-allylamino-N-phenyl-1,8-naphthalimides and their copolymers with methylmethacrylate (MMA), and the effect of substituents in the phenyl ring on the spectral characteristics are described.



I



II

Where:	**a**	**b**	**c**	**D**	**e**
$\mathbf{R_1}$	H	CH_3	OCH_3	Cl	H
$\mathbf{R_2}$	H	H	H	H	OH

Scheme 1. Chemical structure of the 1,8-naphthalimide derivatives **I** and **II**.

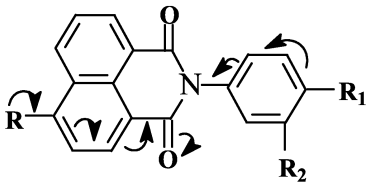
2. Experimental

The structures of the investigated 4-nitro-N-phenyl-1,8-naphthalimide (I) and 4-allylamino-N-phenyl-1,8-naphthalimide (II) derivatives [29] are presented in Scheme 1.

UV-Vis spectrophotometric measurements of **I** and **II** in methanol solution were performed on a Hewlett Packard 8452A spectrophotometer. The fluorescence spectra in methanol solution were obtained with a SFM 25 spectrophotometer (KONTRON Instruments). The quantum yield of fluorescence was determined on the basis of the absorption and fluorescence spectra of the 1,8-naphthallmide derivatives at concentrations 10^{-6} mol l^{-1}, using Rhodamine 6G ($\Phi_0 = 0.88$) [30] as a standard. For all absorption measurements, the dye

Table 1. Photophysical characteristics of 4-allylamino-N-phenyl-1,8-naphthalimide derivatives in methanol solution.

	IIa	IIb	IIc	IId	IIe
λ_A [nm]	444	442	442	444	440
ε [l mol^{-1}cm^{-1}]	12300	12000	12900	12400	13600
λ_F [nm]	532	528	526	528	526
$\nu_A - \nu_F$ [cm^{-1}]	3725	3685	3613	3583	3716
Φ_F	0.55	0.52	0.53	0.60	0.36
f	0.261	0.283	0.291	0.256	0.244
λ_{S1} [nm]	490	489	489	490	488
E_{S1} [kJ mol^{-1}]	249.5	249.0	249.0	249.5	248.5



Scheme 2. Donor-acceptor interaction and the path of charge transfer in **I** and **II**.

concentration in the solution was 10^{-5} mol l^{-1}. The fluorescence measurements were performed at a concentration of 10^{-6} mol l^{-1}. The solid polymer films (25 – 30 μm) were prepared by a solvent evaporation technique. Chloroform was used as solvent for the methylmetacrylate (MMA) based polymers.

3. Results and Discussion

1,8-naphthalimide derivatives can be treated as a combination of two sub-systems; viz. the naphthalene ring and a dicarboximide (-CO-N-CO-) group in a six membered ring. The photophysical properties and the colour characteristics of 1,8-naphthalimides depend basically on the polarization of the molecules. The irradiation induced polarization of 1,8-naphthalimide molecules causes an electron donor-acceptor interaction between the substituents at C-4 and the carbonyl groups from the imide structure of the chromophorous system. On the other hand, the photophysical properties also depend on the interaction between the phenyl ring and the carbonyl groups. The donor-acceptor interaction and the path of charge transfer are given in Scheme 2.

3.1. Photophysical Characteristics of 1,8-naphthalimide Derivatives in Methanol Solution

Table 1 collects the spectral parameters of **IIa-IIe** derivatives in methanol solution: the absorption (λ_A) and fluorescence (λ_F) maxima, the molar extinction coefficient (ε), Stokes shift ($\nu_A - \nu_F$), quantum yield of fluorescence (Φ_F) and the energy of the lowest exited singlet states (E_{S1}).

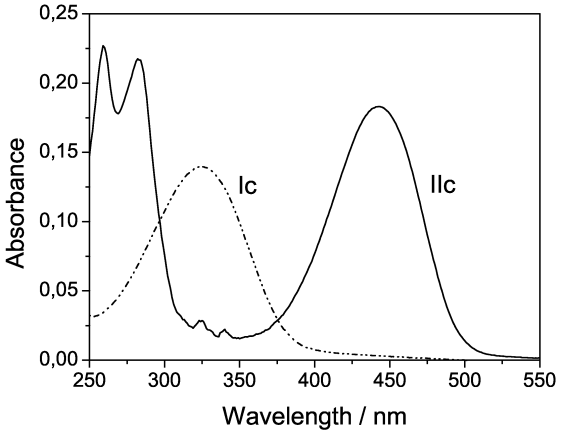


Fig.1. UV-Vis absorption spectra of **Ic** and **IIc** in methanol solution.

Ia – Ie derivatives with a nitro group at C-4 position absorb in the near UV region at λ_A between 318 and 324 nm due to the electron-accepting nature of this group. The substituents in the phenyl ring bonding to the N-amide atom have a small effect on the absorption maxima. As an example, the absorption spectra of **Ic** and **IIc** dissolved in methanol are shown in Figure 1. The replacement of the nitro group by an electron-donating allylamino one leads to a great batochromic shift of the absorption maxima with 122 – 126 nm. The 4-allylamino-N-phenyl-1,8-naphthalimide derivatives in methanol solution at room temperature show absorption maxima at 440 – 444 nm and fluorescence emission maxima at 526 – 532 nm. Figure 2 presents the normalized absorption and fluorescence spectra of **IIb** as an example. In the long-wavelength region the fluorescence spectrum is the mirror image of the absorption one. This is indicative for the preserved planarity of the molecular structure of the derivatives in the exited state. Therefore the fluorescence emission is prevailing in this case. Because the overlap between absorption and fluorescence spectra is small and the concentration of derivative is low, the reabsorption and aggregation effects are negligible. The close values of λ_A and λ_F in methanol solution for the investigated 4-allylamino-N-phenyl-1,8-naphthalimide derivatives show the similar polarization of the chromophoric system of the derivative molecules, caused by charge transfer (CT).

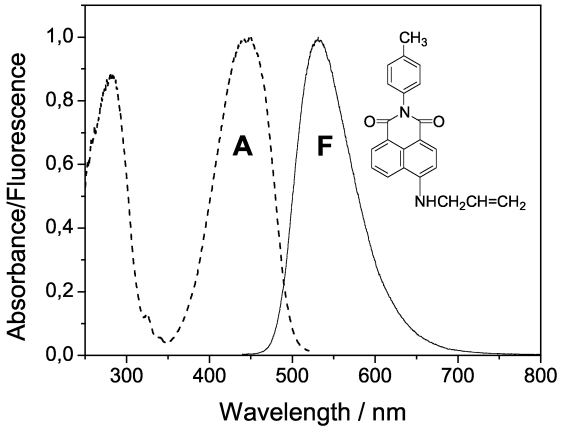


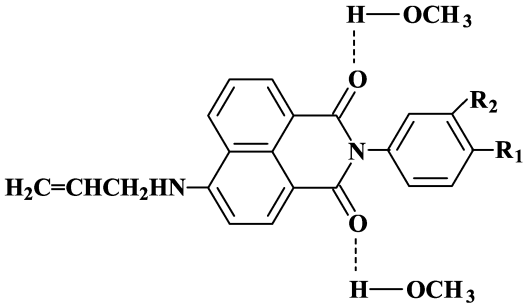
Fig. 2. Normalized absorption (A) and fluorescence (F) spectra of **IIb** in methanol solution.

In the visible region the molar extinction coefficients of **IIa-IIe** are high (ε between 12300 and 13600 $\mathrm{l\,mol^{-1}cm^{-1}}$), indicating that the long wavelength band of the absorption spectra (in the visible region) is a band of charge transfer, due to π,π^* electron transfer on $S_0 \rightarrow S_1$ transition. The 4-nitro substituted derivatives do not produce this band (Fig. 1).

The Stokes shift ($\nu_A - \nu_F$) indicates the difference in the properties and the structure of the dyes between the ground state S_0, and the first exited state S_1. The values of the Stokes shift for **IIa – IIe** are in the region 3585 – 3725 $\mathrm{cm^{-1}}$, which accords with other investigations on similar 1,8-naphthalimide derivatives [10 – 13].

Absorbing light, the investigated 1,8-naphthalimide derivatives pass from the basic singlet S_0 to the first excited state S_1. The energy of the first excited state and the corresponding λ_{S1} have been determined for the 4-allylamino derivatives (Table 1). The energies of the lowest exited singlet state (E_{S1}), 248.5 – 249.5 $\mathrm{kJ\,mol^{-1}}$, are obtained from the locations of intersections of the normalized absorption and fluorescence spectra of **IIa – IIe**. The dye molecules are deactivated on fluorescence light emission and pass from the S_1 to the basic S_0 state. Similar results are obtained for other 4-amino substituted 1,8-naphthalimides [10 – 13, 16].

An important parameter of the fluorophores is the oscillator strength (f). It reveals the effective number of electrons taking part in the transition from the ground to the excited state, and it is proportional to the area under the absorption spectrum. Values of oscillator strengths can be calculated using the formula [31]



Scheme 3. Hydrogen bonds between 4-allylamino-N-phenyl-1,8-naphthalimide and methanol molecules.

$$f = 4.32 \times 10^{-9} \Delta\nu_{1/2} \varepsilon_{max}, \quad (1)$$

where $\Delta\nu_{1/2}$ is the width of the absorption band (in $\mathrm{cm^{-1}}$) at $^1/_2\varepsilon_{max}$. The values of f obtained for II in methanol solution are in the range 0.244 – 0.291.

The quantum yield of fluorescence of **IIa – IIe** is estimated on the basis of the absorption and fluorescence spectra. As seen from the data in Table 1, **IIa – IIe** have fluorescence quantum yields in the range 0.36 – 0.60. Methanol has an interesting effect on the fluorescence of 1,8-naphthalimides. It is due to the interactions between the 1,8-naphthalimide and methanol molecules. The hydrogen bonds between the hydroxyl groups of the methanol and the carboxylic oxygen atom (C=O) from the naphthalimide system occur in the hydroxylated methanol solution (Scheme 3). Those H-bonds favour the radiation-less transition causing a decrease of the fluorescence quantum yield of 1,8-naphthalimides [32]. On the other hand, this effect stabilizes the exited state [33]. The lowest value of Φ_F obtained for **IIe** is probably due to conformation changes in the chromoforic system.

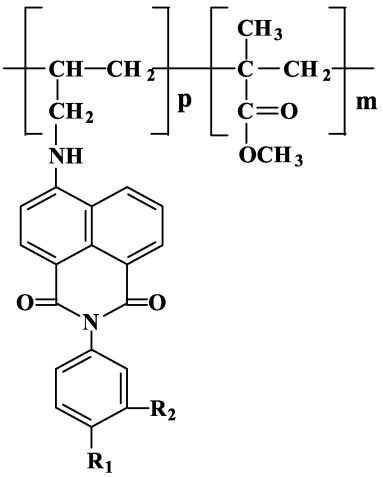
3.2. Photophysical Properties of Copolymers in Solid State

The green fluorescent copolymers of MMA and **IIa – IIe** have the chemical structure presented in Scheme 4 [34].

The PMMA based thin films show very good transmission in the 300 – 800 nm range. Table 2 lists the photophysical parameters of poly(MMA-co-dye) in the solid state. The maxima of the UV-Vis absorption spectra (λ_A) of the copolymers are in the range 419 – 423 nm. Figure 3 presents, as a typical example, the UV-Vis absorption spectrum of poly(MMA-co-dye1) in solid state and the absorption spectrum of **IIa** in

Table 2. Absorption and fluorescence characteristics of the copolymers poly(MMA-co-dyes) in the form of solid films.

Copolymers	λ_A nm	λ_F nm	$\nu_A - \nu_F$ cm^{-1}	E_{S1} $kJmol^{-1}$
Poly(MMA-co-dye**IIa**)	419	515	4449	251.5
Poly(MMA-co-dye**IIb**)	424	520	4354	252.4
Poly(MMA-co-dye**IIc**)	424	520	4354	253.4
Poly(MMA-co-dye**IId**)	420	502	3889	254.0
Poly(MMA-co-dye**IIe**)	420	507	4085	254.1



Scheme 4. Chemical structure of poly(MMA-co-dye) copolymers.

methanol solution, given for comparison. As is seen from Fig. 3, the spectral curves are rather similar each to other in the visible region. This obviously indicates that during the co-polymerization no change in the chemical structure of the chromophoric system occurs. The fluorescence maxima of the thin polymer films are in the region 502 – 520 nm in dependence on the chemical structure of the dyes. For dyes 1 – 3, the fluorescence maxima are at 515 – 520 nm, while for the dyes 4 and 5 they are at 502 – 507 nm, probably due to conformational effects in the solid film. It has been found that the fluorescence spectra for each copolymer in the solid film are identical in shape, irrespective of the excitation wavelength used, which demonstrates the existence of only one fluorescing species. Red shifts of the absorption and fluorescence maxima of all poly(MMA-co-dye)s compared to the respective maxima in the methanol solutions have been observed. This can result from the different polarity and viscosity. Methanol is a more polar solvent than

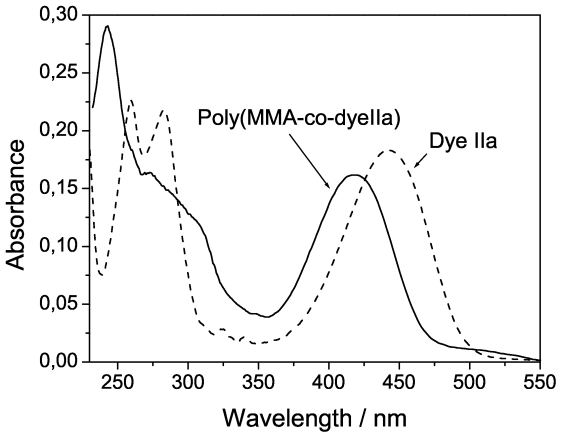


Fig. 3. UV-Vis absorption spectra of Poly(MMA-co-dye**IIa**) in solid state and **IIa** in methanol solution.

PMMA. Hence, in methanol the absorption maxima of **IIa – IIe** are shifted batochromically, if compared to those of poly(MMA-co-dye). The fluorescence in solid films is more intense than that of the monomer dyes. This phenomenon is due to the perfect incorporation of the fluorophores into the polymeric matrix, which hinders the conformational changes in the chromophoric system [34]. On the other hand, the high fluorescence intensity in solid film is due to the high microviscosity of the copolymers [35]. Thus the part of emissionless deactivation during the transition $S_1 \rightarrow S_0$ is smaller. Stokes shifts are in the 3889 – 4449 cm^{-1} range. There is almost no difference in the values for the energy of the first excited state E_{S1}, which are in the 251. – 254.1 kJ mol^{-1} range. The respective values in methanol solution, 248.5 – 249.5 kJ mol^{-1}, are slightly lower.

4. Conclusion

The photophysical characteristics of some recently synthesized 4-nitro- and 4-allylamino-N-phenyl-1,8-naphthalimide derivatives have been investigated in methanol solution. It has been proved that the substituents in the phenyl ring do not affect considerably the spectral properties of the novel derivatives. The copolymers with methylmethacrylate in solid state have yellow-green colour with intense and stable fluorescence, which makes them prospective colorants for polymer dispersed liquid crystals and light-emitting diodes.

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