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Dyes and Pigments, Vol. 38, No. 4, pp. 219–226, 1998

PII: S0143-7208(97)00117-4 0143-7208/98 $19.00+0.00

Photophysical Characteristics of Polymerizable 1,8-Naphthalimide Dyes and their Copolymers with Styrene or Methylmethacrylate*

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(Received 10 November 1997; accepted 4 December 1997)

ABSTRACT

The study presents the photophysical characteristics in ethanol and benzene of four fluorescent 1,8-naphthalimides dyes containing polymerizing groups bound to imide nitrogen atom as well as an amino group in 4-position to naphthalene ring. The polymerization of styrene or methylmethacrylate in the presence of these dyes has been investigated. It was established that 83–90% of polymethylmethacrylate (PMMA) and 79–91% >of polystyrene (PS) are chemically bound to the polymer chain. Absorption and fluorescent spectra of polymers structurally coloured with naphthalimide dyes in organic solvent and solid film are discussed. It was found that the photophysical properties, polymerization rate and specific viscosity of the polymers coloured depend on the nature of the amino group in the structure of the dyes. © 1998 Published by Elsevier Science Ltd. All rights reserved

Keywords: Polymerizable naphthalimide dyes, absorption, fluorescence, chemically coloured polystyrene, polymethylmethacrylate.

INTRODUCTION

Derivatives of 1,8-naphthalimides are of interest in view of their use as fluorescent dyes for solar energy collectors [1] and liquid crystals [2,3]. They have also been described as products in the synthesis of derivatives with photosensiting or chemiluminescent properties [4,5], for markers in molecular biology [6] and for laser active media [7].

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*Dedicated to Professor Pierre Mealliez with best wishes on the occasion of his 60th Birthday.

1,8-Naphthalimide derivatives with amino groups in the 4-position have an excellent yellow colour and emit very intense yellow-green fluorescence [8–10]. They are well known as dyes for synthetic polymer materials. A range of this type has been shown to have good coloration ability on synthetic fibres [11,12]. 4-Acylamino derivatives of 1,8-naphthalimide have blue fluorescence and they can be used as fluorescent brighteners [13]. The presence in such compounds of an unsaturated polymerizable double bond enables their use in copolymerization processes with vinyl monomers, forming a covalent bond in the polymer molecule with resistance to wet treatment and solvents [14–16].

The present work reports investigations of some derivatives of 1,8-naphthalimide containing various amino groups in the 4-position of the naphthalimide ring and an evaluation of their properties.

EXPERIMENTAL

The synthesis of the naphthalimide dyes investigated has been previously described [13,17,18]. UV–VIS absorption spectra were recorded on a Hewlet–Packard 8254 A Spectrophotometer in ethanol and benzene. Fluorescence measurements were recorded on a Perkin Elmer MPF 44.

The polymerization in styrene was carried out in a 5 ml dilatometer with capillary diameter 0.64 mm in the presence of 0.1 wt.% of the corresponding dye against styrene and 1 wt.% of dibenzoylperoxide towards the monomeric mixture at 80°C (±0.5°C) [15]. The bulk polymerization of styrene was carried out in ampoules, previously purged with pure dry nitrogen at 80°C for 8 h in the presence of 0.1 wt.% dye and 1 wt.% initiator dibenzylperoxide. The polymer obtained was reprecipitated 3–4 times from benzene with ethanol [15]. The bulk polymerization of methymethacrylate was carried out in ampoules, previously purged with pure dry nitrogen, at 70°C for 12 h in the presence of 0.1 wt.% dye and 1 wt.% initiator dibenzylperoxide. The polymer obtained was reprecipitated 3–4 times from chloroform with ethanol [14].

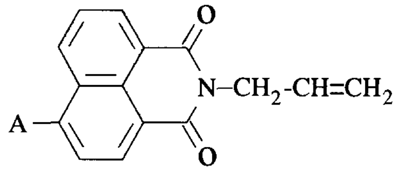
The values (ξ) of the reprecipitate were determined by measuring the specific viscosity of the benzene (PS) and of the chloroform (PMMA) solutions (0.5 wt.%) in an Ubbelohde viscometer, according to the following equation [19].

$$[\eta] = \frac{\sqrt{2}}{c}\sqrt{\eta_s - \ln \eta_r}$$

where c is the concentration of the polymers in benzene or chloroform (g dl^{-1}) η_s is the specific viscosity (cm^3 g^{-1}) and η_r is the relative viscosity (cm^3 g^{-1}).

RESULTS AND DISCUSSION

The dyes studied were of the general formula:



where A = $-NH_2$ (1), $-NHCH_3$ (2), $-N(CH_3)_2$ (3), $NHCOCH_2Cl$ (4)

Spectrophotometeric investigations of the monomeric dyes

Absorption and fluorescence spectra of the compounds were recorded in ethanol and benzene, and the data are presented in Table 1. The polarization of the naphthalimide molecule is governed by the donor–acceptor interactions of the electron-donating substituents in the 4-position and the electron-accepting carbonyl group, while change transfer along the chain of conjugated double bonds leads to absorption in the visible region for dyes 1–3 and in the near-UV region for dye 4. For dyes 1–3 in ethanol, λ_{max} in the visible region was in the range 416–432 nm, while in benzene it was 400–414 nm. Thus the dye having a primary amino group absorbed in ethanol at 430 nm, and in benzene at 414 nm. Whilst substitution of one hydrogen atom of the amino group by a methyl group does not significantly change the absorption maximum (dye 2), the presence of a tertiary amino group (two methyl groups) results in a hypsochromic shift of 16 nm (ethanol) and 10 nm (benzene) in dye 3 compared to dye 1. In the case of dye 4 the carbonyl group causes a strong hypsochromic shift of the absorption maximum. Dye 4 absorbs in the UV region at 360 nm (benzene) and 371 (ethanol).

The effect of π-donating groups in the 4-position of the naphthalimide molecule, and of π-accepting carbonyl groups upon the absorption properties depends on the polarity of solvents. A bathochromic shift of $\pi \longrightarrow \pi*$ and CT absorption bands was observed between benzene and the more polar ethanol.

With respect to the substituent A, the dyes were hypsochromically shifted in the order:

$$-HNCOCH_2Cl > -N(CH_3)_2 > -HNCH_3 \approx -NH_2$$

All dyes 1–3 had a yellow-green fluorescence, with maximum between 518–522 nm (ethanol) and 504–510 nm (benzene). Dye 4 has an intense blue fluorescence with a well pronounced maximum at 450 nm (benzene) and

TABLE 1
Absorption, Fluorescence, Stoke's Shift, Quantum Yield, and Oscillator Strength of Dyes 1–4 in Ethanol and Benzene

	Ethanol				*Benzene*			
	1	*2*	*3*	*4*	*1*	*2*	*3*	*4*
λ_A nm	430	432	416	371	414	410	400	360
lgε	4.02	4.12	3.99	3.70	4.13	4.20	4.09	3.99
λ_F nm	518	522	520	459	507	510	504	450
E_{S1} kJ mol^{-1}	245.3	246.2	251.1	286.5	253.1	254.0	264.7	291.9
Stoke's shift cm^{-1}	3950	3991	4807	5164	4430	4782	5159	5555
Φ_{fl}	0.85	0.83	0.04	0.39	0.90	0.92	0.14	0.53
f	0.213	0.201	0.194	0.293	0.324	0.411	0.343	0.42

459 nm (ethanol) and it is thus suitable for use as a fluorescent brightener. The fluoresce curve shows an approximate mirror image relationship to the absorption curve. The Stoke's shifts of the dyes in ethanol was between 3950–5167 cm^{-1} and 4430–5555 cm^{-1} in benzene, which becomes greater in both solvents in the order:

$$4 > 3 > 2 > 1$$

The dyes studied did not phosphoresce either in ethanol or in an i-pentane–ethanol–diehyl ether mixture (5:2:5) at 77 K, and when excited, they were in the singlet state S_1. Dyes 1–4 pass from the basic singlet S_0 to the first excited state S_1 on light absorption. The energy of the first excited state S_1 and the corresponding λ_{S1} were determined. The energy of E_{S1} found experimentally in ethanol was 245–287 kJ mol^{-1} while in benzene solution it was 243–292 kJ mol^{-1}. The dye molecule is deactivated on fluorescence light emission, and passes from the S_1 to the basic S_0 state.

The quantum fluorescence yield Φ was determined on the basis of absorption and fluorescence spectra of the dyes in ethanol and benzene at a concentration of 1.10^{-5} M. Rhodamine 6G ($\Phi_0 = 0.88$) was used as a standard [20]. From the tabulated data (Table 1), it is seen that the studied dyes have quantum yields of $\Phi = 0.04$–0.85 (ethanol) and $\Phi = 0.14$–0.90 (benzene). The quantum yield for all dyes increases with the transition from ethanol to the less polar benzene. The low value of the fluorescence quantum yield of dye 3 is due to the decrease in coplanarity of the molecule originating from steric factors. It might also be due to the interaction between one of the methyl groups and the hydrogen atom in the 5-position of the naphthalene ring. In this case, for dye 3 the results show that the fluorescence involves non-emission deactivation of the S_1.

An important characteristic of the dyes is the oscillator strength (**f**). The oscillator strength shows the effective number of electrons, transition of which from the ground to excited state gives the absorption area in the electron specrtrum. Values of the oscillator strength were calculated using the following formula [21]:

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

were $\Delta\nu_{1/2}$ is the width of the absorption bond in cm^{-1} at $\varepsilon_{\max}/2$.

The value of f varies from 0.194 to 0.293 in ethanol and from 0.324 to 0.410 in benzene. For all dyes, the calculated value in ethanol is lower that in benzene. This is due to the hypochromic effect of ethanol.

Copolymerization of dyes with styrene or methylmethacrylate

The polymerization of styrene or methylmethacrylate in the presence of 0.1 wt.% of dye was studied. The copolymerization of the dyes with styrene was investigated dilatometrically. The results obtained are shown in Fig. 1 and compared with those for homopolystyrene. On the basis of these data, the polymerization rate was calculated (Table 2). As can be seen, the participation of the monomeric dye 3 (which contains a tertiary amino group) in the copolymerization accelerates the process compared to those of pure styrene. Dyes 1 and 2 decreased the rate of the process. This influence is most significant for dye 1. Modification of the primary amino group in dye 1 with a chloroacetylamino group (dye 4) accelerates the copolymerization rate compared to that of dye 1.

The copolymerization with styrene or methylmethacrylate was carried out in bulk, both in the presence of 1 wt.% of DBP and 0.1 wt.% dyes 1–4. In both cases transparent fluorescent polymers with an intensive yellow-green fluorescence (dyes 1–3) or blue fluorescence (dye 4) were obtained. The coloured polymers were precipitated three–four times to remove unreacted monomers. All of them retained their colour, indicating that the dye was chemically bound to the polymer chain. Absorption and fluorescence spectra of the polymers in benzene for Poly(St-co-dye) and in chloroform for Poly(MMA-co-dye), as well as in a thin polymer film 40 μm thick, were studied. The results are summarized in Tables 2 and 3. The absorption and fluorescent spectra for the precipitated Poly(St-co-dye) and Poly(MMA-co-dye) showed the same λ_A and λ_F as pure dyes 2–4 in the respective solvent. This shows that the basic chromophore of the dye did not change either during the polymerization or as a result of the bonding to the polymer chain. Dye 1 changed its colour and was not suitable for this type of polymerization.

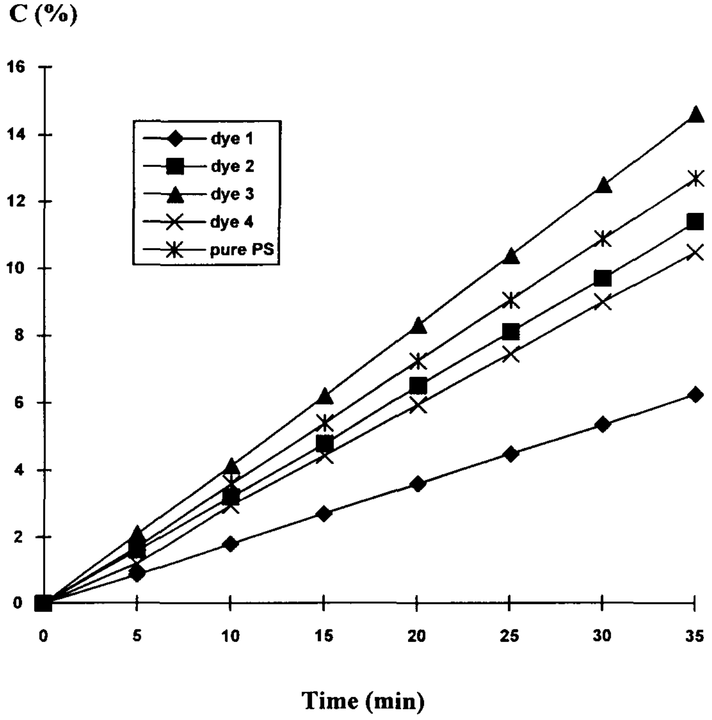


Fig. 1. Conversion curve of polymerization for styrene with 0.1 wt.% of dyes 1–4 and pure polystyrene.

Probably during the process the free radicals of the initiator attack the primary amino group, weakening the donor–acceptor interaction in the dye molecule. Hence the polymerization rate of PS in the presence of dyes is lower.

Using the standard line method, it was determined spectrophotometrically for dyes 2–4 that 79–91% (PS) and 83–90% (PMMA) of the initial amount

TABLE 2
Absorption and Fluorescence Maxima, Polymer Rate and Specific Viscosity of Poly(St-co-dye) and Pure Polystyrene

Dye	*Solid film* λ_A *(nm)*	*Solid film* λ_F *(nm)*	*Benzene* λ_A *(nm)*	*Benzene* λ_F *(nm)*	*Polym. rate* *(mol l^{-1} s^{-1})*	*(ξ)* *(cm^3 g^{-1})*	*Chemically bound dye (%)*
1	389	490	392	491	2.7	0.31	—
2	416	508	412	509	4.9	0.54	79
3	403	500	398	503	5.7	0.57	91
4	364	442	360	451	5.2	0.53	86
Without dye	—	—	—	—	5.3	0.62	—

TABLE 3

Absorption and Fluorescence Maxima, and Specific Viscosity of Poly(MMA-co-dye) and Pure Polymethylmethacrylate

	Monomer		*Polymer*					
	in $CHCl_3$		*in* $CHCl_3$		*Solid film*			
Dye	λ_A *(nm)*	λ_F *(nm)*	λ_A *(nm)*	λ_F *(nm)*	λ_A *(nm)*	λ_F *(nm)*	(ξ) $(cm^3 g^{-1})$	*Chemically bound dye (%)*
1	422	510	392	498	390	493	0.56	—
2	420	508	418	506	413	506	0.90	83
3	406	503	407	501	401	501	0.96	90
4	364	453	362	451	365	450	0.92	85
Without dye	—	—	—	—	—	—	1.04	—

of the dye was incorporated into the macromolecule. Considering that these results were for repeatedly precipitated polymers, where during the precipitation low molecular weight fractions were removed, this value is satisfactory, and thus dyes 2–4 are suitable for the production of coloured polymers resistant to moisture and solvents. The colours obtained are also fluorescent. In the solid polymeric films, dyes 2 and 3 have absorption and fluorescent maxima close to those of the monomeric dyes in the nonpolar solvents benzene and chloroform, and, respectively, a hypsochromic shift with respect to the maxima in the more polar ethanol.

The results for the specific viscosity (ξ) of the colour copolymers show that dyes 2–4 do not affect significantly the molecular weight, if compared to that of homopolymers, while dye 1 considerably decreases (ξ) values both of Poly(St-co-dye1) and Poly(MMA-co-dye1).

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