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Synthesis of Some Unsaturated 1,8-Naphthalimide Dyes

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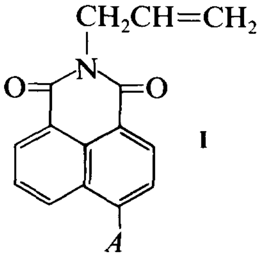
ABSTRACT

Four unsaturated derivatives of 1,8-naphthalimide have been synthesized and their spectrophotometric properties and Cielab colour coordinates determined. They can copolymerize with styrene, and the coloured polymers thus obtained have good resistance to wet treatments and to organic solvents.

1 INTRODUCTION

Amino derivatives of 1,8-naphthalic anhydride have been reported as fluorescent dyes for polymers[1] and in a previous publication[2] we described the synthesis and properties of related dyes containing an unsaturated allylamine group capable of polymerization. These have the general formula **I**, where *A* is a residue of a cyclic amine or an amino group.



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When *A* is the residue of a cyclic amine the dyes have low fluorescence and quantum yields and only when *A* is an amino group do the dyes have

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a high quantum yield approaching that of Rhodamine 6G. Due to the presence of the allylamine group, the dyes can copolymerize with vinylic monomers, thus forming coloured polymers with resistance to wet treatments and to organic solvents.

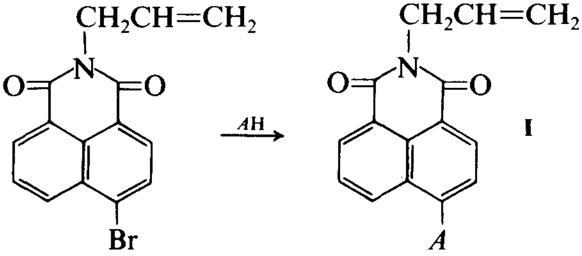
Investigations carried out on the polymerization of styrene in the presence of these dyes showed that they did not decrease the polymerization rate and could even increase it (T. Konstantinova and I. Grabchev, unpublished data); this is a useful property since most dyes usually decrease the polymerization rate.[3–5]

Following these previous results it was of interest to synthesize other derivatives of 1,8-naphthalimide which might have higher quantum yield, more intense fluorescence and an ability to polymerize. This present work reports the synthesis of some derivatives of 1,8-naphthalimide containing various alkylamino groups in the 4-position of the naphthalimide ring and an evaluation of their properties.

2 RESULTS AND DISCUSSION

2.1 Synthesis of dyes

The route employed in the synthesis of these dyes was as follows:



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(where *A* is given in Table 1). The synthesis of 4-Br-*N*-allylnaphthalimide has been reported previously.[2] In this present work methylamine, ethylamine, dimethylamine and diethylamine were used as *A*H. The reaction was carried out in 2-methoxyethanol, giving the respective mono- or dialkylamino derivatives in good yield.

2.2 Spectrophotometric investigations

The absorption and fluorescence spectra of the dyes were recorded in ethanol (5×10^{-5} mol l^{-1} concentration). All dyes had a yellow-green colour with absorption maximum between 416 and 436 nm and fluorescence maximum in the range 520–525 nm. The fluorescence quantum

TABLE 1
Characterization Data for Dyes I

Dye no.	*A*	*Yield (%)*	*Melting point (°C)*	R_f^a
I.1	$—NHCH_3$	93	225–7	0·64
I.2	$—NHC_2H_5$	96	197–9	0·55
I.3	$—N(CH_3)_2$	96	113–5	0·52
I.4	$—N(C_2H_5)_2$	94	102–4	0·76

[a] Using *n*-heptane : acetone = 1 : 1.

yields were calculated using Rhodamine 6G as a standard (quantum yield = 0·88). The results are given in Table 2. In comparison with similar dyes,[2] it was found that the nature of the amine was the main influence on the molar absorption coefficient and on the fluorescence. These two parameters decreased as the substitution of the amino group increased. It should be noted that the replacement of one of the amino hydrogen atoms by alkyl does not significantly affect the absorption and fluorescence maxima.

2.3 Colour assessment

Polyamide fabrics were dyed at 1% depth (owf) and colour assessment of the dyeings was made using the 'Texflach ACS' equipment in the Datacolor laboratory in Sofia. The results are given in Table 3, where Cielab values and other colour parameters are presented. All dyeings were yellow-greenish in colour and the brightness of the dyeings from dyes **I.1** and **I.2** was higher than those of dyeings from dyes **I.3** and **I.4**.

2.4 Polymerization of styrene in the presence of the dyes

The possibility of copolymerization of styrene with dyes **I.1**-**I.4** was investigated; this was effected in bulk at 80°C in the presence of 0·1 wt%

TABLE 2
Spectrophotometric Data for Dyes I

Dye no.	λ_{max} *absorption (nm)*	λ_{max} *fluorescence (nm)*	λ_{sI} *(nm)*	E_{sI} *(kJ)*	*Quantum yield*[a]
I.1	432	522	489	297	0·99
I.2	436	525	488	295	0·88
I.3	416	520	480	249	0·04
I.4	416	523	480	249	0·06

[a] Relative to quantum yield of Rhodamine 6G.

TABLE 3
Colour Data of Dyes on Polyamide[a]

Dye no.	*Chromaticity*		*Luminance Y (%)*	*Cielab coordinates*		
	x	*y*		*L**	*a**	*b**
I.1	0·410	0·469	104·1	103·42	−18·21	74·81
I.2	0·418	0·473	103·27	104·94	−17·40	79·96
I.3	0·394	0·486	91·14	93·31	−12·91	99·08
I.4	0·399	0·489	89·75	95·01	−10·76	94·14

[a] Dyeing at 1% dye (owf).

of the corresponding dye and 0·1 wt% of dibenzoylperoxide (DBP) for 8 h. Yellow polymers with an intense fluorescence were obtained. They were purified by 4–5 fold precipitation with methanol from benzene. All retained their colour, indicating the formation of a covalent bond between the dye and the polymer. The absorption spectra for the precipitated polymers showed the same λ_{max} as the parent dyes. It was established spectrophotometrically, using the standard calibration curve method, that about 85% of the initial amount of the dye in the monomeric mixture was incorporated into the polymer chain.

The properties of dyes **I.1** and **I.2** were better than those previously reported for derivatives of cyclic amines.

3 EXPERIMENTAL

IR spectra were recorded (KBr) on a Perkin Elmer FT-IR spectrophotometer, UV/vis (ethanol) on an HPUV-8452 and fluorescence measurements on a Jobin-Ivon spectrofluorimeter. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker 200. TLC monitoring of the reactions was carried out on Silicagel plates (Fluka F_{60} 254, 20 × 20 cm, 0·2 mm) using *n*-heptane : acetone = 1 : 1 as eluent. 4-Br-*N*-allylnaphthalimide was synthesized as described previously.[2]

3.1 Synthesis of 4-methylamino-*N*-allylnaphthalimide (I.1)

A mixture of 4-Br-*N*-allylnaphthalimide (3·16 g, 0·01 mol) and methylamine (0·12 g, 0·01 mol as 40% aqueous solution) was dissolved in 50 mol of 2-methoxymethanol, and 0·01 mol of triethylamine was then added.

The solution was refluxed for 4 h and, after cooling to room temperature, the liquor was poured into 200 ml of water. The resulting crystals were filtered and dried *in vacuo*.

Yield 93%. IR (KBr): ν = 3214 cm^{-1} (NH), 1691 cm^{-1} (C=O), 1650 cm^{-1} (C=C). ^{1}H NMR (CDCl$_3$): δ = 3·1–3·2 (s, 3H, CH$_3$), 4·7–4·8 (d, 2H, NCH$_2$), 5·2–5·4 (m, 2H, =CH$_2$), 6·0–6·1 (m, 1H, =CH), 7·5–8·6 (m, 5H, ArH).

Dyes **I.2-I.4** were synthesized following the same procedure; characterisation data are shown below.

*4-Ethylamino-*N*-allylnaphthalimide (**I.2**)*
Yield 96%. IR (KBr): ν = 3221 cm^{-1} (NH), 1690 cm^{-1} (C=O), 1645 cm^{-1} (C=O). ^{1}H NMR (CDCl$_3$): δ = 1·3–1·4 (s, 3H, CH$_3$), 3·4–3·5 (m, 2H, NCH$_2$), 4·6–4·7 (d, 2H, NCH$_2$), 5·2–5·3 (m, 2H, =CH$_2$), 6·0–6·1 (m, 1H, =CH), 7·4–8·5 (m, 5H, ArH).

*4-Dimethylamino-*N*-allylnaphthalimide (**I.3**)*
Yield 96%. ^{1}H NMR (CDCl$_3$): δ = 3·1–3·2 (s, 6H, CH$_3$), 4·7–4·8 (d, 2H, NCH$_2$), 5·2–5·4 (m, 2H, =CH$_2$), 6·0–6·1 (m, 1H, =CH), 7·4–8·5 (m, 5H, ArH).

*4-Diethylamino-*N*-allylnaphthalimide (**I.4**)*
Yield 94%. ^{1}H NMR (CDCl$_3$): δ = 1·1–1·2 (t, 6H, CH$_3$), 3·4–3·5 (m, 4H, CH$_2$CH$_3$), 4·7–4·8 (m, 2H, NCH$_2$CH), 5·2–5·4 (m, 2H, =CH$_2$), 5·9–6·0 (m, 1H, =CH), 7·4–8·7 (m, 5H, ArH).

3.2 Polymerization

In an ampoule flushed with dry N$_2$, 10 g of purified styrene, 0·01 g of the appropriate dye and 0·01 g of DBP were mixed. The ampoule was sealed and heated in a thermostat at 80°C for 8 h. Yellow-green polymers with an intense fluorescence were obtained. These polymers were dissolved in benzene and precipitated by methanol (4–5 times) until the filtrate became colourless; the polymers were then dried *in vacuo* at 30°C.

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REFERENCES

1. Peters, A. T. & Bide, M. J., *Dyes and Pigments*, **6** (1985) 349.
2. Konstantinova, T., Meallier, P. & Grabchev, I., *Dyes and Pigments*, **22** (1993) 191.
3. Konstantinova, T., Konstantinov, Hr. & Draganov, A., *Die Agnew. Makromol. Chemie*, **50** (1976) 1.
4. Asquith, R. & Blair, H., *J. Soc. Dyers Col.*, **93** (9) (1977) 114.
5. Mareshal, E., *Progress in Organic Coatings*, **10** (1982) 251.