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The Synthesis of Some 1,8-Naphthalic anhydride Derivatives as Dyes for Polymeric Materials

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ABSTRACT

Four derivatives of 4-amino-1,8-naphthalimide containing an unsaturated group have been synthesized and their fluorescence, quantum yield, photodegradation and Cielab colour coordinates determined their ability to copolymerize with styrene is demonstrated and the coloured polymers thus obtained had good resistance to wet treatment and solvents.

1 INTRODUCTION

Aminonaphthalimides are well known as dyes for synthetic polymer materials and a range of this type have been shown to have good colouration properties on synthetic-polymer fibres.[1]

Methods for the formation of coloured polymers in which the dye is chemically bound to the polymer molecule have been studied in the last 10–15 years and different dyes, which can take part in polymerization or polycondensation processes, have been synthesized,[2–4] the products having good fastness to wet treatments and solvents.

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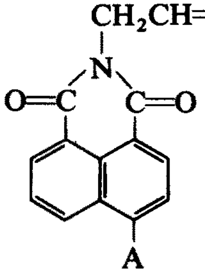
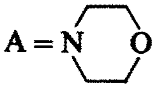
The authors have reported the synthesis and application of some triazine[5,6] and benzanthrone[7] derivatives suitable for such colouration of polymers.

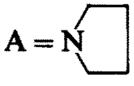
The authors report here the synthesis and properties of some 4-amino derivatives of 1,8-naphthalimide, containing an unsaturated group and which are capable of copolymerization. They are represented by the general formula (**I**), where A is:



I



1



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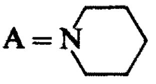


3

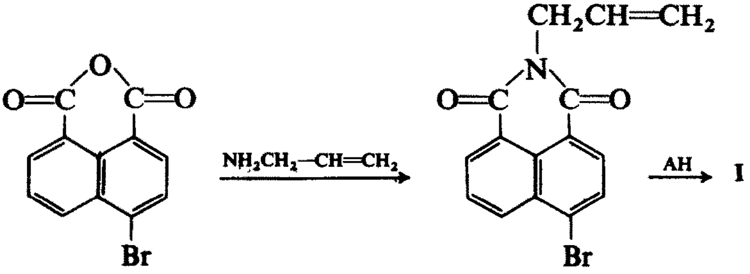
A = $-NH_2$

4

2 RESULTS AND DISCUSSIONS

2.1 Synthesis of dyes

The route employed in the synthesis of dyes **1–3** was as follows:



4-Bromo-1,8-naphthalic anhydride, synthesized as previously described,[8] reacted in molar ratio with allylamine (AAm) in boiling methanol for 4 h. The reaction was monitored by TLC. 4-Bromo-*N*-allylnaphthalimide (**B**) was isolated in good yield (>90%). A mixture of **B** and the corresponding amine (AH) was then refluxed for 4 h in ethanol, with addition of triethylamine to remove HBr. It was interesting to note that the reactivity of the amines AH under the experimental conditions used, i.e. replacing a 4-bromo substituent, was better than similar reactions replacing a 4-chloro

TABLE 1
Characterization Data for the Dyes of Formula I

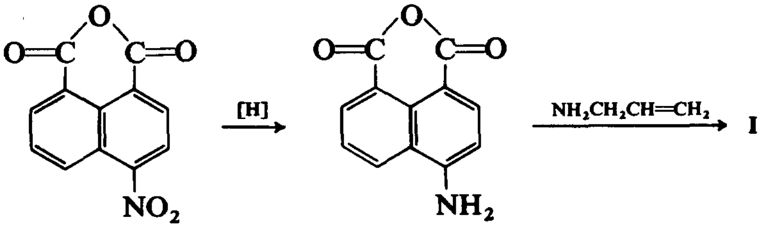
Dye no.	A	Yield (%)	m.p. (°C)	λ_{max} (nm)	ε
1	Morpholine	76	118–20	390	12 600[a]
2	Pyperidine	82	110–12	410	6 900[a]
3	Pyrrolidine	78	163–5	444	15 800[b]
4	Amino	92	228–30	430	10 600[b]

[a] Concentration 2×10^{-4} mol/litre.
[b] Concentration 5×10^{-5} mol/litre.

substituent, although the order of reactivity[1] was the same, viz. pyperidine > pyrrolidine > morpholine.

Characterization data for the dyes are shown in Table 1.

Dye 4 was synthesized following the following scheme:



A mixture of 4-amino-1,8-naphthalic anhydride, obtained as previously described[8,9] and allylamine was refluxed in methanol for 3–4 h, giving 90% of 2-amino-N-allylnaphthalimide.

All dyes were characterized by m.p. R_f, elemental analysis, IR, UV/Vis and ^{1}H-NMR spectra.

It was of interest to note that the presence of an unsaturated group in the dye molecule resulted in no change in the λ_{max} relative to analogous dyes containing N-alkyl or N-hydroxyalkyl substituents.[1]

2.2 Spectrophotometric investigations

The absorption spectra of the dyes in ethanol were recorded and data are shown in Table 2. The dyes were very strongly yellow-orange fluorescent and their fluorescent spectra in the same solvent were recorded, and on the basis

TABLE 2
Absorbtion, Fluorescence, Quantum Yield and Degradation Data of Dyes of Formula I

	1	*2*	*3*	*4*
Concentration in C_2H_5OH (mol/litre)	2×10^{-4}	5×10^{-5}	2×10^{-4}	5×10^{-4}
λ_{max}	390	444	410	430
ε	12 600	15 800	6 900	10 600
$\lambda_{singlestate}$	485	492	478	488
$\lambda_{fluorescence}$	522	546	525	518
E_{st} (kcal/mol)	60	58	61	59
Quantum yield (against Rhodamine 6G)	0·11	0·05	0·05	≈1
Degradation (%)	22	51	13·6	62
Quantum yield of degradation (%)	$1{\cdot}08 \times 10^{-5}$	$1{\cdot}01 \times 10^{-5}$	$1{\cdot}48 \times 10^{-5}$	$1{\cdot}33 \times 10^{-4}$

of the results the energy of the first excited state, and their photostability, were estimated.[10]

From the data in Table 2, it can be seen that the energy level of the excited state is approximately equal for all the dyes (60 kcal). The main difference observed is in the quantum yield of the fluorescence, a result in accord with the fact that the amino group causes a red shift of the benzene fluorescence with an enhanced intensity, and that *N*-heterocyclic compounds do not fluoresce easily.

The photostability of the dyes in ethanol under UV light (λ 550–200 nm) for 8 h and 30 min was investigated. The four compounds were found to have essentially the same photostability, their quantum yield of degradation being of similar order.

On the basis of the experimental data, the values of P_a and ϕ_d were estimated:

$$P_a = P_0(1 - 10^{-\varepsilon cl})$$

From the data in Table 3, the absorption ability of the dyes follows the order: **1** > **4** > **3** > **2**.

2.3 Colour assessment

Polyamide fabrics were dyed by the disperse method at 1% depth o.w.f. The assessment of the colour of the fabrics was made by the 'Texflach ACS' Technique in the Datacolor laboratory in Sofia. Resultant values of the Cielab and other colour parameters are presented in Table 4.

TABLE 3
Values of P_a and θ_d of Dyes of Formula I

Dye no.	P_a	$\phi_d \times 10^{-4}$
1	0·997/P_0	9
2	0·838/P_0	5
3	0·958/P_0	5·7
4	0·705/P_0	8·5

TABLE 4
Colour Data of Dyes on Polyamide[a]

Dye no.	*Chromaticity*		*Luminance Y (%)*	*Cielab coordinates*			C^*
	x	*y*		L^*	a^*	b^*	
1	0·383	0·475	102·87	101·1	−26·67	69·97	74·99
2	0·412	0·487	94·84	97·97	−18·21	83·02	84·99
3	0·445	0·500	92·55	97·05	−10·45	103·6	104·16
4	0·481	−0·471	−54·61	78·82	10·33	88·87	89·47

[a] Dyeings at 1% dye (o.w.f.).

2.4 Copolymerization with styrene

In order to evaluate whether the unsaturated group was capable of copolymerization with styrene, the polymerization of styrene in the presence of the dyes was carried out. The polymerization was effected in bulk at 80°C in the presence of 0·1 wt% of dibenzoylperoxide and 0·1 wt% of the dyes for 8 h. Transparent fluorescent polymers were obtained with dyes **1**, **2** and **3**, but dye **4** lost its colour and was therefore not suitable for this type of polymerization. The coloured polymers were precipitated 4–5 times to remove unreacted monomers; all of them retained their colour, indicating that the dye was chemically bonded to the polymer chain. The absorbtion spectra for the precipitated polymers showed the same λ_{max} as the pure dyes, thus showing 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.

Colorimetrically, by the method of the standard calibration curve, it was established that about 80% of the initial amount of 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 can be considered to be very satisfactory and dyes **1**–**3** are thus suitable for the production of coloured polymers having resistance to wet treatment and solvents, the colourations also being fluorescent.

3 EXPERIMENTAL

All melting points are uncorrected. IR spectra were recorded on an FT-IR Perkin-Elmer 1600 Spectrophotometer (KBr); UV/Vis spectra were recorded in ethanol on a Hewlet Packard 8452A Spectrophotometer and fluorescence measurements were made on a Jobin-Yvon JY3D Spectrofluorimeter; the authors used a low-pressure mercury lamp emitting principally at 254 nm, the intensity of this wavelength being 2×10^{16} photons per second. ^{1}H-NMR spectra were recorded in $CDCl_3$. TLC analyses were made on Silica Gel plates (Fluka $F_{60}254$), using heptane/acetone 1:1 as eluant.

3.1 Synthesis

4-Bromo-naphthalic anhydride[8] and 4-aminonaphthalic anhydride[9] were prepared as previously described.

3.1.1 *4-Bromo-*N*-allylnaphthalimide (**B**)*

4-Bromo-1,8-naphthalic anhydride (2·8, 0·01 mol) was dissolved in ethanol (50 ml) and allylamine (0·01 mol) was added at 55°C. The solution was refluxed for 3–4 h; the liquor was then cooled and the product filtered, washed with water and dried *in vacuo* at 30°C. Yield 90%; m.p. 129–130°C; $R_f = 0{\cdot}65$.

3.1.2 *4-Morpholino-*N*-allylnaphthalimide (**1**)*

A mixture of **B** (0·01 mol) and morpholine (0·01 mol) in ethanol (50 ml) was refluxed; during the reaction an equimolar quantity of triethylamine was added. The reaction was completed after 4 h. After concentration of the liquor, the resultant yellow crystals were filtered, washed and dried *in vacuo*. Yield 75%; m.p. 118–129°C; $R_f = 0{\cdot}57$.

IR(KBr) $\nu = 1690\,cm^{-1}$ (C=O); $1654\,cm^{-1}$ (C=C); 1589, $1513\,cm^{-1}$ (CH—Ar); $1448\,cm^{-1}$ (CH_2).

^{1}H-NMR ($CDCl_3$) $\delta = 3{\cdot}0$–$3{\cdot}2$ (t, 4H, CH_2); 3·8–4·1 (t, 4H, CH_2—); 4·6–4·8 (d, 2H, CH_2=); 5·3–5·5 (m, 2H, CH_2); 5·8–5·9 (m, 1H, CH=); 7·2–8·5 (m, 5H, Ar).

Dyes **2** and **3** were synthesized using the same procedure, as follows.

*3.1.3 4-Piperidino-*N*-allylnaphthalimide (**2**)*

Yield 82%; m.p. 110–112°C, $R_f = 0{\cdot}56$.

IR(KBr) $\nu = 1697\,\mathrm{cm}^{-1}$; $1652\,\mathrm{cm}^{-1}$; $1590\,\mathrm{cm}^{-1}$; $1447\,\mathrm{cm}^{-1}$.

^{1}H-NMR ($CDCl_3$) $\delta = 1{\cdot}8$ (d, 6H); 3·2 (s, 4H); 4·8 (d, 2H); 5·3–5·5 (m, 2H), 5·8–6·0 (m, 1H); 7·2–8·5 (m, 5H).

*3.1.4 4-Pyrrolidino-*N*-allylnaphthalimide (**3**)*

Yield 78%; m.p. 163–5°C; $R_f = 0{\cdot}55$.

IR(KBr) $\nu = 1675\,\mathrm{cm}^{-1}$ (C=O); $1644\,\mathrm{cm}^{-1}$; $1581\,\mathrm{cm}^{-1}$; $1529\,\mathrm{cm}^{-1}$; $1462\,\mathrm{cm}^{-1}$.

^{1}H-NMR ($CDCl_3$) $\delta = 2{\cdot}0$–$2{\cdot}4$ (t, 4H, CH); 3·6–3·9 (t, 4H, CH_2); 4·7–4·9 (d, 2H, CH_2=); 5·0–5·5 (m, 2H, OCH_2); 5·8–6·1 (m, 1H, CH=); 7·2–8·5 (m, 5H, Ar).

*3.1.5 4-Amino-*N*-allylnaphthalimide (**4**)*

A mixture of 4-aminonaphthalic anhydride (0·01 mol, 2·1 g) and allylamine (0·75 ml) was refluxed for 6 h in methanol (100 ml, 0·01 mol). Orange crystals were isolated after removal of solvent under vacuum. Yield 90%; m.p. 228–230°C; $R_f = 0{\cdot}35$.

Analysis $C_{15}H_{12}N_2O_2$: calculated N 10·93%; found N 10·90%.

3.2 Polymerization

In an ampoule flushed with N_2, styrene (10 g) and the appropriate dye (0·01 g) and dibenzoylperoxide (0·01 g) were mixed. The ampoule was sealed and heated for 8 h at 80°C. The coloured transparent polymers thus obtained were dissolved in benzene and precipitated with methanol. This operation was repeated 4–5 times until the filtrate was colourless. The polymers were dried *in vacuo* and spectrophotometrically tested (1 g of polymer in 25 ml of DMF).

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