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# The synthesis, properties and application of some 1,8-naphthalimide dyes

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**Abstract**

The synthesis of two, unsaturated 1,8-naphthalimide derivatives was studied; it was found that the synthesis of the two dyes was more efficient than previously reported. Quantitative thin-layer chromatography (tlc) was used to monitor the process and check the purity of the products. The dyes were copolymerized with methylmethacrylate (MMA) giving polymers with intense colour and fluorescence that were stable to solvent extraction. Wool and polyamide fibres were dyed and the colorimetric characteristics of the dyed fabrics were measured. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Unsaturated 1,8-naphthalimide dyes; Coloured PMMA; Polymerisable dyes; Wool; Nylon

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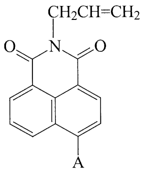
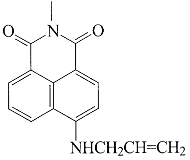
## 1. Introduction

Derivatives of 1,8-naphthalimide are well known as dyes for polymers, for liquid crystal displays, in molecular biology and other applications [1–3]. We have previously reported the synthesis of some unsaturated 1,8-naphthalimide dyes which were capable of copolymerisation with styrene and acrylontrile and of forming a covalent bond in the polymer molecule [4–7]. Some of these dyes were of general formula (1) where A are residues of different aliphatic amines:



(1)

Others are of structure **(2)**, where R are methyl or ethyl residues:



(2)

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Our investigations showed that the dyes have very good fluorescence quantum yield and good photostability [7]. The present study concerns their synthesis, colour characteristics and application to natural and synthetic polyamide fibres.

## 2. Results and discussion

### 2.1. Synthesis

The dyes of the present study have the general formula **(2)**, where R$=$–$CH_3$ (**2a**) and R$=$–$C_2H_5$ (**2b**)

They were obtained according to Scheme 1.

The first stage of the reaction, where 4-Br-1,8-naphthalic anhydride **(3)** reacted with the corresponding $RNH_2$, was performed in our earlier study in boiling, absolute ethanol for 6 h. The corresponding intermediates **(4)** [where R$=$–$CH_3$ (4a) and R$=$–$C_2H_5$ (4b)] were obtained in 72–78% yield. In the present work, we examine the possibility of obtaining these products in higher yield and purity.

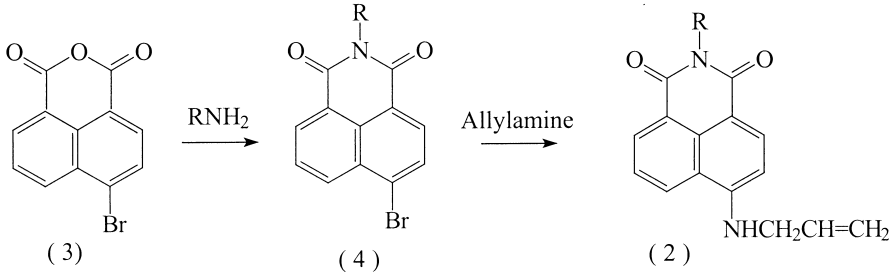
In order to secure rapid, reliable information about the course of the reaction, we developed a quantitative method of analysis. Thin-layer chromatography is widely used for the identification and quantitation of organic compounds. Its versatility, speed and low cost in combination with high resolution and ease of use, make it extremely useful. To monitor the synthesis we experimented with a range of mobile phases to maximise the separation of the final products from the starting materials. *n*-Heptane–acetone (3:1, v/v) was found to provide compact spots of regular shape, giving subsequent detection with high sensitivity. Quantitative analysis was performed by scanning the chromatograms; data for the area of each spot were recorded and the correlation between the spots, derived from each initial staring point, was calculated. On the basis of these data the conversion ratio at a given reaction time was estimated.

Reactions using acetone instead of absolute ethanol as a solvent were undertaken for better solubility of the starting materials. After 6 h reflux, the conversion ratio reached no more then 70%. The use of other solvents such as dimethylsulfoxid (DMSO) and 1,4-dioxan (DOX), allowed the reaction to occur at higher temperature. In boiling DOX, a conversion ratio of >98% was reached within 2 h. Similar results were obtained using DMSO at the same temperature. Temperatures higher than 100°C was found unsuitable because a 4-alkylamino substitution took place. This observation, together with some difficulties in the isolation of products from DMSO, made the use of DOX most suitable.

Thus, in boiling DOX, 98% of anhydride **(3)** was ?twb> converted to the corresponding **4a** or **4b** compound within 2 h and they were isolated in 88–90% yield. Their characteristic data (mp and elemental analysis) were identical to those obtained previously [7]. In addition were recorded $^1$H NMR spectra to confirm their structure.

The subsequent step of the synthesis according to Scheme 1, i.e. the reaction between 4-Br-*N*-alkylnaphthalimide **(4)** and allylamine, was performed again in boiling DOX with the addition of triethylamine to remove HBr. tlc of the reaction

They were obtained according to the scheme:



Scheme 1.

mixture using the same system as before showed 100% conversion of compound **(4)** to compound **(2)** after 4 h and compounds **2a** and **2b** were isolated in 95–96% yield. Their characteristic data (UV/Vis, IR and $^1$HNMR spectra, elemental analysis and mp) were identical to those obtained previously [7].

Thus, using DOX as a solvent and carrying out the synthesis at higher temperature we obtained these two compounds and their intermediates **(4)** in shorter times, with higher yields and purity.

### *2.2. Spectral data*

The absorption spectra of the dyes **(2)** were recorded in a range of solvents and data are presented in Table 1. As the polarity of the solvents increased from toluene to methanol, a bathochromic shift of $\lambda_{max}$ was observed. On the basis of these data we conclude that there is a $\pi \rightarrow \pi^*$ charge transfer transition which is in accordance with the good quantum yield of fluorescence of the dyes [7].

### *2.3. Colour assessment*

Polyamide and wool fabrics were dyed with dyes **2a** and **2b**. After 30 min, materials with an intense yellow-greenish colour and bright fluorescence were obtained. Colorimetric data for the dyeings were obtained using an ACS *Texflash* spectrophotometer and associated software and are displayed in Tables 2 and 3.

The dyeings diplayed poor fastness properties; detailed investigations of the dyeing mechanism and the nature of the dye–fibre linkages formed are necessary and will form part of further work.

Table 1
$\lambda_{max}$ (nm) for the dyes in different solvents

| Dye no. | $C_6H_5CH_3$ | $CHCl_3$ | DMF | $CH_3OH$ |
|---|---|---|---|---|
| **2a** | 416 | 422 | 434 | 440 |
| **2b** | 416 | 422 | 434 | 440 |

Table 2
Colour data of dyes **2a** and **2b** on wool and PA

| Dye no. | Material | *L** | *a** | *b** | *C ** | *h* |
|---|---|---|---|---|---|---|
| **2a** | Wool | 77.2 | −9.9 | 57.3 | 58.2 | 99.8 |
| **2a** | PA | 94.8 | −23.3 | 67.1 | 71.0 | 109.2 |
| **2b** | Wool | 83.6 | −10.2 | 59.3 | 60.1 | 99.9 |
| **2b** | PA | 97.3 | −27.8 | 84.0 | 88.5 | 108.4 |

Table 3
Colourimetric data for wool and PA materials dyed with dyes **(2)**

| Dye no. | Material | $\lambda_{max}^{abs}$ (nm) | Reflectance $R$ (%) at $\lambda_{max}^{abs}$ | $K/S$ at $\lambda_{max}^{abs}$ | Strength of colour (%) |
|---|---|---|---|---|---|
| **2a** | Wool | 420 | 14.8 | > 2.4 | 595.5 |
| **2a** | PA | 420 | 25.6 | 1.1 | 261.6 |
| **2b** | Wool | 420 | 14.1 | 2.6 | 634.0 |
| **2b** | PA | 420 | 16.1 | 2.1 | 529.5 |

### *2.4. Copolymerization with MMA*

PolyMMA is a widely used polymer that enjoys many applications and thus was of interest to the context of securing bright colours with intense fluorescence. The copolymerization of MMA was performed in bulk at 70° C in the presence of 0.5% ABIN and three different concentrations of dyes **2a** and **2b**, namely 0.025, 0.05 and 0.1%. After 8 h, transparent polymers coloured in an intense yellow-greenish fluorescence were obtained, even at the lowest dye concentration used. The polymers retained the colouration even after five-fold precipitation, indicating that the dyes were chemically bonded to the polymer. The absorption spectra of the precipitated polymers show the same $\lambda_{max}$ as the parent dyes, an indication that the basic chromophore did not change either during the polymerization or as a result of its incorporation in the polymer chain. We established that 80% of the initial amount of **2a** and 56% of **2b** in the monomeric mixture were incorporated in the polymer. The participation of the dyes in copolymerization did not affect the yield of the polymers. The viscosimetric data [$\eta$] for the coloured polymers were measured and compared to those of pure PMMA obtained under the same conditions. The data showed a slight, but not significant decrease of molecular mass ([$\eta$] for pure PMMA = $1.55 \times 10^4$ g/cm$^3$, polymer with dye **2a** = 1.35 and with dye **2b** = 1.4). More detailed investigations in the field of polymer chemistry, i.e. the kinetics of the process and the influence of the dyes on some other properties (polydispersity, thermo- and photostability) of the polymers, will be the subject of further study.

## 3. Experimental

### *3.1. Materials, equipment and analysis*

Materials and solvents were of p.a. or analytical grade (Fluka), acenaphthene (98%, Merck). 4-Bromo-naphthalic anhydride **(3)** was synthesized as described elsewhere [8]. tlc analyses were performed on silica gel plates (Fluka, $F_{60}$ 254, 20 ×10 cm, 0.1 mm thickness, ready-to-use), product of Merck (Germany), using *n*-heptane–acetone (3:1, v/v) as eluent and a Camag (Switzerland) TLC system, comprising a Linomat IV device for sample application, a Scanner II and an SP429 Integrator. Electronic spectra were recorded in DMF on a Hewlett Packard 8452A UV/Vis spectrophotometer. $^1$HNMR spectra in $CDCl_3$ were recorded on JEOL-JNM PS100 spectrometer. Colour measurement was performed using a "Texflash ACS" spectrophotometer under illuminant $D_{65}$. The viscometric values [$\eta$] of the polymers were determined by measuring the specific viscosity of solutions (0.5% by mass) in toluene at 25°C in an Ubbelohde viscometer AV-1.

### *3.2. Synthesis of the compounds*

#### *3.2.1. Synthesis of compound* **4a**

4-Bromo-1,8-naphthalic anhydride (0.01 mol) was dissolved in 50 cm$^3$ DOX at room temperature and then methylamine (0.01 mol, as 40% aq. solution) was added. The solution was refluxed and the course of the reaction was monitored using tlc on silica gel with *n*-heptane–acetone (3:1) as eluent. After 2 h, when the reaction was completed, the solution was poured into water and the resulting product **4a** was filtered off, washed with water and dried. Yield 90%; mp 176–177°C; $R_f$ 0.60. $^1$HNMR [$CDCl_3$] $\delta$: 3.5 (s, 3H, $CH_3$) 7.5–8.2 (m, 5H, Ar).

Compound **4b** was obtained following the same procedure and was obtained in 88% yield. mp 160–161°C; $R_f$ 0.52; $^1$HNMR [$CDCl_3$] $\delta$: 1.2–1.4 (t, 3H, $CH_3$) 3.9–4.2 (q, 2H, $\underline{CH_2}CH_3$) 7.5–8.2 (m, 5H, Ar).

#### *3.2.2. Synthesis of compound* **2a**

0.01 mol of 4-bromo-*N*-methylnaphthalimide (**4a**) was dissolved in 60 cm$^3$ of DOX and then allylamine (0.012 mol) and triethylamine (0.01 mol) were added. The solution was refluxed and the reaction followed using tlc as described above. After 4 h, the reaction was complete and the product **2a** was isolated by pouring into water. After filtration, the ensuing crystals were washed with water and dried under vacuum at 40°C. Yield 96%; mp 109–110°C; $R_f$ 0.52 (*n*-heptane–acetone = 1:1) [7].

Following the same procedure, compound **2b** was obtained in 95% yield and mp 149–152°C without purification, $R_f = 0.48$ (*n*-heptane–acetone = 1:1) [7].

### *3.3. Polymerization*

In an ampoule flushed with pure dry nitrogen, 10 g of MMA, 0.05 g of ABIN and 0.01 g of the corresponding dye (**2a** or **2b**) were mixed. After sealing, the ampoules were heated at 70°C. After 8 h, solid, transparent yellow-greenish coloured polymers with intense fluorescence were obtained which were dissolved in chloroform and reprecipitated from ethanol, until colourless filtrates were obtained. The polymers were then dried under vacuum at 30C to constant mass and analyzed.

## 4. Conclusions

On the basis of the results obtained in this present study, more suitable conditions for the synthesis of dyes with formula **(2)** were determined. The dyes were suitable for application to wool and nylon fibres as well as incorporation in PMMA.

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## References

[1] Peters AT, Bide MJ. Dyes and Pigments 1985;6:349.
[2] Quan X, Zhu K, Chen K. Dyes and Pigments 1989;11:13.
[3] Wolarz E, Mortson H, Bauman D. Displays 1992;13:171.
[4] Konstantinova T, Meallier P, Grabchev I. Dyes and Pigments 1993;22:191.
[5] Grabchev I, Meallier P, Konstantinova T, Popova M. Dyes and Pigments 1995;28:41.
[6] Konstantinova T, Grabchev I. Angew Makromol Chemie 1996;196:107.
[7] Grabchev I, Konstantinova T, Guittoneau S, Meallier P. Dyes and Pigments 1997;35(4):361.
[8] Grysham P, Kadhim A, Peters AT. Journal of Heterocyclic Chemistry 1974;11:33.