

SYNTHESIS AND APPLICATION OF BIS-NAPHTHALIMIDE DYE CONTAINING UV ABSORBER AND POLYMERIZABLE GROUPS

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ABSTRACT

New bis-naphthalimide dye (BND), containing an UV absorber and two unsaturated allylic groups in its molecule has been synthesized. It was evaluated for applicability on polyamide fibres and sample with intensive yellow-orange colour and yellow fluorescence has been obtained. The degree of exhaustion and fixation were assessed. The colour characteristics and optical properties from the CIE Lab colour space have been examined of the textile sample. The photostability of the dye in solution, as well as of dyed textile material was determined. The possibility for copolymerization of the dye with methyl methacrylate has been investigated and a polymethyl methacrylate with intensive colour and fluorescence has been obtained. It was spectrophotometrically estimated that 82 % of the initial amount of the compound was chemically bonded in the copolymer. Results obtained lead to the conclusion that the synthesized dye have good photostability and can be applied both as fluorescent dye for dyeing of polyamide fibres and as colour fluorescent monomer for obtaining of coloured polymethyl methacrylate.

Keywords: naphthalimide dye, dyeing of polyamide, copolymerization with methyl methacrylate.

INTRODUCTION

Naphthalimide fluorophores are widely used in different fields: in analytical chemistry [1 - 10], biology and medicine [11 - 20], materials chemistry [21 - 27], textile and polymer industries [18 - 21, 25, 28] because of their excellent photostability, good structural flexibility, beautiful and bright colour and fluorescence, excellent fluorescent characteristics.

The simultaneous coloration and UV light stabilization of textile and polymer materials is a very promising direction in dye chemistry. One way to accomplish this is the introduction of a UV absorber into the dye molecule [29]. It is known that stilbene derivatives are some of the most widely used UV-absorbing compounds. The evidence for this is some manuscripts in which fragments of these derivatives are included in the structure of several optical brighteners, dyes, UV absorbers and antioxidants [30 - 35].

Based on above mentioned and my own experience in simultaneous coloration and UV light stabilization of textile, paper and polymer materials it was of interest to synthesize a bis-naphthalimide dye (BND), containing UV absorber and a polymerizable group in its molecule and examination of its application [33 - 35]. Therefore, this was the aim of the present study.

EXPERIMENTAL

Materials and methods

N-allyl-4-hydrazine-1,8-naphthalimide has been synthesized according to a method described before [27]. 4,4'-dinitrostilbene-2,2'-disulphonic acid was product of Alfa Aesar; methyl methacrylate and dimethylformamide used as solvent were products of Fluka; azo-bis-iso-butyronitrile (98 %) was product of Sigma Aldrich (Merck).

Thin-layer chromatography (TLC) measurements

were performed on silica gel plates (Merck). Electronic spectra were recorded on a DLAB SP-UV1100 spectrophotometer (DLAB Scientific Co., Ltd., China); IR - on a Varian 660 instrument (Varian, USA); $^1\text{H-NMR}$ spectra - on DRX - 400 Bruker equipment and fluorescent spectra – on spectrometer FS-2 (Scinco Co. Ltd, Korea).

The photodegradation of the dye in solution of dimethylformamide with concentration $2 \cdot 10^{-4} \text{ g mL}^{-1}$ was performed in a Suntest equipment (Heraeus, Germany), fitted with an air-cooled Xenon lamp (Hanau, 1.1 kW, 765 W m^{-2} , wavelength $\lambda_{\text{max}} = 290 \text{ nm}$). The kinetic of photodegradation was monitored spectrophotometrically (by the method of standard calibration curve).

The colour characteristics of the dyed polyamide fibers were recorded using ElektroPhysik ColorTest (Germany) with illuminant D65.

Photostability of the dyed polyamide fibers was studied by exposure with a xenon light source on a test camera Q-SUN Xe-1 (Q-Lab, USA) using BDS EN ISO 4892-2.

The copolymerization of the dye with methyl methacrylate was performed using traditional recipe [36].

Synthesis of BND

N-allyl-4-hydrazine-1,8-naphthalimide (1.34 g, 0.005 mol) was dissolved in 25 mL dimethylformamide. To this solution, 1.08 g (0.0025 mol) of 4,4'-dinitrostilbene-2,2'-disulfonic acid was added. The reaction mixture was stirred for 16 h while boiling. The reaction was monitored by TLC (system hexane : acetone = 1 : 1 on silica gel). After cooling to room temperature, the reaction mixture was poured into 50 mL water. The precipitate of BND was filtered off, washed with water

till pH 7 and dried in vacuum at 40°C . The purified with column chromatography (above mentioned system) product was underwent further research.

RESULTS AND DISCUSSION

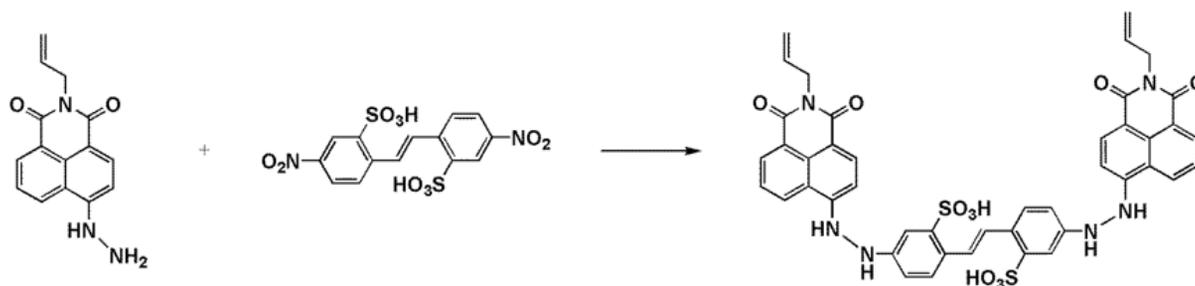
The synthesis of BND was accomplished using the reaction Scheme 1.

The synthesized BND was isolated with 75 % yield. This yield value is due to the partial water solubility that the product possesses due to the presence of two residues of sulphonic acid in the molecule.

The purified with column chromatography BND was characterized by TLC (above-mentioned system) - $R_f = 0.47$; UV-vis spectrum - λ_{max} (dimethylformamide) = 432 nm; fluorescent spectrum - λ_{max} (dimethylformamide) = 526.2 nm; IR (KBr), cm^{-1} : 3602 ($\nu\text{-OH}$); 3435 ($\nu\text{-NH}$); 3085 ($\nu\text{-CH=CH}$); 1687 ($\nu\text{-C=O}$); 1644 (νAr); 1582 ($\delta\text{-NH}$); 1528 ($\nu\text{-CH}$); 1471 ($\delta_{\text{as}}\text{-CH}_2$); 1345 ($\delta\text{-CH=CH-}$); 1205 and 1028 ($\nu\text{-SO}_3$); 894 (δAr) and $^1\text{H NMR}$ (dimethyl sulfoxide, δ/ppm): 8.60 (d, 1H, ArH), 8.58 (d, 1H, ArH), 8.55 (d, 1H, ArH), 8.53 (d, 1H, ArH), 8.52-8.51 (d, 1H, ArH), 8.49 (d, 1H, ArH), 8.43-8.38 (m, 1H, ArH), 8.36 (s, 1H, ArH), 8.34 (s, 1H, ArH), 8.16 (d, 1H, ArH), 8.13 (d, 1H, ArH), 7.98-7.95 (d, 1H, ArH), 7.80-7.76 (m, 1H, ArH), 7.70-7.68 (m, 3H, ArH), 5.98-5.87 (m, 3H, 2 x -CH= , -OH), 5.28-5.23 (m, 7H, 2 x -NCH_2 , -OH , 2 x -NH), 4.76-4.72 (m, 6H, 2 x =CH_2 , 2 x -NH), 3.04 (s, 4H, 2 x -CH=CH-).

Photostability of the BND

The solutions of synthesized BND and the starting compound N-allyl-4-hydrazine-1,8-naphthalimide using as a comparative compound in dimethylformamide



Scheme 1. Synthesis of BND.

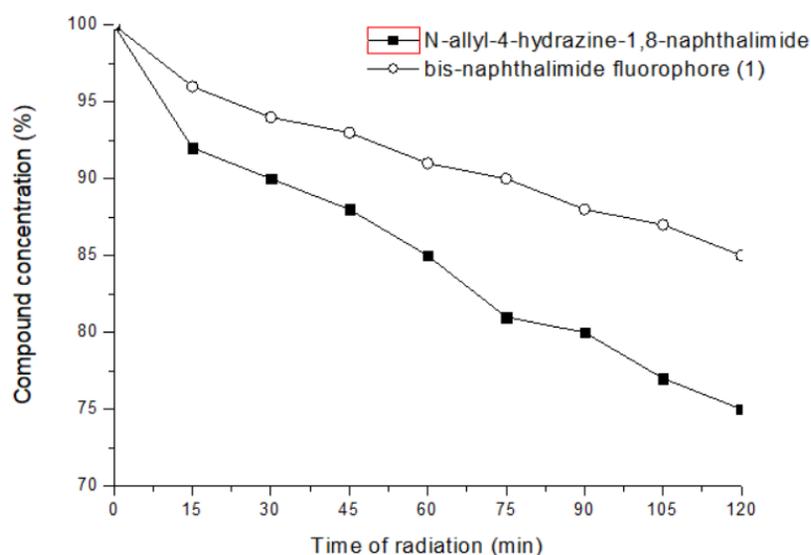


Fig. 1. Concentration of the corresponding compound in dimethylformamide (wt. %) during the radiation under UV light, min.

Table 1. Colour coordinates of dyed polyamide fibres during the radiation.

Time of radiation, h	L*	a*	b*	ΔE	X	Y	Z
0	66.56	-9.61	65.55	73.91	29.49	33.89	6.12
2	63.93	-6.96	56.07	66.72	27.09	30.20	6.65
4	62.71	-2.22	35.85	51.45	26.39	28.86	6.68
6	61.41	-4.51	48.48	61.81	25.58	28.51	7.03
8	60.79	-6.21	51.01	64.32	25.39	27.93	12.13
10	59.81	-6.84	52.45	65.32	25.17	27.26	11.93

were radiated with UV light for 2 h. Using the method of the standard calibration curve, the concentration of the corresponding compound in the solution during the radiation was recorded spectrophotometrically every 15 min. The results obtained are presented graphically in Fig. 1.

As could be seen from the Fig. 1, the concentration of the BND at the end of radiation is 85 % in comparison with N-allyl-4-hydrazine-1,8-naphthalimide, which concentration at the end of radiation is 75 %. The increase in the photostability of the dye by 10 % is a result of the introduction of 4,4'-diaminostilbene-2,2'-disulphonic acidic fragment in its molecule.

Dyeing of polyamide fibres and determination of their photostability

Polyamide fibres were dyed with BND at 1 % depth o.w.f. according to traditional recipe [37]. The fibres with yellow-greenish colour and yellow fluorescence were

obtained. The colour coordinates of dyed polyamide fibres were determined and given in Table 1. The exhaustion (80 %) and fixation ratio (95 %) of BND were calculated after spectrophotometrical determination of concentration of the dye solution before and after dyeing and washing.

Using ElektroPhysik ColorTest (Germany) with illuminant D65 the change in the colour characteristics of radiated coloured fibres were determined. Data is given in Table 1.

From the results in the Table 1, the colour does not change during the radiation (it remains in the yellow-green range), which is an indication for good photostability of the dyed sample. The values of L* were changed in direction of black. This is probably due to cross-linking and microcracks of the test surface as a result of the intense radiation. Further research is needed for better explanation of this.

Copolymerization of BND

The copolymerization with methyl methacrylate with 0.1 wt. % of the BND was performed for 8 h using a standard procedure [34]. A copolymer with yellow-green color and an intense fluorescence was obtained. The copolymer was analysed and it was observed that the quantity of the chemically bonded compounds is 82 %.

CONCLUSIONS

New bis-naphthalimide dye, containing an UV absorber and two polymerizable groups has been synthesized. Polyamide fibres were dyed with the synthesized dye and chemical coloured copolymer with methyl methacrylate were obtained. The photostability of the dye in solution of dimethylformamide and dyed polyamide fibres was investigated. Results obtained lead to the conclusion that the investigated dye is appropriate for simultaneous coloration and stabilization of polyamide fibres and polymethyl methacrylate.

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Authors' contributions

All studies described in the manuscript are prepared by P.M.

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