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# Synthesis and Properties of Some Fluorescent 1,8-Naphthalimide Derivatives and Their Copolymers with Methyl Methacrylate

T. N. Konstantinova, P. M. Miladinova

*Organic Synthesis Department, University of Chemical Technology and Metallurgy, 8 Ohridsky Street, Sofia 1756, Bulgaria*

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**ABSTRACT:** Six new fluorescent derivatives of 1,8-naphthalimide were synthesized. Three were dyes, and three were fluorescent whitening agents (FWAs) containing a tetramethylpiperidine (TMP) stabilizer fragment. The FWAs were obtained under phase-transfer catalysis conditions. Five of the compounds were copolymerized with methyl methacrylate, so copolymers with an intense color and/or fluorescence stable against solvents were obtained. The chemical bonding of the synthesized monomers in the polymers was confirmed spectrophotometrically. The participation of the monomer compounds did not significantly affect the process of copolymerization or the molecular masses of the obtained copolymers. The quantity of chemically bonded naphthalimide monomer in the copolymers was determined to be over 60%. The spectral properties of the compounds and their photostability in solution and in the copolymers were studied. The influence of the compounds on the photostability of the copolymers was determined. The compounds, especially those containing a stabilizer

(TMP) fragment in their molecules, showed a positive stabilizing effect on the photodegradation of poly(methyl methacrylate). Polyamide fabrics with 2-allyl-6-hydrazino-benzo[de]isoquinoline-1,3-dione, 2-allyl-6-(2-aminoethylamino)-benzo[de]isoquinoline-1,3-dione, and 2-chloro-*N'*-(2-methyl)-1,3-dioxo-2,3-dihydro-1*H*-benzo[de]isoquinoline-6-yl) acetohydrazide were dyed, and materials with an intense yellow color and fluorescence were obtained. Cotton fabrics were whitened with 2-(2,2,6,6-tetramethyl-piperidin-4-yl)-6-methoxy-benzo[de]isoquinoline-1,3-dione, 2-(2,2,6,6-tetramethyl-piperidin-4-yl)-6-allyloxybenzo[de]isoquinoline-1,3-dione, and 2-[2-(2,2,6,6-tetramethyl-piperidin-4-yl)-1,3-dioxo-2,3-dihydro-1*H* benzo[de]isoquinoline-6-oxy]ethyl-2-methacrylate, and materials with bright whiteness and intense bluish fluorescence were obtained. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1991–1998, 2009

**Key words:** chromatography; copolymerization; dyes/pigments; fluorescence; stabilization

## INTRODUCTION

Stable coloration of polymers is of great importance for their application. One possibility for achieving this is the use of functional dyes to obtain chemically colored materials. For textiles, a rather successful decision is the synthesis and application of reactive dyes.<sup>1,2</sup> For polymers, it is the application of functional dyes able to take part in polymerization or polycondensation; thus, self-colored materials can be obtained. During the last 25 years, different functional dyes have been synthesized and applied.<sup>3–5</sup> In this direction, we have reported the synthesis and application of some reactive dyes for textiles<sup>6,7</sup> and monomer dyes for

polymers.<sup>8–10</sup> Among them, the fluorescent dyes are of special interest because of their pure color and intense fluorescence. Recently, they have been widely applied in high technology such as solar energy cells, liquid-crystal displays, and lasers.<sup>1,2,11</sup> The fluorescent whitening agents (FWAs) are also of special interest and have been applied not only for whitening of materials but also in high technology.<sup>12</sup>

Having this in mind, we directed our investigations to the synthesis and application of different luminophores, FWAs or dyes,<sup>13–16</sup> some of which are 1,8-naphthalimide derivatives. Along with the coloration, the stabilization of materials is also important. In the last years, different functional stabilizers have been synthesized and applied.<sup>17–19</sup> In previously published articles,<sup>20,21</sup> we reported the synthesis and application of different monomer stabilizers. The possibility of one-step coloration and stabilization of materials was of special interest.<sup>22,23</sup>

On the basis of this, the synthesis of some new functional fluorescent dyes and FWAs [1,8-

Correspondence to: T. N. Konstantinova (konst@uctm.edu).

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naphthalimide derivatives that can be applied as polymerizable and/or active dyes or as intermediates for other products] and their copolymers with methyl methacrylate (MMA) and their influence on the photostability of the copolymers were the objects of this study.

## EXPERIMENTAL

### Materials, analysis, and equipment

4-Br-1,8-naphthalic anhydride was synthesized by a method described before.<sup>16</sup> All solvents and reagents were products of Fluka (Seelze, Germany) (pro analysis or analytical grade). MMA, a product of Agrochim (Bulgaria), was purified<sup>15</sup>; azobisisobutyronitrile (ABIN), used as an initiator, was 99.9% pure. All melting points were uncorrected (a Kofler melting-point microscope). The electronic absorption spectra were recorded in dimethylformamide (DMF;  $2 \times 10^{-4}$  g/mL) on a Hewlett-Packard 8452A spectrophotometer with 2-nm resolution. Fluorescent spectra were recorded on a Varian Eclipse fluorescent spectrophotometer in DMF ( $2 \times 10^{-4}$  g/mL). <sup>1</sup>H-NMR spectra were measured on Bruker equipment operating at 250 MHz in dimethyl sulfoxide (DMSO; chemical shifts are given as  $\delta$  in parts per million). The quantitative thin-layer chromatography (TLC) measurements were performed with ready-to-use plates (20 cm  $\times$  20 cm) precoated with a 0.2-mm layer of silica gel 60F<sub>254</sub> (Merck, Germany) and with Camag (Switzerland) equipment comprising a Linomat IV device for sample application and a Scanner II equipped with an SP 4290 integrator. The chromatograms were developed with the appropriate mobile phases; the spots were monitored under ultraviolet (UV) illumination (wavelength at 245 nm), the retention factor ( $R_f$ ) values were measured, and the spots were scanned. The chemically bound percentage in the polymer compounds (dyes and FWAs) was determined by the method of the standard curve with solutions in DMF with a concentration of  $2 \times 10^{-4}$  g/mL for the compounds and with a concentration of  $1 \times 10^{-2}$  g/mL for the polymers. The photostability of both the compounds and copolymers was studied by the irradiation of their DMF solutions at the aforementioned concentrations in Suntest equipment (Heraeus, Germany) fitted with an air-cooled xenon lamp (1.1 kW, 765 W/m<sup>2</sup>). The process was monitored spectrophotometrically. Photodegradation of the polymers was followed viscosimetrically. Values of the limiting viscosity numbers for the polymers and their molecular weights were determined by the measurement of the specific viscosity of their solutions (0.5 wt % in toluene) at 25°C in an Ubbelohde AV-1 viscometer.

### Synthesis of the compounds

#### Synthesis of 2-allyl-6-hydrazino-benzo[de]isoquinoline-1,3-dione (compound 1)

To a solution of 2.8 g (1 mmol) of 2-allyl-6-bromobenzo[de]isoquinoline-1,3-dione (**a**) in 100 mL of 2-methoxyethanol, 0.65 g of hydrazine (2 mmol) was added, and the mixture was heated at 100°C. Every 15 min, a sample from the solution was taken and analyzed by quantitative TLC with silica gel plates and an *n*-heptane/acetone (3 : 1 v/v) eluent system. After 90 min, when the reaction was completed, the solution was cooled, and the yellow-orange crystals were filtered off with a 96% yield. They were washed with water, dried *in vacuo* at 40°C, and analyzed.

mp: 242–245°C.  $R_f$ : 0.60 (silica gel plates, 3 : 1 v/v *n*-heptane/acetone system). Maximum absorption wavelength ( $\lambda_{\text{max}}^{\text{abs}}$ ): 458 nm (solution in DMF,  $2 \times 10^{-4}$  g/mL). Molar absorptivity ( $\epsilon$ ): 2787 L g mol<sup>-1</sup> cm<sup>-1</sup>. Maximum fluorescence wavelength ( $\lambda_{\text{max}}^{\text{fls}}$ ): 560 nm. <sup>1</sup>H-NMR (DMSO,  $\delta$ , ppm): 7.0–8.6 (m, 5H, ArH), 5.8–6.0 (m, 1H, CH=), 5.0–5.2 (m, 2H, CH<sub>2</sub>=), 4.6–4.8 (m, 3H, CH<sub>2</sub>N, NH), 2.5 (s, 2H, NH<sub>2</sub>).

#### Synthesis of 2-allyl-6-(2-amino-ethylamino)-benzo[de]isoquinoline-1,3-dione (compound 2)

With the same procedure, to a solution of 2.8 g (1 mmol) of **a** in 100 mL of 2-methoxyethanol, 2.8 g (4 mmol) of ethylenediamine was added, and the mixture was heated at 100°C. After 4 h (TLC control with the 2 : 1 v/v *n*-heptane/acetone eluent system), the reaction was completed, the mixture was filtered, and the filtrate was poured into water. The resultant yellow-orange crystals were isolated, purified by recrystallization from chlorobenzene (45% yield), dried, and analyzed.

mp: 121–124°C.  $R_f$ : 0.20 (silica gel plates and 2 : 1 v/v *n*-heptane/acetone system).  $\lambda_{\text{max}}^{\text{abs}}$ : 442 nm (solution in DMF).  $\epsilon$ : 4331 L g mol<sup>-1</sup> cm<sup>-1</sup>.  $\lambda_{\text{max}}^{\text{fls}}$ : 535 nm. <sup>1</sup>H-NMR (DCI<sub>3</sub>,  $\delta$ , ppm): 7.8–8.7 (m, 5H, ArH), 5.9–6.1 (m, 1H, CH=), 5.3–5.5 (d, 2H, CH<sub>2</sub>=), 5.2–5.3 (d, 2H, CH<sub>2</sub>N), 4.7–4.9 (d, 5H, 2x CH<sub>2</sub> + NH), 1.8 (s, 2H, NH<sub>2</sub>).

#### Synthesis of 2-chloro-*N'*-(2-methyl)-1,3-dioxo-2,3-dihydro-1*H*-benzo[de]isoquinoline-6-yl)-acetohydrazide (compound 3)

Compound **1** (2.7 g, 1 mmol) was dissolved in 50 mL of acetic acid, and to this solution at 50°C, 2 mL of ClCH<sub>2</sub>COCl was added dropwise. The mixture was stirred at this temperature, and after 2 h (TLC control), the product was isolated by the pouring of the solution into water, filtering, and drying at 40°C *in vacuo*.

Yield: 80%. mp: 228–230°C.  $R_f$ : 0.40 (silica gel plates and 2/1 v/v *n*-heptane/acetone eluent system).  $\lambda_{\text{max}}^{\text{abs}}$ : 404 nm (DMF solution,  $2 \times 10^{-4}$  g/mL).  $\epsilon$ : 2067 L g mol<sup>-1</sup> cm<sup>-1</sup>.  $\lambda_{\text{max}}^{\text{fl}}$ : 507 nm. <sup>1</sup>H-NMR (DMSO,  $\delta$ , ppm): 9.6 (s, 1H, NH), 7.0–8.6 (m, 5H, ArH), 5.8–6.0 (m, 1H, CH=), 5.0–5.2 (m, 2H, CH<sub>2</sub>), 4.6–4.7 (m, 2H, CH<sub>2</sub>N), 4.2–4.4 (d, 2H, CH<sub>2</sub>CO), 2.0 (s, 1H, NH).

Synthesis of 2-(2,2,6,6-tetramethyl-piperidin-4-yl)-6-methoxy-benzo[de]isoquinoline-1,3-dione (compound 4)

To a solution of 7.5 g of 2-(2,2,6,6-tetramethyl-piperidin-4-yl)-6-bromobenzo[de]isoquinoline-1,3-dione (**b**) in 80 mL of 1,2-dichloromethane, a mixture of 0.8 mL of CH<sub>3</sub>OH, 0.36 g of tetrabutylammonium bromide (TBAB), and 2 mL of 50% aqueous sodium hydroxide was added. The mixture was stirred at 25°C and after 4 h was diluted with water. The product (colorless crystals) was isolated according to the described procedure<sup>24</sup> with an almost quantitative yield.

mp: 118–120°C.  $R_f$ : 0.30 (silica gel plates and 2/1 v/v *n*-heptane/acetone eluent system). Absorption wavelength ( $\lambda^{\text{abs}}$ ): 342 (356) nm (solution in DMF,  $2 \times 10^{-4}$  g/mL).  $\epsilon$ : 4209 L g mol<sup>-1</sup> cm<sup>-1</sup>. Fluorescence wavelength ( $\lambda^{\text{fl}}$ ): 413 nm. <sup>1</sup>H-NMR (DMSO,  $\delta$ , ppm): 7.0–8.7 (m, 5H, ArH), 5.1–5.2 (m, 1H, CH piperidine), 3.7 (s, 3H, CH<sub>3</sub>O), 3.1 (s, 1H, NH piperidine), 2.0–2.1 (m, 2H, CH<sub>2</sub> piperidine), 1.4–1.3 (m, 2H, CH<sub>2</sub> piperidine), 1.2 (s, 6H, 2xCH<sub>3</sub> piperidine), 1.1 (s, 6H, 2xCH<sub>3</sub> piperidine).

Synthesis of 2-(2,2,6,6-tetramethyl-piperidin-4-yl)-6-allyloxybenzo[de]isoquinoline-1,3-dione (compound 5)

Compound 5 was obtained with a similar procedure. To a solution of 7.5 g of **b** in 80 mL of 1,2-dichloromethane, a mixture of allylic alcohol (1.2 g), TBAB (0.36 g), and 2 mL of 50% aqueous sodium hydroxide was added. The mixture was stirred at 25°C, and after 10 h, the conversion rate of 70% (TLC analysis) was determined. The colorless crystals were isolated as mentioned previously, purified by preparative thin-layer chromatography (PTLC) on a silica gel plate and with a 2/1 v/v *n*-heptane/acetone eluent system, and analyzed.

mp: 129–132°C.  $R_f$ : 0.40 (silica gel plates and 2/1 v/v *n*-heptane/acetone eluent system).  $\lambda^{\text{abs}}$ : 342 (356) nm (solution in DMF,  $2 \times 10^{-4}$  g/mL).  $\epsilon$ : 4448 L g mol<sup>-1</sup> cm<sup>-1</sup>.  $\lambda^{\text{fl}}$ : 410 nm. <sup>1</sup>H-NMR (DMSO,  $\delta$ , ppm): 7.1–8.6 (m, 5H, ArH), 6.1–6.0 (m, 1H, CH=), 5.4–5.3 (m, 2H, CH<sub>2</sub>=), 5.1–5.0 (m, 1H, CH piperidine), 4.7–4.6 (m, 2H, CH<sub>2</sub>O), 2.8 (s, 1H, NH piperidine), 2.4–2.3 (m, 2H, CH<sub>2</sub> piperidine), 1.5–1.4 (m,

2H, CH<sub>2</sub> piperidine), 1.25 (s, 6H, 2xCH<sub>3</sub> piperidine), 1.15 (s, 6H, 2xCH<sub>3</sub> piperidine).

Synthesis of 2-[2-(2,2,6,6-tetramethyl-piperidin-4-yl)-1,3-dioxo-2,3-dihydro-1H benzo[de]isoquinoline-6-oxy]ethyl-2-methacrylate (compound 6)

Compound 6 was obtained according to a similar procedure. A mixture of 2-hydroxyethyl ester of methacrylic acid (HEMA; 2.6 g), TBAB (0.36 g), and 2 mL of 50% aqueous sodium hydroxide was added to a solution of 7.5 g of **b** in 80 mL of 1,2-dichloromethane. The resulting mixture was stirred at 50°C, and after 8 h (TLC analysis), 40% conversion was determined. The colorless crystals were isolated, purified by PTLC on silica gel plates and with a 2/1 v/v *n*-heptane/acetone eluent system, and analyzed.

mp: 133–135°C.  $R_f$ : 0.20 (silica gel plates and 2/1 v/v *n*-heptane/acetone eluent system).  $\lambda^{\text{abs}}$ : 344 (356) nm (solution in DMF,  $2 \times 10^{-4}$  g/mL).  $\epsilon$ : 4176 L g mol<sup>-1</sup> cm<sup>-1</sup>.  $\lambda^{\text{fl}}$ : 407 nm. <sup>1</sup>H-NMR (DMSO,  $\delta$ , ppm): 7.1–8.7 (m, 5H, ArH), 6.2–6.1 (m, 2H, CH<sub>2</sub>=), 5.5–5.6 (m, 1H, CH piperidine), 4.5–4.4 (m, 2H, CH<sub>2</sub>O), 4.3–4.2 (m, 2H, CH<sub>2</sub>O), 2.1 (s, 1H, NH piperidine), 1.9 (s, 3H, CH<sub>3</sub>), 1.5–1.4 (m, 2H, CH<sub>2</sub> piperidine), 1.4–1.3 (m, 2H, CH<sub>2</sub> piperidine), 1.25 (s, 6H, 2xCH<sub>3</sub> piperidine), 1.15 (s, 6H, 2xCH<sub>3</sub> piperidine).

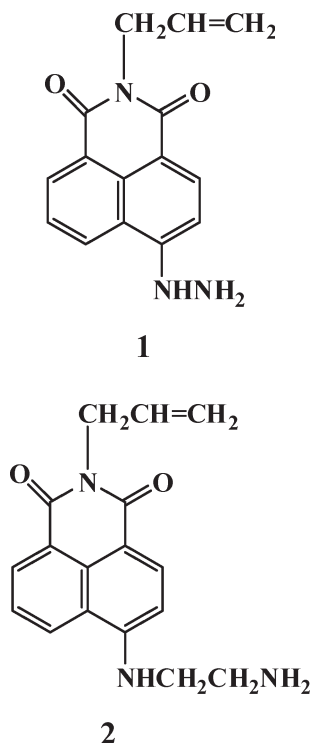
## Polymerization with MMA

MMA (10 g), corresponding compounds 1–6 (0.1 wt % versus MMA), and 0.5 wt % ABIN were mixed in an ampule flushed with dry and pure nitrogen. The ampules were sealed and heated at 70°C. After 8 h, the transparent polymers, colored with an intense yellow fluorescence for compounds 1–3 and colorless with bluish fluorescence for compounds 4–6, were obtained. The polymers were dissolved in CHCl<sub>3</sub> and precipitated with CH<sub>3</sub>OH, which is a good solvent for the compounds. This operation for copolymers with compounds 1–3, 5, and 6 was repeated four times until colorlessness without fluorescence under UV-light filtrates was obtained. The polymer with compound 4 was precipitated once. The polymers thus purified were dried *in vacuo* and analyzed.

## RESULTS AND DISCUSSION

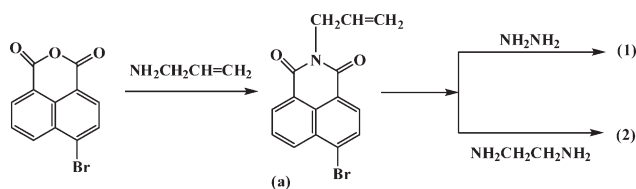
### Synthesis of the compounds

The first two compounds of this study can be presented with formulas 1 and 2:



Their synthesis was performed according to Scheme 1. According to the scheme, first 1 mmol of 4-Br-naphthalic anhydride (6-bromobenzo[de]isochromene-1,3-dione) was reacted with 1 mmol of allylamine (a procedure previously described by us),<sup>16,23</sup> and thus product **a** was obtained. Furthermore, by the reaction of 1 mmol of **a** with 2 mmol of hydrazine in boiling 2-methoxyethanol, compound **1** was obtained. The course of the reaction was monitored by quantitative TLC (see the Experimental section), and it was completed after 90 min. The product (yellow-orange crystals) was isolated by filtration. Compound **2** was obtained with the same procedure when 1 mmol of product **a** was reacted with 4 mmol of ethylenediamine. After 4 h under the same conditions (TLC control), product **2** was isolated and purified by recrystallization.

Products **1** and **2** were analyzed with melting-point measurements, TLC, and ultraviolet-visible (UV-vis), fluorescent, and <sup>1</sup>H-NMR spectra. The characteristic data are presented in the Experimental section. The compounds have an intense yellow-orange fluorescence in solution.



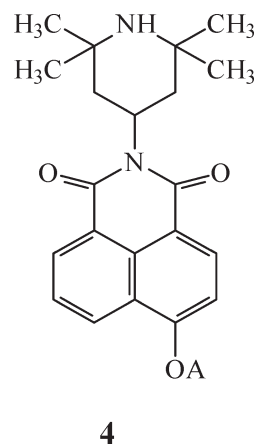
Scheme 1

In our previous articles, we reported the synthesis of the FWA *N*-(2-allyl-1,3-dioxo-2,3-dihydro-1*H*-benzo[de]isoquinolin-6-yl)-2-chloroacetamide.<sup>25</sup> For practice, we thought that it would be interesting to synthesize some similar compounds that were dyes instead. Thus, the next step of our study was the synthesis of compound **3**, which is presented with formula 3:



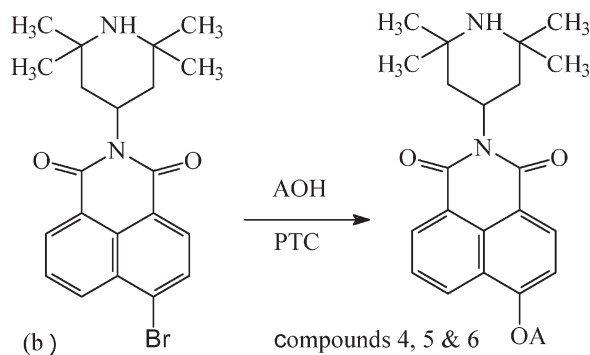
The synthesis of the compound was achieved by a reaction of 1 mmol of dye **1** with 2 mmol of chloroacetyl chloride (ClCH<sub>2</sub>COCl) at 50°C according to a procedure described by us previously.<sup>25</sup> After 2 h, when the reaction was completed (TLC control), yellow crystals with an 80% yield were isolated, characterized, and identified by melting-point measurements, TLC, and UV-vis, fluorescence, and <sup>1</sup>H-NMR spectra (see the Experimental section). As one can see from these data, the compound retained the color after acylation and could be applied as a reactive dye.<sup>2</sup>

As mentioned previously, the method of one-step coloration and stabilization of polymers is important. It was interesting to obtain some compounds that absorbed in the near-UV region, emitted in the visible region, and contained a stabilizer fragment suitable for one-step whitening and stabilization of polymers. The next step of our study was the synthesis of the compounds presented with general formula 4:



The meanings of A in the formula are as follows: —CH<sub>3</sub> for compound **4**, —CH<sub>2</sub>CH=CH<sub>2</sub> for





Scheme 2

compound 5, and  $-\text{CH}_2\text{CH}_2\text{OCOC}(\text{CH}_3)=\text{CH}_2$  for compound 6.

The synthesis of the compounds is presented in Scheme 2. According to the scheme, **b**, obtained by us previously,<sup>26,27</sup> was reacted with  $\text{CH}_3\text{OH}$ , allylic alcohol, or HEMA under phase-transfer catalysis conditions.

Product **4** was obtained by the reaction of **b** with  $\text{CH}_3\text{OH}$  at  $25^\circ\text{C}$  in a 1,2-dichloromethane/50% aqueous sodium hydroxide two-phase system with the use of 5 mol % TBAB as a catalyst.<sup>24</sup> At the end of the 4th hour, starting compound **b** was entirely converted into the target product (**4**). It was isolated with an almost quantitative yield and analyzed (data are presented in the Experimental section).

The synthesis of compounds **5** and **6** was performed with a similar procedure, but the reaction of product **b** with allylic alcohol was completed after 10 h at  $25^\circ\text{C}$  with 70% conversion (TLC data), whereas that with HEMA was completed after 8 h at  $50^\circ\text{C}$  (40% conversion). The isolated colorless crystals were purified by PTLC, and the pure products were characterized and identified by melting-point measurements,  $R_f$  measurements, and UV-vis, fluorescence, and  $^1\text{H}$ -NMR spectra. They have an intense bluish fluorescence in solution. The data are presented in the Experimental section.

### Spectrophotometric measurements

The absorption UV-vis spectra of the compounds were recorded in a range of solvents, and the data are presented in Table I.

On the basis of these data, the following conclusions could be made. For compounds **1** and **2**, when the polarity of the solvents increased from toluene to DMF, a bathochromic shift of the maximum wavelength ( $\lambda_{\text{max}}$ ) was observed, which was an indication for a  $\pi \rightarrow \pi^*$  electron charge-transfer transition in their molecules.<sup>28</sup> For compounds **3–6**, neither a bathochromic shift nor a hypsochromic shift in  $\lambda_{\text{max}}$  was registered, and we concluded that there was an  $n \rightarrow \pi^*$  charge-transfer transition. After acylation of

TABLE I  
Spectrophotometric Data for Compounds 1–6 in Different Solvents

Compound	$\lambda_{\text{max}}^{\text{abs}}$ (nm)			
	$\text{C}_6\text{H}_5\text{CH}_3$	$\text{CHCl}_3$	$\text{C}_2\text{H}_5\text{OH}$	DMF
1	430	436	446	458
2	410	414	440	442
3	404	406	408	404
4	342 (354)	344 (356)	342 (356)	342 (356)
5	342 (354)	344 (356)	342 (354)	342 (356)
6	342 (354)	344 (356)	344 (356)	344 (356)

the  $-\text{NHNH}_2$  group in compound **1** to  $-\text{NHNHCOCH}_2\text{Cl}$  (compound **3**), a hypsochromic shift in the absorption was registered, but  $\lambda_{\text{max}}$  remained in the visible region of the spectrum, and the compound was colored. This represents the possibility of its application as a fluorescent dye (including as an active one for textiles) or as a semiproduct for other colored derivatives such as dendrimers and polymerizable dyes.

### Photostability of the compounds

To study the photostability of the synthesized compounds, they were subjected to irradiation under UV light in a DMF solution. Just as during the irradiation, no change in the absorption maxima ( $\lambda_{\text{max}}$ ) was registered; the process was followed spectrophotometrically with the method of the standard calibration curve. The dependence of the compound's concentration on the time of irradiation is presented in Figure 1; the initial concentration of the compounds was accepted to be 100%.

One can see from Figure 1 that compounds **4–6**, which contained a tetramethylpiperidine (TMP)

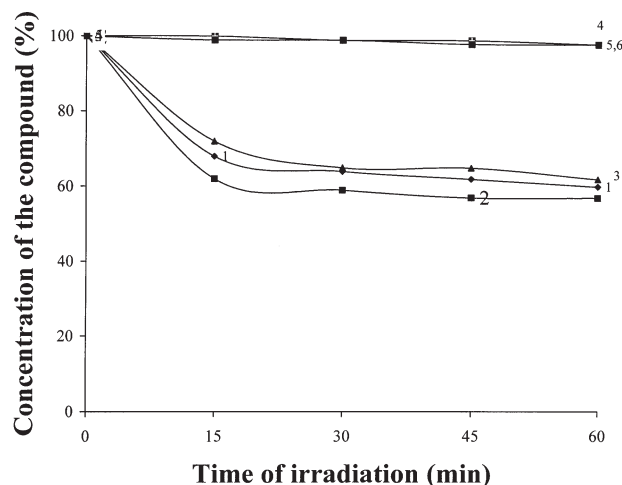


Figure 1 Dependence of the concentration of compounds 1–6 (%) on the time of irradiation under UV light (min). The numbers of the curves correspond to the numbers of the compounds.

fragment in their molecules, exhibited the highest photostability ( $\approx 98\%$  until the end of the 1st hour). Compounds 1–3 had good photostability as well.<sup>27</sup>

### Color assessment

It was interesting to study the ability of the synthesized compounds for dyeing or whitening textile materials. With compounds 1–3, polyamide fabrics were dyed at 1% depth (owf).<sup>2</sup> Materials with an intense yellow-orange color and a bright yellow fluorescence were obtained.

With the same standard procedure, 100% cotton fabrics with compounds 4–6 at 1% depth (owf) were treated. Materials with a bright whiteness and an intense bluish fluorescence were obtained.

These results confirmed the possibility of the application of compounds 1–3 as dyes and compounds 4–6 as FWAs for the textiles.

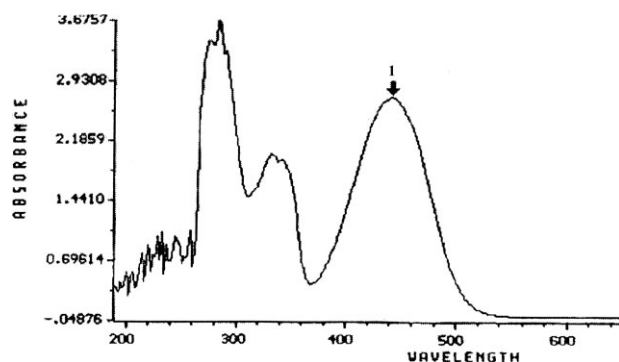
As compounds 1–3, 5, and 6 each possessed an unsaturated group in their molecules, it was important to study the following:

- The ability of the compounds to copolymerize with MMA so that inherently colored or whitened polymers are obtained.
- The photostability of the compounds in the polymers.
- The influence of the compounds on the photostability of the copolymers themselves.

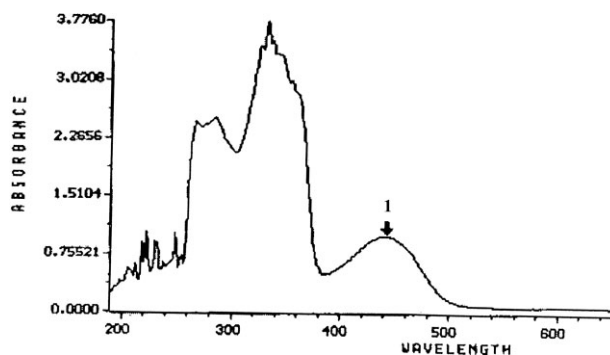
The obtained results will enable us to recommend the most suitable compounds for coloration or whitening and stabilization of polymers

### Copolymerization with MMA

Poly(methyl methacrylate) (PMMA) is a widely used polymer that enjoys many applications, and it was interesting to study the copolymerization of MMA with the synthesized compounds. Experiments for the copolymerization of MMA with compounds 1–3,



**Figure 2** Absorption spectrum of compound 2 (solution in DMF). 1 indicates  $\lambda_{\max} = 442$  nm and  $A = 2.7279$ .

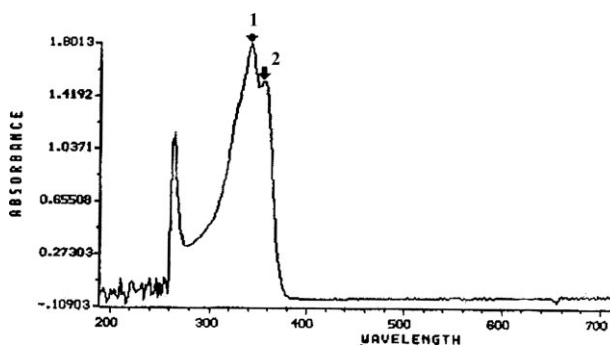


**Figure 3** Absorption spectrum of the copolymer of MMA with compound 2 (in DMF). 1 indicates  $\lambda_{\max} = 442$  nm and  $A = 0.9886$ .

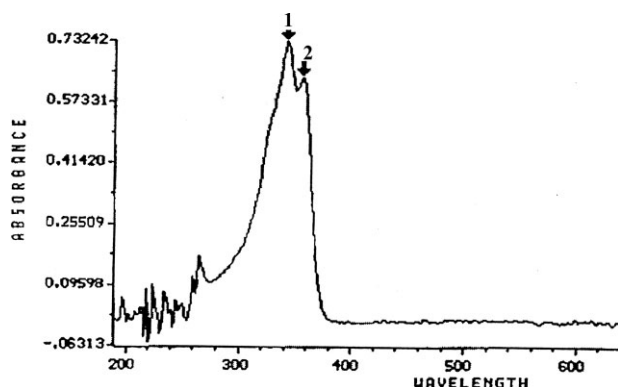
5, and 6 were carried out in bulk with 0.1 wt % of the corresponding compound and 0.5 wt % ABIN according to a procedure described elsewhere.<sup>23</sup> With compounds 1–3, solid and transparent yellow-orange polymers with an intense yellow fluorescence were obtained. Colorless polymers with an intense bluish fluorescence with compounds 5 and 6 were obtained. All polymers were purified by reprecipitation (TLC control; see the Experimental section). After fourfold precipitation, the polymers retained their color and/or fluorescence, and this indicated that the compounds were chemically bonded to the polymer chain. UV-vis absorption spectra (DMF solutions) of the precipitated polymers were compared to those of the pure monomer compounds. In these spectra, no change in  $\lambda_{\max}$  was registered (Figs. 2–5).

This was an indication that there were no changes in the basic chromophore either during the polymerization or as a result of its bonding to the polymer chain. Furthermore, the percentage of chemically bonded compounds was calculated by the method of the standard calibration curve. The obtained data are presented in Table II.

One can see from these data that the quantity of the chemically bonded compounds in the copolymer was between 55 and 66%. Bearing in mind that this



**Figure 4** Absorption spectrum of compound 6 (solution in DMF). 1 indicates  $\lambda_{\max} = 342$  nm and  $A_1 = 1.0812$ ; 2 indicates  $\lambda_{\max} = 354$  nm and  $A_2 = 1.5251$ .



**Figure 5** Absorption spectrum of the copolymer of MMA with compound 6 (solution in DMF). 1 indicates  $\lambda_{\text{max}} = 342$  nm and  $A_1 = 0.7324$ ; 2 indicates  $\lambda_{\text{max}} = 356$  nm and  $A_2 = 0.6385$ .

refers to the reprecipitated polymers, from which during the precipitation some of the lower molecular fractions bound to the polymer dye or FWA were removed, we can consider this content satisfactory.

The course of the polymerization was monitored (time–yield dependence) and showed that the participation of the monomer compounds in the polymerization did not affect the polymerization rate (the yield for pure PMMA was  $\approx 85\%$ , and for the copolymers, it was between 80 and 85%).

#### Photostability of the compounds in the copolymer

To study the photostability of the compounds in the copolymers, solutions of the reprecipitated polymers were irradiated with UV light under the same conditions used for the solutions of the pure compounds. The process was monitored spectrophotometrically because, during the irradiation, no changes in the absorption maxima of the chromophores were observed. The data are presented in Table III.

One can see from these data that the photostability of the compounds increased by 15–25% when they were incorporated into the polymer chain.

#### Influence of the compounds on the photostability of the copolymers

To study the influence of the compounds on the photostability of the copolymers (purified by precipi-

**TABLE II**  
Data for the Chemically Bonded Fractions in the PMMA Compounds

Compound	1	2	3	5	6
Chemically bounded fraction (%)	60	55	66	65	56

Data for the reprecipitated polymers are given; the concentration of each compound in the initial monomer mixture was 100%.

**TABLE III**  
Spectrophotometric Data (%) for Compounds 1–3, 5, and 6 in the Copolymer After Irradiation Under UV Light (h)

Compound	Pure compound (1 h) <sup>a</sup>	In the copolymer (1 h) <sup>b</sup>
1	60	74
2	57	79
3	62	87
5	98	98
6	98	98

The concentration of each compound before irradiation was 100%.

<sup>a</sup> Solution in DMF ( $2 \times 10^{-4}$  g/mL).

<sup>b</sup> Solution in DMF ( $1 \times 10^{-2}$  g/mL).

tation), the latter were irradiated for 8 h and analyzed. Under the same conditions, we studied PMMA whitened with compound 4 in the mass (0.1% concentration), and this enabled us to see the influence of the covalent bonding of the compound on the photostability of the polymer. The process of photodegradation was followed viscosimetrically. Values of the limiting viscosity numbers of the copolymers before and after irradiation were calculated. The data are presented in Table IV.

One can see from these data that all of the compounds had a stabilizing effect on the photodegradation of PMMA. Better stability was observed for the copolymers with compounds 4–6 containing a TMP fragment in the molecule. In this connection, it is interesting to note the differences between compound 4, which was in the mass of the polymer, and compounds 5 and 6, which were chemically bonded (copolymer). Obviously, the covalent bonding of the compounds is of significant importance.

#### CONCLUSIONS

As a result of this study, 6 compounds, 3 of them dyes and 3 FWAs containing a TMP stabilizer fragment, were obtained. Five of them were able to copolymerize with MMA, so self-colored or whitened

**TABLE IV**  
Data for the  $[\eta]$  Values  $\times 10^5$  (g·mL<sup>-3</sup>) of the Polymers of MMA with Compounds 1–6 Before and After 8 h Irradiation

Polymer	$[\eta] \cdot 10^5$ (g·mL <sup>-3</sup> ) before irradiation	$[\eta] \cdot 10^5$ (g·mL <sup>-3</sup> ) after irradiation	S*
PMMA	1.10	0.61	1.14
Co-MMA + 1	0.81	0.74	0.11
Co-MMA + 2	0.95	0.80	0.18
Co-MMA + 3	1.01	0.80	0.28
PMMA + 4	1.10	1.02	0.10
"in mass"			
Co-MMA + 5	1.05	1.03	0.05
Co-MMA + 6	0.82	0.80	0.01

\* Calculated.<sup>29</sup>



polymers with an intense fluorescence were obtained. The compounds were able to dye or whiten textiles with good color characteristics and fluorescence. All the compounds had a good stabilizing effect on the photodegradation of PMMA, especially those that had a TMP fragment in their molecules and were covalently bound to the polymer. They are suitable for one-step whitening and stabilization of PMMA.

## References

1. Zollinger, H. *Color Chemistry*; VHC: Zurich, 1989.
2. Warning, D.; Hallas, E. *The Chemistry and Application of Dyes*; Plenum: London, 1990.
3. Asquit, R.; Blair, H. *J Soc Dyers Colour* 1977, 93, 114.
4. Mareshal, E. *Prog Org Coat* 1982, 10, 251.
5. Guthrie, J. T. *Rev Prog Color* 1990, 20, 120.
6. Konstantinova, T.; Petrova, P. *Dyes Pigm* 2002, 52, 115.
7. Konstantinova, T.; Petrova, P. *J Univ Chem Technol (Sofia)* 2004, 39, 151.
8. Konstantinova, T.; Draganov, A.; Konstantinov, C. *Angew Makromol Chem* 1975, 43, 29.
9. Konstantinov, C.; Konstantinova, T.; Draganov, A.; Kabaivanov, V. *J Appl Polym Sci* 1972, 16, 725.
10. Konstantinova, T.; Grabchev, I. *J Appl Polym Sci* 1996, 62, 447.
11. Gregory, P. *High-Technology Application of Organic Colorants*; Plenum: London, 1992.
12. *Florescent Whitening Agents*; Anliker, R.; Muler, G., Eds.; Thieme: Stuttgart, 1975.
13. Konstantinova, T.; Grabchev, I. *Polym Int* 1997, 43, 39.
14. Konstantinova, T.; Konstantinov, H.; Betcheva, R. *Dyes Pigm* 1999, 43, 197.
15. Konstantinova, T.; Lazarova, R. *Dyes Pigm* 2006, 74, 208.
16. Konstantinova, T.; Meallier, P.; Grabchev, I. *Dyes Pigm* 1993, 22, 191.
17. Shuhaibar, K.; Rasoul, F.; Pasch, H.; Mobasher, A. *Angew Makromol Chem* 1991, 193, 147.
18. Malik, J.; Ligner, G.; Avar, L. *J Polym Degrad Stab* 1998, 60, 205.
19. Bojinov, V. *Photochem Photobiol Sci* 2002, 1, 340.
20. Konstantinova, T.; Bogdanova, A.; Stanimirov, S.; Konstantinov, H. *J Polym Degrad Stab* 1994, 43, 187.
21. Bojinov, V.; Konstantinova, T.; Konstantinov, H. *Angew Makromol Chem* 1998, 260, 17.
22. Bojinov, V.; Konstantinova, T. *J Polym Degrad Stab* 2000, 68, 295.
23. Konstantinova, T.; Lazarova, R.; Bojinov, V. *J Polym Degrad Stab* 2003, 82, 115.
24. Bojinov, V.; Grabchev, I. *Dyes Pigm* 2001, 51, 57.
25. Grabchev, I.; Konstantinova, T. *Dyes Pigm* 1997, 33, 197.
26. Bojinov, V.; Konstantinova, T. *Dyes Pigm* 2002, 54, 239.
27. Konstantinova, T.; Lazarova, R.; Venkova, A.; Vassileva, V. *Polym Degrad Stab* 2004, 84, 405.
28. Braun, A.; Maurette, M.; Oliveros, E. *Technologie Photochimique*; Press Polytechniques Romandes: Lausanne, Switzerland, 1986.
29. Dan, E.; Somersall, A.; Guillet, J. *Macromolecules* 1973, 6, 228.