

Novel functionalized 2-(2-hydroxyphenyl)-benzotriazole – benzo[*de*]isoquinoline-1,3-dione fluorescent UV absorbers Synthesis and photostabilizing efficiency

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Abstract

Two novel yellow–green emitting adducts of 2-(2-hydroxyphenyl)-benzotriazole and benzo[*de*]isoquinoline-1,3-dione, have been synthesized for the first time by combination of benzotriazole UV absorber and 1,8-naphthalimide fluorescent unit in one molecule. The new compounds have shown very good photostabilizing efficiency, indicating a high potential for simultaneously dyeing and stabilization of polymer materials. The chemical bonding of the synthesized monomers in the polymer chain was confirmed spectrophotometrically. The influence of these additives on the photostability of the co-polymers was studied. The participation of combined molecules in the polymerization did not affect considerably the co-polymers' molecular weight.

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1. Introduction

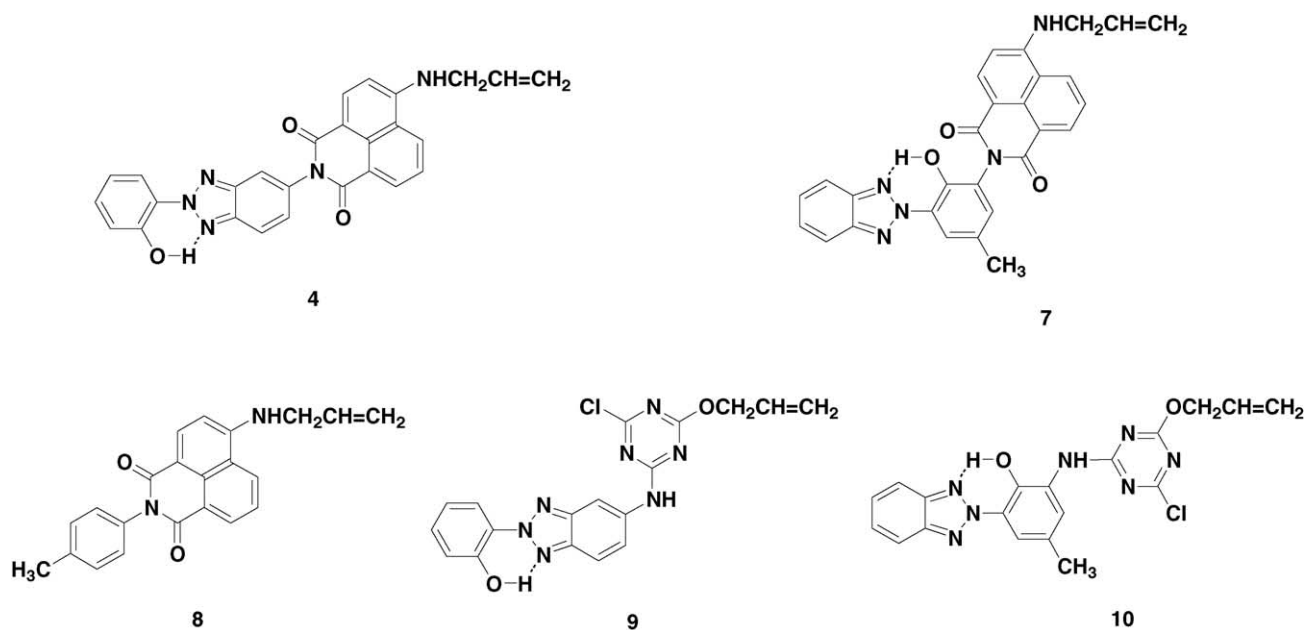
Fluorescent benzo[*de*]isoquinoline-1,3-diones due to their good spectral properties have found application in a number of areas including laser active media [1], potential photosensitive biologically units [2], fluorescent markers in biology [3], analgesics in medicine [4], light emitting diodes [5], photo-induced electron sensors [6], fluorescence switchers [7], electroluminescent materials [8], liquid crystal displays [9] and ion probes [10]. The comparatively low molecular mass of the benzo[*de*]isoquinoline-1,3-dione dyes as well as their high photostability and intensive fluorescence makes these dyes preferable to other types of disperse and covalently bound dyes for coloration of polymers. The introduction of a polymerizable allyl group into the benzo[*de*]isoquinoline-1,

3-dione molecule could provide the capability of covalent bonding to the polymer chain. During the last years, some polymerizable 6-substituted-benzo[*de*]isoquinoline-1,3-dione derivatives have been synthesized and investigated for their ability to co-polymerize with different monomers [6a,6d,8c,9b,11]. The advantage of using polymerizable dyes over conventional dyes is that the dye becomes chemically bonded to the polymer. The dye, therefore, cannot be extracted from the polymer. The solvent-fastness of a polymer colored with a polymerizable dye is, as a consequence, much greater than a polymer colored with conventional dyes [12].

Photostability of the polymers is one of their most important properties. To solve the problem of polymer stabilization, a number of different stabilizers have successfully been applied [13]. Among them, 2-hydroxyphenylbenzotriazole UV absorbers are of a great interest due to their high photostabilizing efficiency. They are transparent to visible light and

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Scheme 1.

are supposed to dissipate the absorbed energy in a harmless manner, i.e. to convert the absorbed photon energy into heat without being chemically affected [14].

A combination of 2-(2-hydroxyphenyl)-benzotriazole UV absorber and 6-amino-substituted benzo[*de*]isoquinoline-1,3-dione units in one molecule could result in a new type of fluorescent dyes (FDs) capable of photostabilizing the polymer materials. In this paper, we report the synthesis of novel yellow–green emitting benzo[*de*]isoquinoline-1,3-diones **4,7** (Scheme 1), containing an allyl group and a 2-(2-hydroxyphenyl)-benzotriazole fragment, and their potential for simultaneously chemically dyeing and photostabilization of side-group co-polymers. In order to receive a more complete comparative picture for the influence of the benzotriazole fragment in the molecule of the examined compounds on the polymer photostability, a benzo[*de*]isoquinoline-1,3-dione derivative **8** (not containing a 2-(2-hydroxyphenyl)-benzotriazole moiety in its molecule) and 2-(2-hydroxyphenyl)-benzotriazole derivatives **9** and **10** (not containing a benzo[*de*]isoquinoline-1,3-dione moiety in their molecules), synthesized before [9c,15,16], was involved in the present study (Scheme 1).

2. Experimental

2.1. Materials

The starting 2-(2-hydroxyphenyl)-5-amino-benzotriazole **1** [15] and 2-(2-hydroxy-3-amino-5-methylphenyl)-benzotriazole **5** [16] as well as 4-nitro-1,8-naphthalic anhydride **2** [3,9c] were prepared according to the reported procedures. Allylamine (Fluka), p.a. grade, was used without purification. Commercial methyl methacrylate (MMA,

Merck) was distilled under reduced pressure in nitrogen atmosphere before use. Dibenzoylperoxide (DBP, Fluka, 99.6%) re-crystallized from chloroform was used as an initiator of the free radical co-polymerization. All solvents (Fluka, Merck) were of p.a. or analytical grade.

2.2. Methods

FT-IR spectra were recorded on a Bruker IFS-113 spectrometer at 2 cm^{-1} resolution using KBr discs. The ^1H NMR spectra (chemical shifts are given as δ in ppm) were recorded on a Bruker DRX-250 spectrometer, operating at 250.13 MHz. The UV–vis spectra were recorded on a Hewlett Packard 8452A spectrophotometer with 2 nm resolution at room temperature in chloroform. The fluorescence spectra were taken on a SFM 25 spectrophotometer (KONTRON instruments). Fluorescence quantum yields were determined on the basis of the absorption and fluorescence spectra. Rhodamine 6G was used as standard ($\Phi_0 = 0.88$). TLC was performed on silica-gel, Fluka F60254, 20×20 , 0.2 mm, using as eluant the solvent systems *n*-heptane/acetone (1:1). The melting points were determined by means of a Kofler melting point microscope.

2.3. Synthesis of monomers

2.3.1. General preparation procedure for intermediates **3** and **6**

A suspension of 4-nitro-1,8-naphthalenedicarboxylic acid anhydride **2** (15 mmol) and benzotriazole **1,5** (15 mmol) in 90 ml of glacial acetic acid was stirred at 110°C for 8 h. The crude product that precipitated on cooling was filtered off, washed with water and treated with 50 ml of 5% aqueous

sodium carbonate. The solid phase was filtered off, washed with water and dried. Re-crystallization from acetic acid afforded the intermediate **3** or **6** as pale yellow–brown crystals.

2.3.1.1. 2-[2-(2-Hydroxy-phenyl)-2H-benzotriazol-5-yl]-6-nitro-benzo[de]isoquinoline-1,3-dione (3). FT-IR (KBr), cm^{-1} : 3160 (νOH); 3078 ($\nu\text{CH}=\text{}$); 1712 ($\nu^{\text{as}}\text{C}=\text{O}$); 1673 ($\nu^{\text{s}}\text{C}=\text{O}$); 1596 ($\nu\text{C}=\text{C}$); 1528 ($\nu^{\text{as}}\text{NO}_2$); 1369 ($\nu^{\text{s}}\text{NO}_2$); 1344 ($\nu\text{N}-\text{C}-\text{N}$).

^1H NMR (250.13 MHz, $\text{CDCl}_3 + \text{DMSO}-d_6$) ppm: 11.09 (s, 1H, OH); 8.87 (d, 1H, $J = 8.7$ Hz, benzo[de]isoquinoline 7-H); 8.76 (d, 1H, $J = 7.4$ Hz, benzo[de]isoquinoline 9-H); 8.72 (d, 1H, $J = 8.0$ Hz, benzo[de]isoquinoline 5-H); 8.43 (d, 1H, $J = 7.6$ Hz, phenyl 6-H); 8.42 (d, 1H, $J = 8.0$ Hz, benzo[de]isoquinoline 4-H); 8.36 (dd, 1H, $J = 9.0$ Hz, $J = 1.4$ Hz, benzotriazole 6-H); 8.07 (d, 1H, $J = 9.0$ Hz, benzotriazole 7-H); 8.02 (dd, 1H, $J = 8.7$ Hz, $J = 7.4$ Hz, benzo[de]isoquinoline 8-H); 7.93 (d, 1H, $J = 1.4$ Hz, benzotriazole 4-H); 7.35 (dd, 1H, $J = 8.9$ Hz, $J = 1.8$ Hz, phenyl 5-H); 7.17 (dd, 1H, $J = 8.3$ Hz, $J = 1.1$ Hz, phenyl 3-H); 7.03 (m, 1H, phenyl 4-H).

Elemental analysis: Calculated for $\text{C}_{24}\text{H}_{13}\text{N}_5\text{O}_5$ (MW 451.39) C 63.86, H 2.90, N 15.52%; found C 64.12, H 2.85, N 15.61%.

2.3.1.2. 2-(3-Benzotriazol-2-yl-2-hydroxy-5-methyl-phenyl)-6-nitro-benzo[de]isoquinoline-1,3-dione (6). FT-IR (KBr), cm^{-1} : 3180 (νOH); 3070 ($\nu\text{CH}=\text{}$); 1710 ($\nu^{\text{as}}\text{C}=\text{O}$); 1674 ($\nu^{\text{s}}\text{C}=\text{O}$); 1598 ($\nu\text{C}=\text{C}$); 1540 ($\nu^{\text{as}}\text{NO}_2$); 1360 ($\nu^{\text{s}}\text{NO}_2$); 1336 ($\nu\text{N}-\text{C}-\text{N}$).

^1H NMR (250.13 MHz, $\text{CDCl}_3 + \text{DMSO}-d_6$) ppm: 11.59 (s, 1H, OH); 8.90 (dd, 1H, $J = 8.8$ Hz, $J = 0.9$ Hz, benzo[de]isoquinoline 7-H); 8.81 (dd, 1H, $J = 7.4$ Hz, $J = 0.9$ Hz, benzo[de]isoquinoline 9-H); 8.77 (d, 1H, $J = 8.1$ Hz, benzo[de]isoquinoline 5-H); 8.48 (d, 1H, $J = 8.0$ Hz, benzo[de]isoquinoline 4-H); 8.41 (d, 1H, $J = 1.4$ Hz, phenyl 4-H); 8.08 (dd, 1H, $J = 8.7$ Hz, $J = 7.4$ Hz, benzo[de]isoquinoline 8-H); 7.92 (dd, 2H, $J = 9.7$ Hz, $J = 3.1$ Hz, benzotriazole 4-H and 7-H); 7.51 (dd, 2H, $J = 9.7$ Hz, $J = 3.1$ Hz, benzotriazole 5-H and 6-H); 7.24 (d, 1H, $J = 1.9$ Hz, phenyl 6-H); 2.50 (s, 3H, CH_3).

Elemental analysis: Calculated for $\text{C}_{25}\text{H}_{15}\text{N}_5\text{O}_5$ (MW 465.42) C 64.52, H 3.25, N 15.05%; found C 64.80, H 3.19, N 15.16%.

2.3.2. General preparation procedure for fluorescent dyes **4** and **7**

To a solution of intermediate **3** or **6** (5 mmol) in 50 ml of DMF 0.43 g of allylamine ($d = 0.76$, 7.5 mmol) was added at room temperature. After 36 h (TLC control in a solvent system *n*-heptane:acetone = 1:1), the resulting solution was poured into 300 ml of water. The precipitate was filtered off and washed with water. The crude product was dissolved in a mixture solvent of minimum water and ethanol (100 ml), and the undissolved residue was filtered off. The filtrate then was diluted in 100 ml of

water and the precipitated product was filtered off and dried. Re-crystallization from ethanol–water (50:50 vol.%) afforded 1.57 g of 6-allylamino-2-[2-(2-hydroxy-phenyl)-2H-benzotriazol-5-yl]-benzo[de]isoquinoline-1,3-dione **4** or 1.66 g of 6-allylamino-2-(3-benzotriazol-2-yl-2-hydroxy-5-methyl-phenyl)-benzo[de]isoquinoline-1,3-dione **7** as yellow–orange crystals.

2.3.2.1. 6-Allylamino-2-[2-(2-hydroxy-phenyl)-2H-benzotriazol-5-yl]-benzo[de]isoquinoline-1,3-dione (4). FT-IR (KBr), cm^{-1} : 3178 (νOH); 3369 (νNH); 3080 ($\nu\text{CH}=\text{}$); 2922 (νCH); 1696 ($\nu^{\text{as}}\text{C}=\text{O}$); 1657 ($\nu^{\text{s}}\text{C}=\text{O}$); 1584 ($\nu\text{C}=\text{C}$); 1365 ($\nu\text{N}-\text{C}-\text{N}$).

^1H NMR (250.13 MHz, $\text{CDCl}_3 + \text{DMSO}-d_6$) ppm: 11.20 (s, 1H, OH); 8.60 (dd, 2H, $J = 8.5$ Hz, $J = 7.2$ Hz, benzo[de]isoquinoline 7-H and 9-H); 8.44 (d, 1H, $J = 8.5$ Hz, benzo[de]isoquinoline 4-H); 8.38 (dd, 1H, $J = 8.3$ Hz, $J = 1.3$ Hz, benzotriazole 6-H); 8.07 (d, 1H, $J = 9.0$ Hz, phenyl 6-H); 7.94 (d, 1H, $J = 1.0$ Hz, benzotriazole 4-H); 7.66 (dd, 1H, $J = 8.2$ Hz, $J = 7.6$ Hz, benzo[de]isoquinoline 8-H); 7.40 (m, 2H, benzotriazole 7-H and phenyl 5-H); 7.21 (dd, 1H, $J = 8.3$ Hz, $J = 1.1$ Hz, phenyl 3-H); 7.08 (td, 1H, $J = 8.3$ Hz, $J = 1.2$ Hz, phenyl 4-H); 6.71 (d, 1H, $J = 8.6$ Hz, benzo[de]isoquinoline 5-H); 6.02 (m, 1H, allyl $\text{CH}=\text{}$); 5.35 (dd, 1H, $J_{\text{trans}} = 17.3$ Hz, $J = 1.3$ Hz, allyl *trans* = CH_2); 5.27 (dd, 1H, $J_{\text{cis}} = 10.3$ Hz, $J = 1.3$ Hz, allyl *cis* = CH_2); 4.12 (d, 2H, $J = 4.9$ Hz, allyl NCH_2); 3.51 (br.s, 1H, allyl NH).

Elemental analysis: Calculated for $\text{C}_{27}\text{H}_{19}\text{N}_5\text{O}_3$ (MW 461.47) C 70.27, H 4.15, N 15.18%; found C 70.60, H 4.21, N 15.06%.

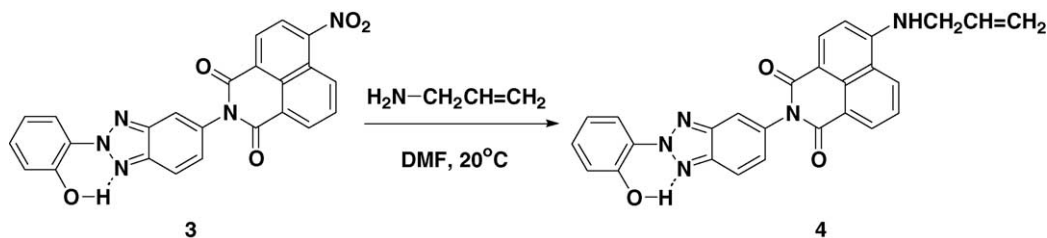
2.3.2.2. 6-Allylamino-2-(3-benzotriazol-2-yl-2-hydroxy-5-methyl-phenyl)-benzo[de]isoquinoline-1,3-dione (7). FT-IR (KBr), cm^{-1} : 3380 (νNH); 3166 (νOH); 3078 ($\nu\text{CH}=\text{}$); 2920 (νCH); 1700 ($\nu^{\text{as}}\text{C}=\text{O}$); 1662 ($\nu^{\text{s}}\text{C}=\text{O}$); 1592 ($\nu\text{C}=\text{C}$); 1338 ($\nu\text{N}-\text{C}-\text{N}$).

^1H NMR (250.13 MHz, CDCl_3) ppm: 11.58 (s, 1H, OH); 8.67 (dd, 2H, $J = 8.2$ Hz, $J = 7.5$ Hz, benzo[de]isoquinoline 7-H and 9-H); 8.60 (d, 1H, $J = 8.3$ Hz, benzo[de]isoquinoline 4-H); 8.40 (d, 1H, $J = 1.2$ Hz, phenyl 4-H); 7.92 (dd, 2H, $J = 9.5$ Hz, $J = 2.9$ Hz, benzotriazole 4-H and 7-H); 7.70 (dd, 1H, $J = 8.2$ Hz, $J = 7.5$ Hz, benzo[de]isoquinoline 8-H); 7.47 (dd, 2H, $J = 9.6$ Hz, $J = 3.0$ Hz, benzotriazole 5-H and 6-H); 7.01 (d, 1H, $J = 1.7$ Hz, phenyl 6-H); 6.70 (d, 1H, $J = 8.3$ Hz, benzo[de]isoquinoline 5-H); 6.08 (m, 1H, allyl $\text{CH}=\text{}$); 5.29 (dd, 1H, $J_{\text{trans}} = 17.3$ Hz, $J = 1.4$ Hz, allyl *trans* = CH_2); 5.16 (dd, 1H, $J_{\text{cis}} = 10.5$ Hz, $J = 1.3$ Hz, allyl = CH_2); 4.30 (dd, 2H, $J = 5.2$ Hz, $J = 1.5$ Hz, allyl NCH_2); 2.49 (s, 3H, CH_3); 1.70 (br.s, 1H, allyl NH).

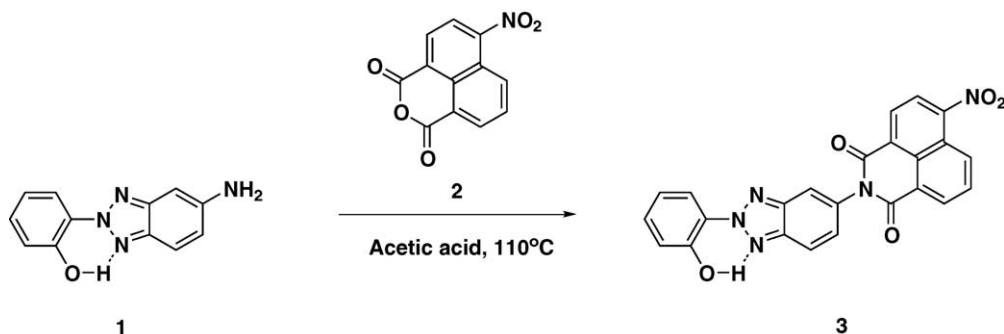
Elemental analysis: Calculated for $\text{C}_{28}\text{H}_{21}\text{N}_5\text{O}_3$ (MW 475.50) C 70.73, H 4.45, N 14.73%; found C 71.04, H 4.39, N 14.81%.

2.4. Synthesis of polymers

The radical co-polymerization of the FDs **4**, **7** and **8** as well as monomeric stabilizers **9** and **10** with MMA was carried out



Scheme 2.



Scheme 3.

in ampoules, previously purged with dry and pure nitrogen. The process of co-polymerization was conducted at 70 °C for 12 h in the presence of 0.1 wt.% of the monomeric compounds **4**, **7–10** and 0.5 wt.% of DBP. The transparent side-chain co-polymers thus obtained were several times re-precipitated with ethanol from toluene until the filtrate was colorless. The precipitated co-polymers were repeatedly washed with ethanol, recovered by filtration and dried in vacuum to constant weight. All spectrophotometric measurements were carried out with precipitated polymers.

2.5. Photodestruction of co-polymers

The studies on the photodegradation of the fluorescent co-polymers were performed in a solar simulator SUNTEST CPS equipment (Heraeus, Germany), supplied with an air-cooled Xenon lamp (Hanau, 1.1 kW, 765 W m⁻²), protected with an adequate filter to simulate the solar spectrum between 290 and 800 nm. The photodestruction of the co-polymers was followed by measuring the changes in the molecular weight (weight-average M_w and number-average M_n) and polydispersity (M_w/M_n) before and after irradiation of their solid films using GPC. The polymeric films of poly(MMA-co-FD)s and PMMA were of 60 μm thickness.

2.6. Determination of polymer molecular weights

The polymer molecular weights were determined on a GPC Waters 244 apparatus equipped with a combination of 100, 1000 Å, linear Ultrastaygel columns; the solvent was THF at a flow rate of 1.0 ml min⁻¹ at 45 °C. Both differential refractive index and UV–vis absorption detectors were used.

Polystyrene calibration was used for all molecular weight calculations.

3. Results and discussion

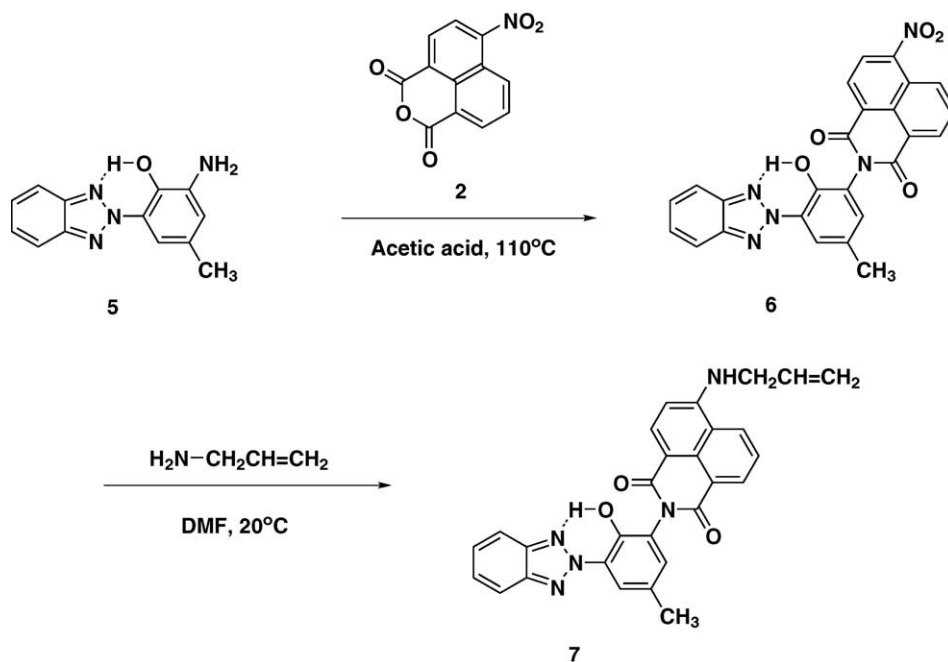
The aim of the present study was to synthesize 1,8-naphthalimide fluorescent dyes, containing a 2-(2-hydroxyphenyl)-benzotriazole stabilizer fragment and a polymerizable allyl group for simultaneously chemically dyeing and stabilization of PMMA. It was of interest to obtain combined compounds in which the 1,8-naphthalimide unit is situated at a different position (at the benzotriazole or at the 2-hydroxyphenyl moiety) with a view to study the position effect of the benzo[*de*]isoquinoline-1,3-dione fragment on the absorption properties of the 2-(2-hydroxyphenyl)-benzotriazole UV absorbers.

3.1. Synthesis

The synthesis of 2-[2-(2-hydroxyphenyl)-2H-benzotriazol-5-yl]-benzo[*de*]isoquinoline-1,3-dione **4** is displayed in [Scheme 2](#) using a procedure described before [17].

In order to obtain fluorescent 1,8-naphthalimide dye **4** and functionalize it with a polymerizable group, the nitro group in the intermediate **3** was nucleophilic substituted with the commercially available allylamine in DMF at room temperature for 36 h [9c].

The intermediate compound **3** was obtained by condensation of 2-(2-hydroxyphenyl)-5-amino-benzotriazole **1** with 4-nitro-1,8-naphthalic anhydride **2** in glacial acetic acid at 110 °C for 8 h ([Scheme 3](#)). The results obtained showed that



the strong electron-accepting nitro group considerably improve the reaction ability of the starting 1,8-naphthalic anhydride **2**.

In order to study the position effect of the benzo[de]isoquinoline-1,3-dione fragment on the absorption properties of the 2-(2-hydroxyphenyl)-benzotriazole UV absorbers, a new combined molecule was synthesized (**7**), in which the 1,8-naphthalimide unit is linked to the 2-hydroxyphenyl moiety of the benzotriazole ring system.

The novel yellow–green emitting UV absorber (**7**) was synthesized in two steps as was already described above in the synthesis of compound **4** (Scheme 4).

All of the synthesized compounds were characterized by their melting points, TLC (R_f values) and UV–vis spectra (Table 1) and identified by elemental analysis data, FT-IR and ^1H NMR spectra. Dyes **4** and **7** were additionally characterized by fluorescence maxima, Stokes shifts ($\nu_A - \nu_F$) and

quantum yields of fluorescence (Φ_F). The data are presented in Table 2.

The absorption spectra of the compounds **4** (Fig. 1) and **7** (Fig. 2) clearly show the participation of both UV absorber and 1,8-naphthalimide units in the combined molecules. Benzotriazole fragments absorb in the UV region at $\lambda_1 = 336\text{--}342\text{ nm}$, while the benzo[de]iso-quinoline-1,3-dione absorption is shifted from UV ($\lambda_2 = 350\text{--}351\text{ nm}$, intermediates **3**, **6**) to visible region at $\lambda_2 = 422\text{--}424\text{ nm}$ (FDs **4** and **7**), which is surely connected with the substitution of the electron-withdrawing nitro group.

The position effect of the benzo[de]isoquinoline-1,3-dione fragment on the absorption properties of the 2-(2-hydroxyphenyl)-benzotriazole can be seen in the UV–vis spectra (Figs. 1 and 2).

The absorption maximum of benzotriazole **1** is 36 nm bathochromically shifted than those of benzotriazole **5**. This

Table 1

Yields and characteristic data of benzotriazoles **1**, **5**, **9** and **10** and 2-[2-(2-hydroxyphenyl)-2H-benzotriazol-5-yl]-benzo[de]isoquinoline-1,3-diones **3**, **4**, **6** and **7** in a chloroform solution

Compound	Yield (%)	mp (°C)	R_f	λ_1^a (nm)	$\log \epsilon$ ($1\text{ mol}^{-1}\text{ cm}^{-1}$)	λ_2^a (nm)	$\log \epsilon$ ($1\text{ mol}^{-1}\text{ cm}^{-1}$)
1	76	211–2	0.48	360	4.26		
3	62	>260	0.47	342	4.47	351	4.40
4	68	>260	0.44	338	4.38	424	4.10
5	81	213–6	0.51	324	4.27		
6	69	>260	0.49	342	4.42	350	4.34
7	72	144–5	0.45	336	4.31	422	4.02
9^b	89	127–9	0.49	342	4.14		
10^b	87	133–5	0.49	348	4.12		

^a λ_1 and λ_2 represent the absorption maxima of 2-(2-hydroxyphenyl)-benzotriazole and benzo[de]isoquinoline-1,3-dione units in the combined molecules, respectively.

^b Synthetic details for compounds **9** and **10** were reported in the previous works [15,16].

Table 2
Photophysical characteristics of compounds **4**, **7** and **8** in a chloroform solution

Compound	λ_A (nm)	$\log \varepsilon$ ($l \text{ mol}^{-1} \text{ cm}^{-1}$)	λ_F (nm)	$\nu_A - \nu_F$ (cm^{-1})	Φ_F
4	424	4.10	516	4205	0.62
7	422	4.02	512	4165	0.66
8	420	4.06	508	4124	0.63

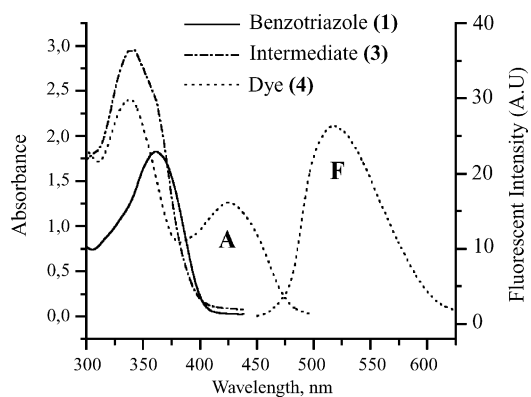


Fig. 1. UV-vis spectra of compounds **1**, **3** and **4** and fluorescence emission of dye **4** in a chloroform solution.

may be related to the position of the electron-donating amino group in the benzotriazole moiety, and in this connection, to the increased strength of the intramolecular hydrogen bond. In the benzotriazole **5**, the amino group is situated in the 2-hydroxyphenyl moiety, which leads to decreased strength of the intramolecular hydrogen bond. In confirmation of the discussed above, after acylation with 1,8-naphthalic anhydride (intermediates **3** and **6**) the electron-donating activity of the amino group decrease strongly and the benzotriazole absorption of compounds **3** and **4** is shifted hypsochromically, while those of compounds **6** and **7** – bathochromically.

Data presented in Table 2 shows that the different substituents at the *N*-imide atom have a small effect on both the absorption and the fluorescence maxima. Stokes shift and quantum yield of fluorescence Φ_F values were common for this class of 1,8-naphthalimide derivatives [9c]. The Stokes shift is a parameter that indicates the differences in the properties and structure of the fluorophores between the ground state S_0 and the first excited state S_1 . The Stokes shifts (cm^{-1}) were calculated by Eq. (1).

$$\nu_A - \nu_F = \left(\frac{1}{\lambda_A} - \frac{1}{\lambda_F} \right) \times 10^7 \quad (1)$$

Table 3
Spectrophotometric data for co-polymers of MMA with monomeric compounds **4**, **7**–**10** in a chloroform solution

Polymer	λ_A (nm)	λ_F (nm)	$\nu_A - \nu_F$ (cm^{-1})	Φ_F	Yield (wt.%)	Chem. bonded monomer (wt.%/mol $\times 10^{-4}$)
PMMA					90	
Poly(MMA-co- 4)	428	518	4059	0.68	74	0.071/1.54
Poly(MMA-co- 7)	426	516	4094	0.69	83	0.080/1.68
Poly(MMA-co- 8)	422	512	4165	0.67	85	0.084/2.45
Poly(MMA-co- 9)	346				78	0.079/2.00
Poly(MMA-co- 10)	350				83	0.081/1.98

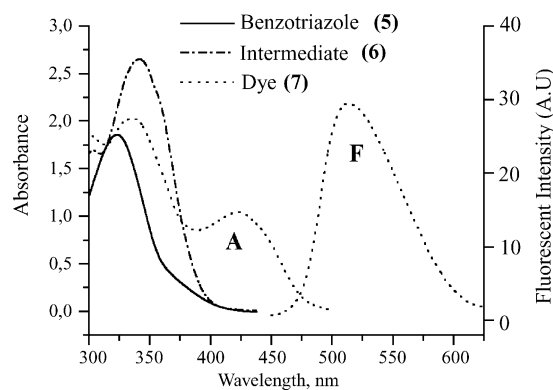


Fig. 2. UV-vis spectra of compounds **5**, **6** and **7** and fluorescence emission of dye **7** in a chloroform solution.

The ability of the molecules to emit the absorbed light energy is characterized quantitatively by the fluorescence quantum yield. Comparison of the fluorescence quantum yields of 6-allylamino-2-(4-methylphenyl)-benzo[*de*]isoquinoline-1,3-dione **8** with those of compounds **4** and **7** (they are approximately the same, Table 2) clearly show that the combination of the two different structural units (compounds **4** and **7**) does not result in their interaction as an intramolecular quenching due to an electronic energy transfer.

3.2. Polymerization

The applicability of the new fluorescent compounds for simultaneously coloring and stabilization of polymers was examined on the basis of their ability to co-polymerize with methyl methacrylate (MMA). The co-polymerization process was conducted under conditions used with other similar benzo[*de*]isoquinoline-1,3-dione derivatives [18]. Transparent fluorescent co-polymers have been obtained. To receive a complete comparative picture for the influence of the 2-(2-hydroxyphenyl)-benzotriazole moiety in the molecules of the examined compounds on the polymer photostability,

Table 4

Molecular characteristics of poly(MMA-co-**4**, **7–10**)s and PMMA before and after of 12 h irradiation

	Before irradiation			After irradiation			A
	$M_{wo} \times 10^{-5}$	$M_{no} \times 10^{-5}$	M_{wo}/M_{no}	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	M_w/M_n	
Poly(MMA-co- 4)	2.43	1.28	1.9	2.42	1.24	2.0	0.032
Poly(MMA-co- 7)	2.56	1.35	1.9	2.52	1.29	2.0	0.047
Poly(MMA-co- 8)	2.60	1.41	1.8	2.18	0.90	2.4	0.567
Poly(MMA-co- 9)	2.49	1.30	1.9	2.50	1.27	2.0	0.024
Poly(MMA-co- 10)	2.55	1.33	1.9	2.53	1.29	2.0	0.031
PMMA	2.72	1.61	1.7	2.29	0.74	3.1	1.176

co-polymers of the benzo[de]isoquinoline-1,3-dione **8** and 2-(2-hydroxyphenyl)-benzotriazoles **9** and **10** with MMA were also obtained. The polymer yields were 74–85 wt.% for poly(MMA-co-**4**, **7–10**)s and 90 wt.% for PMMA (Table 3). It can be seen that monomer compounds **4** and **7–10** did not affect significantly the process of the co-polymerization.

UV–vis spectroscopic and TLC techniques proved the presence of a covalent bond between the monomeric FD units and the polymer chain. The unprecipitated co-polymers (they comprise also some amount of unreacted monomers), precipitated co-polymers, monomeric compounds **4**, **7–10** and mixtures of a homopolymer with the same monomers were studied by TLC. After the chromatography development, it was established that the monomers in the mechanical mixtures (a mechanical blend of both homopolymer and monomer) moved at the same speed as the monomeric compounds did and had the same values of retention factor R_f (Table 1), while the monomers in the co-polymers, where they should be chemically bound, remained at the start together with the polymer ($R_f = 0$). This indicates the different absorbencies of bound and unbound monomers and qualitatively confirms the binding of the combined compounds to the polymer chain.

The UV–vis absorption spectra of the precipitated polymers had similar absorption maxima as the monomeric compounds, showing that the basic chromophore did change, neither during the polymerization nor as a result of its bonding to the polymer chain. This is why the percentage of the chemically bonded monomers in the polymer chain was determined spectrophotometrically using the method of the calibration curve (Table 3).

The synthesized polymers were soluble in the solvents common for the PMMA. Table 3 presents the data obtained from the absorption and fluorescence spectra of the side-group co-polymers in a chloroform solution. The absorption λ_A and fluorescence λ_F maxima of the poly(MMA-co-FDs **4**, **7** and **8**)s have been observed at 422–428 nm and at 512–518 nm, respectively, while the absorption λ_A maxima of the poly(MMA-co-**9**, **10**)s have been at 346–350 nm. They were very similar to those of the monomeric compounds in the same solvent indicating further the preservation of the chromophoric system during the co-polymerization. The poly(MMA-co-FDs **4**, **7** and **8**)s' quantum yield of fluorescence ($\Phi_F = 0.67–0.69$) was higher than that of the corresponding monomeric FDs. This is connected with the

decrease of emissionless processes and is obviously related to the bonding of the fluorophores to the polymer chain.

3.3. Photostability of PMMA and co-polymers

The influence of the monomers **4**, **7–10** upon the photodegradation of PMMA was studied by GPC with prior irradiation of their co-polymers with MMA in a SUNTEST CPS equipment for 12 h. The number of chain breaks per molecule A was calculated by Eq. (2) where M_{no} and M_n are the number-average molecular weights before and after irradiation, respectively [19].

$$A = \frac{M_{no}}{M_n} - 1 \quad (2)$$

The results are listed in Table 4. As it is seen poly(MMA-co-**4**, **7**, **9** and **10**)s did not change significantly their polydispersity and molecular weight distribution while the same values for poly(MMA-co-**8**)s and especially for PMMA decreased strongly. FD **8**, not containing a benzotriazole unit, displayed passable photostabilizing efficiency as a result of re-emitting the absorbed UV light as a long wave visible fluorescent emission.

The stabilizer compounds **9** and **10**, not containing a benzo[de]isoquinoline-1,3-dione fragment, showed the best stabilizing efficiency among the tested compounds. However, their mole content in the co-polymer was higher than those of the combined compounds **4** and **7** (Table 3). Therefore, we can suppose that the efficiency against photodegradation of the compounds **4**, **7**, **9** and **10** is approximately the same and the contribution of the benzo[de]isoquinoline-1,3-dione moiety in the combined compounds **4** and **7** to the polymer photostability is negligible.

The high photostabilizing efficiency of the compounds **4**, **7**, **9** and **10**, containing a 2-hydroxyphenylbenzotriazole fragment, can be related to a rapid excited state intramolecular proton transfer (ESIPT) between the phenolic hydroxyl group and the benzotriazole nitrogen when the compounds are excited into the benzotriazole absorption band [20,21].

The data obtained manifest the potential of the novel benzo[de]isoquinoline-1,3-diones **4** and **7** for simultaneously coloring and stabilization of PMMA. They improved considerably the co-polymer photostability in spite of their low content in the co-polymer. On the other hand, there was not

a substantial difference in the photostabilizing efficiency of the novel compounds.

4. Conclusions

As a result of this investigation, it can be assumed that the novel compounds **4** and **7** a combination of a 2-(2-hydroxyphenyl)-benzotriazole UV absorber and a polymerizable group through the molecule of the fluorescent benzo[*de*]isoquinoline-1,3-dione were successfully synthesized. The position effect of the benzo[*de*]isoquinoline-1,3-dione fragment on the absorption properties of the 2-(2-hydroxyphenyl)benzotriazole was investigated spectrophotometrically. The new compounds were suitable for preparing PMMA-based co-polymers with intensive yellow–green fluorescence and high photostability.

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