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Design and synthesis of polymerizable, yellow-green emitting 1,8-naphthalimides containing built-in *s*-triazine UV absorber and hindered amine light stabilizer fragments

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Abstract

Two novel yellow-green emitting polymerizable 1,8-naphthalimide fluorophores, containing an UV absorber and a hindered amine light stabilizer (HALS) component were synthesized by combination of 2-hydroxyphenyl-1,3-5-triazine, 2,2,6,6-tetramethylpiperidine and allylamine. The combination of the two structural units in one molecule did not result in intramolecular fluorescence quenching. The compounds were copolymerized with acrylonitrile to yield polyacrylonitriles of intense color and fluorescence, indicating that the novel compounds offer potential for the ‘‘one-step’’ chemical coloration and stabilization of polymers.

Keywords: 1,8-Naphthalimide; Fluorescence; Hindered amine light stabilizer (HALS); 2-(2-Hydroxyphenyl)-1,3,5-triazine UV absorbers; Polymerization; Polyacrylonitrile (PAN)

1. Introduction

1,8-Naphthalimide derivatives carrying amino groups at the C-4 position usually exhibit yellow-green fluorescence emission on irradiation [1–11]. Owing to their good spectral properties, 4-alkylamino-1,8-naphthalimides enjoy application in several areas including the coloration of polymers [1], laser active media [2], potential photosensitive biologically units [3], fluorescent markers in biology [4], analgesics in medicine [5], light emitting diodes [6], photo-induced electron sensors [7], fluorescence switchers [8], electroluminescent materials [9], liquid crystal displays [10] and ion probes [11].

Plastics and organic coatings used outdoors are exposed to ultraviolet (UV) radiation in the range 295–400 nm which is a common cause of degradation and weathering. The stabilization of such materials to light has for many years been a challenge and a wide range of stabilizers have been examined, such as UV absorbers and hindered amines (HALS) [12]. These two types of photodegradation stabilizers, however, differ from each other in their action; hindered amines such as 2,2,6,6-tetramethylpiperidines inhibit autoxidation by the transformation of the parent amine to *N*-oxyl radicals, either by reaction with peroxyl radicals or occasionally by reaction with singlet oxygen, which halts oxidative degradation by the coupling of alkyl radicals [13]. In contrast, UV absorbers are transparent to visible light and dissipate the absorbed energy in a harmless manner, i.e. to convert the absorbed photon energy into heat without being chemically affected [14]. In this context, 2-hydroxyphenyl-*s*-triazines are of interest due to their high thermal stability and surprisingly high extinction coefficients, which makes them of especial value for stabilizing polymer substrates, especially automotive coatings [14b].

Recently, a number of papers devoted to the problem of the synthesis of combined stabilizers containing fragments able to

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function according to different stabilizing mechanisms have been published. Thus, hindered amine fragments have been combined with either 2-hydroxybenzophenone [15,16] or 2-hydroxyphenylbenzotriazole UV absorbers [17]. A significant synergistic stabilizing effect against photodegradation was demonstrated [17d].

In previous papers the synthesis and properties of 1,8-naphthalimide fluorophores, containing either a UV absorber moiety [18] or a hindered amine fragment [19] were reported. As the combination of 2,2,6,6-tetramethylpiperidine and 2-hydroxyphenyl-*s*-triazine fragments together with a polymerizable group in one molecule through a fluorophore unit could result in a novel type of fluorescent dye (FDs) that is capable of the "one-step" coloration and photostabilization of polymeric materials. In this paper we report the synthesis and photophysical properties of novel yellow-green emitting 1,8-naphthalimides **3** and **5**, containing a 2-(2-hydroxyphenyl)-1,3,5-triazine and a 2,2,6,6-tetramethylpiperidine fragments, capable to polymerize with vinyl monomers (Scheme 1).

2. Results and discussion

The aim of the present study was to synthesize multifunctional 1,8-naphthalimide fluorescent dyes, containing both a 2-(2-hydroxyphenyl)-1,3,5-triazine UV absorber and a 2,2,6,6-tetramethylpiperidine radical scavenger fragments as well as an unsaturated allyl group for simultaneous chemically fluorescent dyeing and stabilization of polymers.

It was of interest to synthesize two different dyes in which the piperidine moiety is binding to the *s*-triazine ring either through an imine spacer (compound **3**) or directly to the piperidine nitrogen (compound **5**), because the efficiency of polymer bonded radical scavengers (such as HALS) in comparison with freely moving low molecular additive has frequently been questioned. Thus, during the formation of nitroxyl radicals the piperidine moiety in compound **3** will remain intact to the polymer chain, which is impossible for compound **5** due to the cleavage of the chemical bond between the piperidine nitrogen and *s*-triazine.

2.1. Synthesis of dyes

First, the synthesis of the polymerizable 1,8-naphthalimide dyes **3** and **5** was performed following Scheme 2.

According to Scheme 2, target dyes **3** and **5** were obtained by Friedel–Crafts acylation of previously synthesized 4-allylamino-*N*-(3-hydroxyphenyl)-1,8-naphthalimide **1** [10c] with corresponding *s*-triazinylpiperidines (**2** and **4**) in xylene. The TLC analysis showed considerable amount of blue emitting side-product probably due to acylation of the aromatic nitrogen atom at the C-4 position of 1,8-naphthalimide, responsible for the wavelength of fluorescence. This was the reason to change the synthetic route as it is presented in Scheme 3.

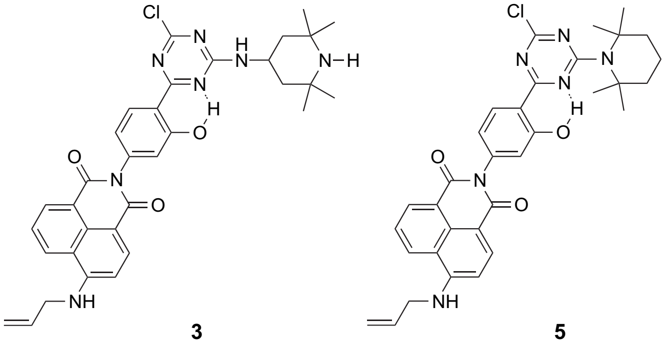
Following Scheme 3 the intermediate compounds **9** and **10** were synthesized in two steps by condensation of 4-nitro-1,8-naphthalic anhydride **6** with 3-aminophenol **7** in glacial acetic acid at 110 °C for 8 h using a procedure described before [10c,18] and subsequent Friedel–Crafts acylation in xylene of obtained 4-nitro-*N*-(3-hydroxyphenyl)-1,8-naphthalimide **8** with *s*-triazinylpiperidines **2** and **4**.

In order to obtain fluorescent 1,8-naphthalimide dyes **3** and **5** and functionalize them with polymerizable group in one step, the nitro group in the intermediates **9** and **10** were nucleophilic substituted with the commercially available allylamine (Fluka) in DMF at room temperature for 36 h by analogy with a method described before [19a].

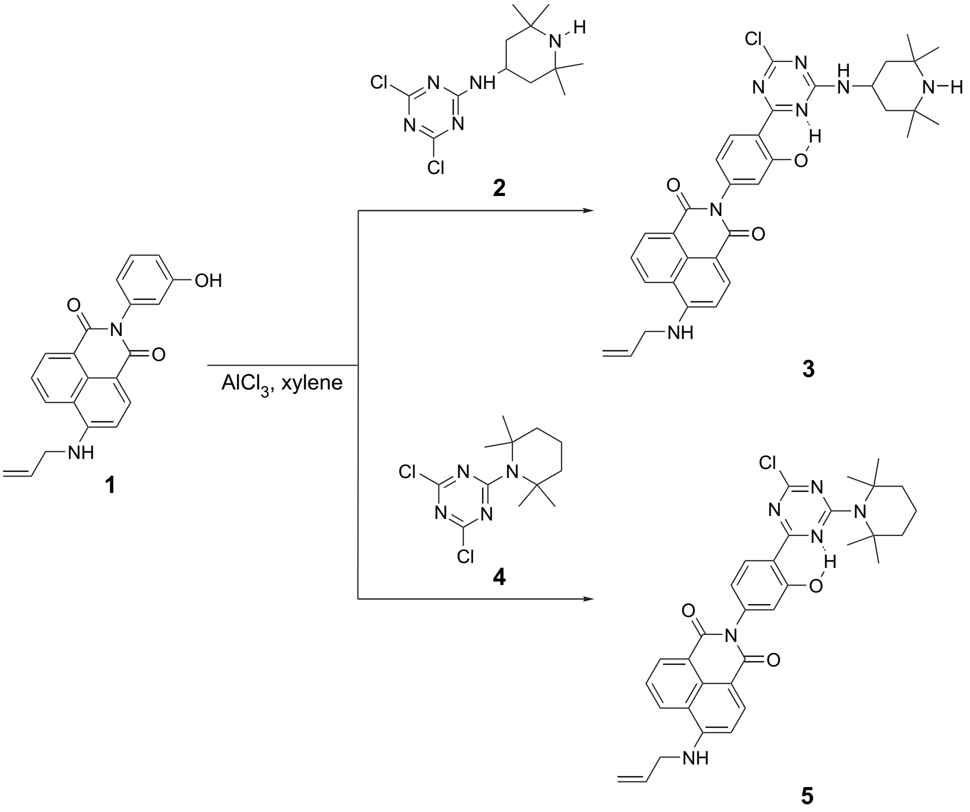
Triazinylpiperidines **2** and **4** were synthesized by methods described before [17a,20] following Scheme 4.

Target 2-(2,2,6,6-tetramethylpiperidin-4-ylamino)-4,6-dichloro-1,3,5-triazine **2** and 2-(2,2,6,6-tetramethylpiperidin-1-yl)-4,6-dichloro-1,3,5-triazine **4** were obtained by acylation of the corresponding 4-amino-2,2,6,6-tetramethylpiperidine **12** [20a] and 2,2,6,6-tetramethylpiperidine **13** [17a,20b] with commercially available cyanuric chloride **11** (Merck) in water/acetone suspension at 5 °C and in xylene at 110 °C, respectively.

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, ^{1}H and ^{13}C NMR spectra. Dyes **3** and **5** were additionally characterized by fluorescence maxima, Stokes shifts (ν_A–ν_F) and quantum yields of fluorescence (Φ_F). The data are presented in Table 2.



Scheme 1.



Scheme 2.

2.2. Photophysical characterization of dyes

The absorption spectra of the dyes **3** and **5** (Fig. 1) clearly show the participation of both *s*-triazine UV absorber and fluorophore units in the combined molecules. The 2-(2-hydroxyphenyl)-1,3,5-triazine UV absorber fragment showed two absorption maxima in the UV region at $\lambda_{A1} = 286-290$ nm and 340 nm, while the 1,8-naphthalimide absorption is shifted from UV to visible region at $\lambda_{A2} = 436-438$ nm, which is surely connected with the substitution of the C-4 electron-withdrawing nitro group in the intermediates **9** and **10** (Scheme 3). These absorption data are usual for the 1,8-naphthalimide dyes (see comparative data presented in Table 1 for dye **1**, not containing UV absorber fragment) [1–11] and 2-hydroxyphenyl-1,3,5-triazine UV absorbers [14b], which indicates that the incorporation of a *s*-triazine fragment in the fluorophore structure did not affect the absorption properties of both the dye and UV absorber, combined in one molecule.

Data presented in Table 1 and the graphic plotted in Fig. 1 also showed that the different binding of the 2,2,6,6-tetramethylpiperidine moiety to the *s*-triazine ring (through an imine spacer in dye **3** and directly to the piperidine nitrogen in compound **5**) practically has no effect on the dye's absorption properties.

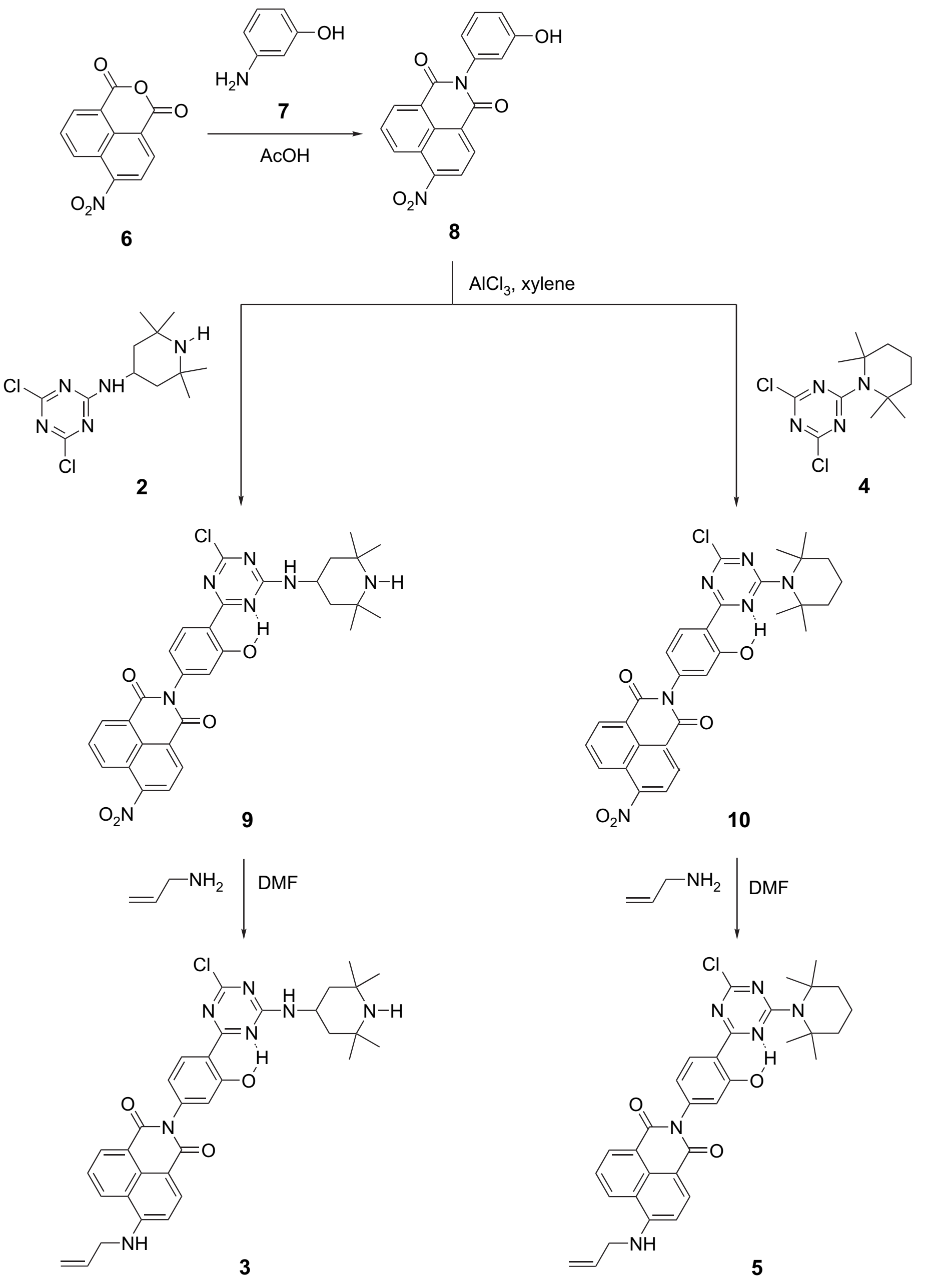
Basic fluorescent characteristics of the target dyes (**3** and **5**) and of comparative dye **1** [21] such as the fluorescence (λ_F) maxima, Stokes shift ($\nu_A - \nu_F$), oscillator strength (f), fluorescence both quantum (Φ_F) and energy (E_F) yields were measured in DMF solution and presented in Table 2.

In DMF solution FDs displayed intense yellow-green fluorescence at $\lambda_F = 526-527$ nm (Fig. 2) due to the charge transfer in the 1,8-naphthalimide moiety from the electron-donating amino group at C-4 position to the carbonyl groups (λ_{A2}). Data presented in Table 2 and the graphic plotted in Fig. 2 show that both different substitution of the piperidine moiety to the *s*-triazine ring and incorporation of a UV absorber fragment in the combined molecule have a negligible effect on the position of fluorescence maxima.

Fig. 3 presents the normalized absorption and fluorescence spectra of dye **3** in DMF solution as an example. In the long-wavelength region, the fluorescence spectrum is the mirror image of the absorption one. This is indicative for the preserved planarity of the molecular structure of the dye in the exited state. The overlap of the absorption and fluorescence spectra is small and an aggregation effect has not been observed at the studied concentration of the dye.

The Stokes shift ($\nu_A - \nu_F$) and oscillator strength (f) are important characteristics for the fluorescent compounds. 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) where $\nu_A = \nu_{A2}$.

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



Scheme 3.

The Stokes shift values of the FDs under study between 3960 cm^{-1} and 4066 cm^{-1} were usual for the 1,8-naphthalimide derivatives [22].

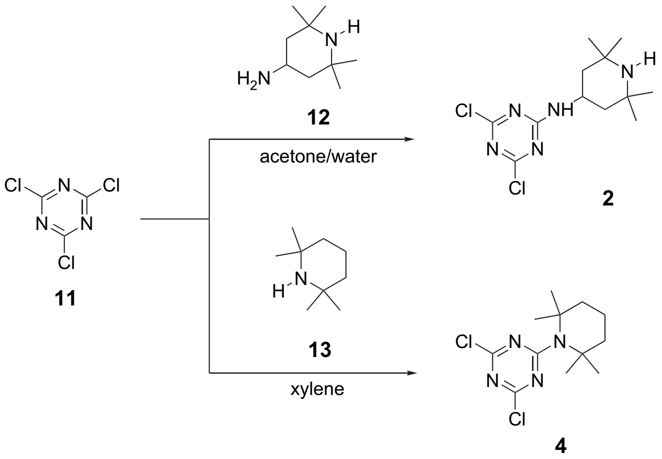
The oscillator strength (f) shows the effective number of electrons whose transition from ground to excited state gives the absorption area in the electron spectrum. Values of the oscillator strength were calculated using Eq. (2) where $\Delta\nu_{1/2}$ is the width of the absorption (λ_{A2}) band (cm^{-1}) at $1/2\varepsilon_{max}$ [23].

$$f = 4.32 \times 10^{-9} \Delta\nu_{1/2}\varepsilon_{max} \tag{2}$$

The values of the oscillator strength for the 1,8-naphthalimide dyes **3** and **5** were closed to that of dye **1** − 0.236 and 0.246, respectively, which conform to previous investigations where 1,8-naphthalimide derivatives have oscillator strength values in the range 0.15–0.35 depending on the experimental conditions [24].

The ability of the molecules to emit the absorbed light energy is characterized quantitatively by the fluorescence quantum yield (Φ_F). The quantum yields of fluorescence were calculated using Coumarin 6 ($Q_F = 0.78$ in ethanol) as a standard according to Eq. (3) [25],

$$\Phi_F = \Phi_{ref}\left(\frac{S_{sample}}{S_{ref}}\right)\left(\frac{A_{ref}}{A_{sample}}\right)\left(\frac{n^2_{sample}}{n^2_{ref}}\right) \tag{3}$$



Scheme 4.

where A_{ref}, S_{ref}, n_{ref} and A_{sample}, S_{sample}, n_{sample} represent the absorbance at the exited wavelength, the integrated emission band area and the solvent refractive index of the standard and the sample, respectively.

The energy yield of fluorescence E_F (Table 2) calculated by Eq. (4) could also be used instead of Φ_F [26].

$$E_F = \Phi_F \frac{\lambda_A}{\lambda_F} \tag{4}$$

Comparison of the fluorescence quantum yields of 4-allylamino-*N*-(3-hydroxyphenyl)-1,8-naphthalimide **1** ($\Phi_F = 0.52$), not containing hindered amine and 2-hydroxyphenyl-1,3,5-triazine fragments, with those of dyes **3** and **5** ($\Phi_F = 0.48–0.49$), a combination of 1,8-naphthalimide with UV absorber and HALS fragments in one molecule, clearly shows (the values are approximately the same) that the combination of the different structural units (compounds **3** and **5**) does not result in their interaction as an intramolecular quenching due to an electronic energy transfer.

2.3. Synthesis of fluorescent copolymers

The applicability of the new fluorescent dyes **3** and **5** for simultaneously coloring and stabilization of polymers was examined on the basis of their ability to copolymerize with acrylonitrile (AN). The free radical polymerization of AN in the presence of dyes **3** and **5** was investigated. To receive a more complete comparative picture for the influence of the *s*-triazine and HALS moieties in the molecule of the examined compounds on the polymerization process, 1,8-naphthalimide dye **1** (not containing both fragments in its molecules) was involved in the present study. In all cases solid, brightly colored transparent polymers with an intense fluorescence were obtained. All polymers obtained were subjected to several times of re-precipitation from DMF by methanol in order to remove the unreacted monomers. The colored polymers retained their color after this operation, which indicated that the dyes were chemically bound to the polymer chain. The polymer yields were 81 wt% for poly(AN-*co*-**1**), 72–74 wt% for poly(AN-*co*-**3**, **5**)s and 90 wt% for PAN (Table 3). It can be assumed that monomer dyes did not affect the process of copolymerization significantly, especially comparative dye **1**, not containing stabilizer fragments in its molecule. In the case of FDs **3** and **5** the retardation process was relatively stronger, which is surely connected with the larger steric volume of these dyes due to the participation of both UV-*s*-triazine absorber and sterically hindered amine fragments in their molecules.

Table 1
Yields, melting points, retention factors and absorption data for intermediates **1**, **2**, **4**, **8–10** and fluorescent dyes **3** and **5** in DMF solution

Compound	Yield (%)	Mp (°C)	R_f	λ_{A1}[a] (nm)	log ε (l mol^{-1} cm^{-1})	λ_{A2}[a] (nm)	log ε (l mol^{-1} cm^{-1})
1	69	153–154	0.48[b]	–	–	436	4.097
2	79	144–146	0.86[c]	–	–	–	–
3	70	>260	0.56[d]	286, 338	4.577, 4.428	434	4.093
4	82	113–115	0.68[c]	–	–	–	–
5	73	>260	0.52[d]	290, 340	4.580, 4.417	436	4.104
8	75	>260	0.44[b]	–	–	346	3.942
9	68	>260	0.49[d]	288, 340	4.563, 4.419	348	3.938
10	70	>260	0.47[d]	286, 338	4.529, 4.413	348	3.982

[a] λ_{A1} and λ_{A2} represent the absorption maxima of 2-(2-hydroxyphenyl)-1,3,5-triazine and 1,8-naphthalimide units in the combined molecules, respectively.

[b] TLC in a solvent system *n*-heptane/acetone (1:1).

[c] TLC in a solvent system *n*-propanol/ammonia = (1:1).

[d] TLC in a solvent system chloroform/methanol = (9:1).

Table 2
Fluorescence characteristics of FDs **1**, **3** and **5** in DMF solution at $\lambda_{Ex} = \lambda_{A2}$

Compound	λ_{Ex} (nm)	λ_F (nm)	$\nu_A - \nu_F$ (cm^{-1})	f	Φ_F	E_F
1	436	526	3924	0.218	0.52	0.43
3	434	527	4066	0.236	0.49	0.40
5	436	527	3960	0.246	0.48	0.40

The presence of a covalent bond between the monomer dye units and the polymer chain has been proved by TLC technique. The unprecipitated copolymers (they comprise also some amount of unreacted monomers), precipitated copolymers, monomer dyes **1**, **3** and **5** as well as mixtures of a homopolymer with the monomers **1**, **3** and **5** were studied by TLC. After the chromatography development, it was established that the dyes **1**, **3** and **5** in the mechanical mixtures (a mechanical blend of both homopolymer and monomer) moved at the same speed as the monomer dyes did and had the same values of retention factor R_f (Table 1), while the monomers in the copolymers, where they should be chemically bound, retained 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 compounds **1**, **3** and **5** to the polymer chain.

The UV–vis absorption spectra of the precipitated copolymers showed similar absorption maxima as those of the monomer dyes **1**, **3** and **5** (Table 4), which was an indication that no changes occurred in their basic chromophore systems, neither during the polymerization, nor as a result of their incorporation to the polymer chain. That is why the method of the standard calibration curve was used for spectrophotometrical determination of the content of a chemically bonded monomer in the polymer (Table 3).

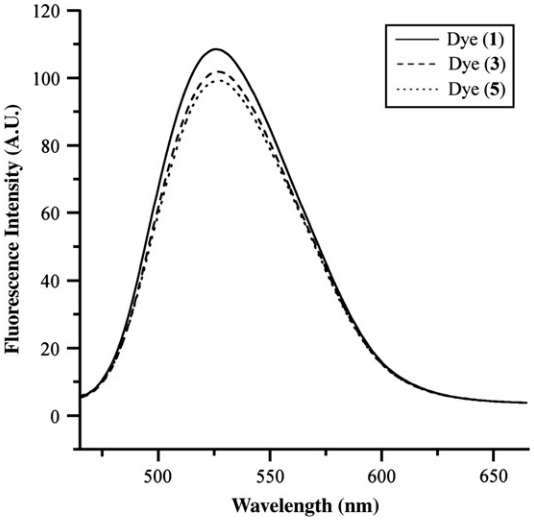


Fig. 2. Fluorescence spectra of FDs **1**, **3** and **5** at concentration 10^{-5} mol l^{-1} in DMF solution.

As it is seen from the data presented in Table 3, the amount of the chemically bonded dyes **3** and **5** is relatively smaller (0.068 wt% and 0.069 wt%, respectively) probably because of the lower activity of the polymerizable group in these compounds or it is bonded partially in the lower molecular weight fractions, which were removed during the precipitation. The reason for such behavior may be the large steric volume of the combined dye-stabilizer molecules. In contrast to dyes **3** and **5**, the content of the chemically bonded dye **1** (0.078 wt%) is higher with respect to the dyes, containing two different stabilizer fragments, which can be explained in a similar way, i.e. by the smaller steric volume of dye **1**. Nevertheless, bearing in mind that the data are referred to re-precipitated polymers and that during the re-precipitation not only the unreacted monomers, but also a part of the lower molecular fractions, containing a bound dye were removed, the results obtained are rather satisfactory and

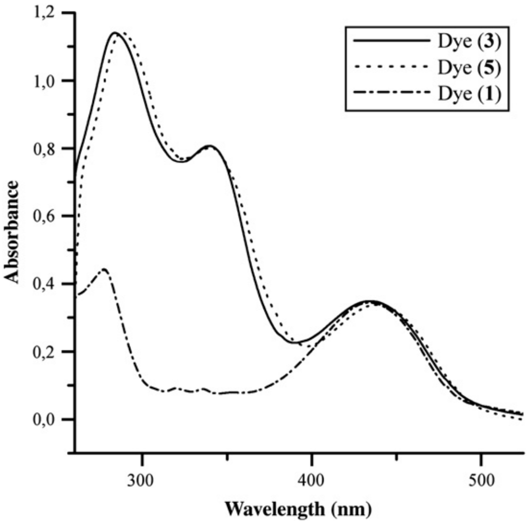


Fig. 1. Absorption spectra of FDs **1**, **3** and **5** at concentration 3.0×10^{-5} mol l^{-1} in DMF solution.

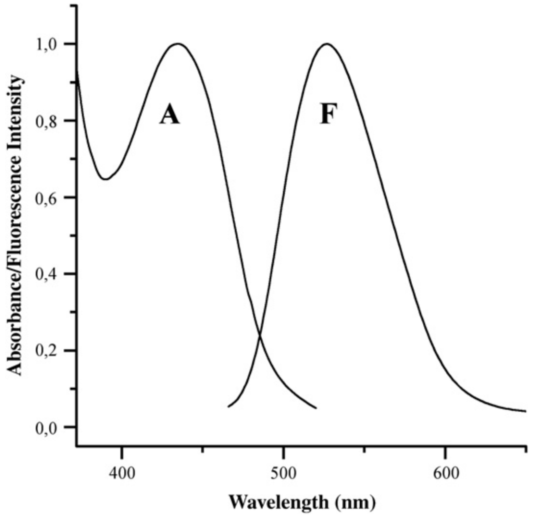


Fig. 3. Normalized absorption and fluorescence spectra of dye **3** in DMF solution at concentration 10^{-5} mol l^{-1} in DMF solution.

Table 3
Chemically bonded dye and yields for copolymers poly(AN-*co*-**1**, **3** and **5**)

Copolymer	Yield	FDs feed		Chemically bonded dye		
	(%)	(wt%)	(mmol%)	(wt%)[a]	(mmol%)[a]	(mol 10^6)[b]
PAN	90					
Poly(AN-*co*-**1**)	81	0.1	15.41	0.078	12.02	2.796
Poly(AN-*co*-**3**)	72	0.1	8.67	0.068	5.89	1.542
Poly(AN-*co*-**5**)	74	0.1	8.89	0.069	6.13	1.561

[a] Chemically bonded dye in respect to the starting monomer mixture.
[b] Content of the chemically bonded dye per 1 g of the precipitated copolymer.

imply that the new FDs **3** and **5** are suitable for production of fluorescent polyacrylonitrile copolymers. Data presented in Table 3 also show that the mole content of the chemically bonded dyes **3** and **5** in the precipitated copolymer is lower because of their relatively higher molecular weights (55–56% towards the mole content of dye **1**), which is particularly important for assessment the photostabilizing efficiency of novel compounds.

Detailed investigation for the influence of novel dyes on both polymerization process and polymer photostability will be the subject of our further work.

2.4. Photophysical characterization of fluorescent copolymers

Photophysical characteristics of yellow-green emitting copolymers were investigated in DMF solution. Table 4 presents the data obtained from the absorption and fluorescence spectra of the side-chain poly(AN-*co*-FDs **1**, **3** and **5**)s.

Absorption (λ_{A1} and λ_{A2}) and fluorescence (λ_F) maxima were observed at $\lambda_{A1} = 340–342$ nm (FDs **3** and **5**), $\lambda_{A2} = 440–442$ nm (FDs **1**, **3** and **5**) and $\lambda_F = 522–524$ nm, respectively. It is evident that the absorption and fluorescence maxima of the copolymers in solution are very similar to those of the monomeric FDs in the same solvent, which is an indication for further preservation of the dyes' chromophoric system during the process of copolymerization. The copolymers' quantum yield of fluorescence ($\Phi_F = 0.56–0.59$) was higher than that of the corresponding monomeric FDs (Table 2). This could be related to the decrease of emissionless processes and is obviously connected with the chemical bonding of the fluorophores to the polymer chain.

The yellow-green fluorescence of the poly(AN-*co*-FDs)s was more intense than that of the monomeric FDs. This phenomenon is due to the perfect incorporation of the FDs into the polymeric matrix, which hinders the conformational changes in the dyes' chromophoric system [28]. Thus, the part of emissionless deactivation during the transition $S_1 \rightarrow S_0$ is smaller.

Table 4
Absorption and fluorescence ($\lambda_{Ex} = \lambda_{A2}$) characteristics of copolymers poly(AN-*co*-**1**, **3** and **5**) in DMF solution

Copolymer	λ_{A1} (nm)	λ_{A2} (nm)	λ_F (nm)	$\nu_A - \nu_F$ (cm^{-1})	Φ_F	E_F
Poly(AN-*co*-**1**)	–	440	522	3570	0.59	0.497
Poly(AN-*co*-**3**)	342	442	524	3540	0.58	0.489
Poly(AN-*co*-**5**)	340	442	523	3504	0.56	0.473

3. Experimental

3.1. Materials

The starting 4-allylamino-*N*-(3-hydroxyphenyl)-1,8-naphthalimide **1** [10c,21], 2-(2,2,6,6-tetramethylpiperidin-4-ylamino)-4,6-dichloro-1,3,5-triazine **2** [20a], 2-(2,2,6,6-tetramethylpiperidin-1-yl)-4,6-dichloro-1,3,5-triazine **4** [17a,20a] and 4-nitro-1,8-naphthalic anhydride **6** [4,10c] were prepared according to the reported procedures. 3-Aminophenol **7**, cyanuric chloride **11**, 4-amino-2,2,6,6-tetramethylpiperidine **12**, 2,2,6,6-tetramethylpiperidine **13** and allylamine (Fluka), p.a. grade, were used without purification. All solvents (Fluka, Merck) used for the synthesis were of analytical grade. Commercial acrylonitrile (AN) was distilled before use. Dibenzoylperoxide (DBP, Fluka, 99.6%) re-crystallized from chloroform was used as an initiator of the free radical copolymerization.

3.2. Methods

FT-IR spectra were recorded on a Bruker IFS-113 spectrometer at 2 cm^{-1} resolution using KBr discs The NMR spectra were recorded on a Bruker DRX-250 spectrometer, operating at 250.13 MHz and 62.90 MHz for ^{1}H and ^{13}C, respectively, using a dual 5 mm probe head. The measurements were carried out in DMSO-d_6 solution at ambient temperature. The chemical shifts (given as δ in parts per million) were referenced to tetramethylsilane (TMS) standard. Experiments with 30° pulses, 1 s relaxation delays, 16 K time domain points, zero-filled to 64 K for protons and 32 K for carbons were performed. The distortionless enhancement by polarization transfer (DEPT) spectra were recorded under the conditions used for the ^{13}C NMR spectra at $\tau = (2^1J_{CH})^{-1} = 3.45$ µs. The UV–vis spectra were recorded on a Hewlett Packard 8452A spectrophotometer with 2 nm resolution at room temperature. The fluorescence spectra were taken on a Perkin Elmer LS55 spectrofluorimeter. The fluorescence quantum yields (Q_F) were measured relatively to Coumarin 6 ($Q_F = 0.78$ in ethanol) [27]. TLC was performed on silica gel, Fluka F60 254, 20 × 20, 0.2 mm, using as eluant the solvent systems *n*-heptane/acetone (1:1), *n*-propanol/ammonia = (1:1) and chloroform/methanol = (9:1). The melting points were determined by means of a Kofler melting point microscope.

3.3. Synthesis of fluorescent dyes

3.3.1. Preparation of 4-nitro-N-(3-hydroxyphenyl)-1,8-naphthalimide *8*

A suspension of 4-nitro-1,8-naphthalic anhydride **6** (3.65 g, 15 mmol) and 3-aminophenol **7** (1.64 g, 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 3.76 g (75%) of pure 4-nitro-*N*-(3-hydroxyphenyl)-1,8-naphthalimide **8** as pale yellow-brown crystals.

FT-IR (KBr), cm^{-1}: 3300 (νOH); 3078 (νArCH=); 1708 (ν^{as}C=O); 1669 (ν^{s}C=O); 1590 (νC=C); 1532 ($\nu^{as}NO_2$); 1370 ($\nu^{s}NO_2$); 1344 (νN–C–N).

^{1}H NMR (250.13 MHz, $CDCl_3$) δ (ppm): 8.67 (dd, 1H, $J = 7.3$, 1.1 Hz, naphthalimide 5-H); 8.54 (dd, 1H, $J = 8.1$, 1.1 Hz, naphthalimide 7-H); 8.40 (d, 1H, $J = 8.0$ Hz, naphthalimide 3-H); 8.15 (d, 1H, $J = 8.0$ Hz, naphthalimide 3-H); 7.80 (dd, 1H, $J = 8.1$, 7.3 Hz, naphthalimide 6-H); 7.14 (m, 3H, phenyl 2-H, 5-H and 6-H); 6.74 (dd, 1H, $J = 7.9$, 1.7 Hz, phenyl 4-H); 5.18 (br s, 1H, OH).

Elemental analysis: calculated for $C_{18}H_{10}N_2O_5$ (MW 334.28) C 64.67%, H 3.02%, N 8.38%; Found C 64.93%, H 2.97%, N 8.47%.

3.3.2. General preparation procedure for intermediates **9** and **10**

To a solution of *s*-triazinylpiperidine **2** or **4** (10 mmol) and 1.34 g of $AlCl_3$ (10 mmol) in 100 ml of xylene, 3.34 g of 4-nitro-*N*-(3-hydroxyphenyl)-1,8-naphthalimide **8** were added at room temperature. The resulting mixture was heated slowly to 60 °C and stirred at this temperature for 3 h. Then the reaction mixture was heated slowly to 90 °C, held at this temperature for 5 h and finally, the mixture was stirred under reflux for 8 h. After cooling the resulting solution was poured into 150 g of ice. Organic phase (xylene) was removed and the water phase was acidified to pH 2 with 10% hydrochloric acid. The solid was filtered off, washed with fresh water and dried to give 3.61 g (58%) of intermediate **9** or 3.64 g (62%) of intermediate **10** as a pale brown solid.

*3.3.2.1. 2-{4-[4-Chloro-6-(2,2,6,6-tetramethylpiperidin-4-ylamino)-1,3,5-triazin-2-yl]-3-hydroxyphenyl}-6-nitro-1H-benzo[de]isoquinoline-1,3(2H)-dione (**9**).* FT-IR (KBr), cm^{-1}: 3298, 3280 (νNH); 3076 (νCH=); 3014 (νOH···N); 2882 (νCH_3); 1710 (ν^{as}C=O); 1674 (ν^{s}C=O); 1596 (νC=C); 1528 ($\nu^{as}NO_2$); 1369 ($\nu^{s}NO_2$); 1344 (νN–C–N).

^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 9.72 (s, 1H, OH); 8.88 (dd, 1H, $J = 8.7$, 1.2 Hz, naphthalimide 5-H); 8.76 (dd, 1H, $J = 7.4$, 1.2 Hz, naphthalimide 7-H); 8.72 (d, 1H, $J = 8.0$ Hz, naphthalimide 3-H); 8.42 (d, 1H, $J = 8.0$ Hz, naphthalimide 2-H); 7.92 (dd, 1H, $J = 8.7$, 7.4 Hz, naphthalimide 6-H); 7.41 (d, 1H, $J = 8.2$ Hz, phenyl 5-H); 7.24 (m, 2H, phenyl 2-H and 5-H); 5.03 (m, 1H, piperidine CH); 3.64 (br s, 1H, NH); 2.58 (t, 2H, $J = 12.1$ Hz, piperidine CH_2); 2.24 (br s, 1H, NH); 1.62 (dd, 2H, $J = 12.1$, 2.2 Hz, piperidine CH_2); 1.31 (s, 6H, piperidine $2 \times CH_3$); 1.20 (s, 6H, piperidine $2 \times CH_3$).

Elemental analysis: calculated for $C_{30}H_{28}ClN_7O_5$ (MW 602.04) C 59.85%, H 4.69%, N 16.29%; Found C 60.13%, H 4.76%, N 16.18%.

*3.3.2.2. 2-{4-[4-Chloro-6-(2,2,6,6-tetramethylpiperidin-1-yl)-1,3,5-triazin-2-yl]-3-hydroxyphenyl}-6-nitro-1H-benzo[de]isoquinoline-1,3(2H)-dione (**10**).* FT-IR (KBr), cm^{-1}: 3066 (νCH=); 3012 (νOH···N); 2876 (νCH_3); 1708 (ν^{as}C=O); 1670 (ν^{s}C=O); 1598 (νC=C); 1540 ($\nu^{as}NO_2$); 1360 ($\nu^{s}NO_2$); 1336 (νN–C–N).

^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 9.79 (s, 1H, OH); 8.89 (dd, 1H, $J = 8.8$, 1.0 Hz, naphthalimide 5-H); 8.81 (dd, 1H, $J = 7.4$, 1.0 Hz, naphthalimide 7-H); 8.78 (d, 1H, $J = 8.1$ Hz, naphthalimide 3-H); 8.46 (d, 1H, $J = 8.1$ Hz, naphthalimide 2-H); 7.93 (dd, 1H, $J = 8.7$, 7.4 Hz, naphthalimide 6-H); 7.44 (d, 1H, $J = 8.1$ Hz, phenyl 5-H); 7.26 (m, 2H, phenyl 2-H and 5-H); 2.82 (m, 6H, piperidine $3 \times CH_2$); 1.36 (s, 6H, piperidine $2 \times CH_3$); 1.22 (s, 6H, piperidine $2 \times CH_3$).

Elemental analysis: calculated for $C_{30}H_{27}ClN_6O_5$ (MW 587.03) C 61.38%, H 4.64%, N 14.32%; Found C 61.17%, H 4.58%, N 14.45%.

3.3.3. General preparation procedure for fluorescent dyes **3** and **5**

To a solution of intermediate **9** or **10** (5 mmol) in 50 ml of DMF, 0.38 ml of allylamine (0.29 g, $d = 0.76$, 5 mmol) was added at room temperature. After 36 h (TLC control in a solvent system chloroform/methanol = 9:1), 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 hot mixture solvent of water (5 ml) 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 2.14 g (70%) of dye **3** and 2.18 g (73%) of dye **5** as a yellow-orange solid.

*3.3.3.1. 6-(Allylamino)-2-{4-[4-chloro-6-(2,2,6,6-tetramethylpiperidin-4-ylamino)-1,3,5-triazin-2-yl]-3-hydroxyphenyl}-1H-benzo[de]isoquinoline-1,3(2H)-dione (**3**).* FT-IR (KBr), cm^{-1}: 3304, 2976 (νNH); 3066 (νCH=); 3018 (νOH···N); 2880 (νCH_3); 1696 (ν^{as}C=O); 1668 (ν^{s}C=O); 1658 (νC=N); 1600 (νC=C).

^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 9.70 (s, 1H, OH); 8.54 (dd, 1H, $J = 7.6$, 1.1 Hz, naphthalimide 7-H); 8.42 (dd, 1H, $J = 8.1$, 1.1 Hz, naphthalimide 5-H); 8.12 (d, 1H, $J = 8.4$ Hz, naphthalimide 2-H); 7.61 (dd, 1H, $J = 8.1$, 7.6 Hz, naphthalimide 6-H); 7.29 (d, 1H, $J = 8.3$ Hz, phenyl 5-H); 7.20 (m, 2H, phenyl 2-H and 5-H); 6.69 (d, 1H, $J = 8.4$ Hz, naphthalimide 3-H); 6.04 (m, 1H, allyl CH=); 5.49 (br s, 1H, NH); 5.36 (d, 1H, $J_{trans} = 17.1$ Hz, allyl H*CH*=); 5.29 (d, 1H, $J_{cis} = 10.4$ Hz, allyl H*CH*=); 5.03 (m, 1H, piperidine CH); 4.08 (dd, 2H, $J = 4.9$, 0.9 Hz, allyl NCH_2); 3.41 (br s, 1H, NH); 2.60 (t, 2H, $J = 12.1$ Hz, piperidine CH_2); 2.17 (br s, 1H, piperidine NH); 1.66 (dd, 2H, $J = 12.1$, 2.2 Hz, piperidine CH_2); 1.38 (s, 6H, piperidine $2 \times CH_3$); 1.22 (s, 6H, piperidine $2 \times CH_3$).

^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 171.8 (triazine Ar–C=N); 164.4 (triazine N=C–Cl); 163.1 (Ar–C–OH); 160.1 (triazine N=C–NH); 157.8 ($2 \times$ C=O); 149.9 (Ar–C–NH); 143.5 (Ar–*C*–N–C=O); 137.5 (Ar–C); 136.3 (allyl CH=); 131.4; 129.8; 128.3; 127.2; 119.7;

114.4; 106.1 and 92.4 (Ar CH); 124.2 and 120.3 (Ar C); 116.3 (allyl $CH_2{=}$); 104.2 (Ar $2 \times C{-}C{=}O$); 55.8 (piperidine $2 \times C{-}Me$); 49.6 (piperidine $2 \times CH_2$); 46.2 (allyl NCH_2); 43.9 (piperidine CH); 34.7 and 27.9 (piperidine $4 \times CH_3$).

Elemental analysis: calculated for $C_{33}H_{34}ClN_7O_3$ (MW 612.12) C 64.75%, H 5.60%, N 16.12%; Found C 65.01%, H 5.52%, N 15.90%.

*3.3.3.2. 6-(Allylamino)-2-{4-[4-chloro-6-(2,2,6,6-tetramethylpiperidin-1-yl)-1,3,5-triazin-2-yl]-3-hydroxyphenyl}-1H-benzo[de]isoquinoline-1,3(2H)-dione (**5**).* FT-IR (KBr), cm^{-1}: 3292 (νNH); 3060 (νCH=); 3014 (νOH···N); 2878 (νCH_3); 1700 ($\nu^{as}C{=}O$); 1666 ($\nu^{s}C{=}O$); 1656 ($\nu C{=}N$); 1598 ($\nu C{=}C$).

^1H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 9.39 (s, 1H, OH); 8.55 (dd, 1H, $J = 7.5$, 1.2 Hz, naphthalimide 7-H); 8.41 (dd, 1H, $J = 8.2$, 1.2 Hz, naphthalimide 5-H); 8.11 (d, 1H, $J = 8.5$ Hz, naphthalimide 2-H); 7.62 (dd, 1H, $J = 8.2$, 7.5 Hz, naphthalimide 6-H); 7.27 (d, 1H, $J = 8.4$ Hz, phenyl 5-H); 7.19 (m, 2H, phenyl 2-H and 5-H); 6.68 (d, 1H, $J = 8.5$ Hz, naphthalimide 3-H); 5.96 (m, 1H, allyl CH=); 5.35 (d, 1H, $J_{trans} = 17.3$ Hz, allyl H*CH*=); 5.28 (d, 1H, $J_{cis} = 10.5$ Hz, allyl H*CH*=); 4.17 (d, 2H, $J = 7.2$ Hz, allyl NCH_2); 3.11 (br s, 1H, NH); 1.83 (m, 6H, piperidine $3 \times CH_2$); 1.39 (s, 6H, piperidine $2 \times CH_3$); 1.21 (s, 6H, piperidine $2 \times CH_3$).

^{13}C NMR (62.90 MHz, DMSO-d_6) δ (ppm): 170.9 (triazine Ar−C=N); 163.9 (triazine N=C−Cl); 161.2 (triazine N=C−NH); 1593.5 (Ar−C−OH); 157.1 ($2 \times C{=}O$); 149.5 (Ar−C−NH); 144.1 (Ar−*C*−N−C=O); 137.2 and 124.2 (Ar−C); 135.5 (allyl CH=); 130.9; 129.5; 128.1; 123.6; 118.8; 114.1; 106.5 and 91.4 (Ar CH); 119.4 (Ar C−C=N); 116.2 (allyl $CH_2{=}$); 104.8 (Ar $2 \times C{-}C{=}O$); 57.6 (piperidine $2 \times C{-}Me$); 46.4 (allyl NCH_2); 42.5 (piperidine $2 \times CH_2$); 27.8 and 26.5 (piperidine $4 \times CH_3$). 18.5 (piperidine CH_2).

Elemental analysis: calculated for $C_{33}H_{33}ClN_6O_3$ (MW 597.11) C 66.38%, H 5.57%, N 14.07%; Found C 66.13%, H 5.66%, N 13.95%.

3.4. Polymerization of the dyes with AN

The free radical copolymerization of the monomer dyes **1**, **3** and **5** with AN was carried out in ampoules, purged with pure nitrogen before use. The process of copolymerization was conducted in a thermostat for 12 h at 70 °C in the presence of 0.5 wt% of DBP and 0.1 wt% of the corresponding monomers (**1**, **3** or **5**). The solid transparent side-chain colored copolymers thus obtained were several times re-precipitated with methanol from DMF in order to remove the non-reacted monomers. This process was controlled by TLC until filtrates were free of monomers **1**, **3** or **5**. The precipitated copolymers poly(AN-*co*-**1**, **3** or **5**) were repeatedly washed with methanol and dried in vacuum to constant weight at 40 °C. All spectroscopic measurements were carried out with precipitated copolymers.

4. Conclusions

Two novel polymerizable yellow-green emitting 1,8-naphthalimide dyes, combination of hindered amine light stabilizer and 2-(2-hydroxyphenyl)-1,3,5-triazine UV absorber fragments into the fluorophore structure have been successfully synthesized. The basic photophysical properties of the new compounds in solution have been determined and discussed. They were customary for the 1,8-naphthalimide derivatives. Also the combination of different structural units in one molecule did not result in their interaction as an intramolecular fluorescence quenching due to an electronic energy transfer. The ability of the synthesized dyes to copolymerize with AN was demonstrated. As a result of our investigation it can be concluded that the new dyes, containing both allyl function and free *s*-triazine chlorine, represent possibility for "one-step" chemical coloration and stabilization of polymers and/or textile materials.

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