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Synthesis and photophysical properties of polymerizable 1,8-naphthalimide dyes and their copolymers with styrene

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Abstract

Two highly fluorescent 4-alkylamino-*N*-allyl-1,8-naphthalimide dyes have been synthesised and their basic photophysical properties in ethanol and toluene solution have been determined. Synthesis and characterization of new side-group copolymers of styrene with the fluorescent 1,8-naphthalimide have been described. It has been established that 0.90–0.92% of the dyes are chemically bonded to the polymer chain. The absorption and fluorescent characteristics of copolymers in toluene and in the solid state are discussed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polymerizable 1,8-naphthalimides; Fluorescent side-group copolymers; Photophysical properties

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1. Introduction

The structural coloration of synthetic polymer materials gives the possibility of obtaining polymers with a colour stable to wet treatment and solvents [1–3]. The copolymers of traditional monomers with some polymerizable fluorescent units display intensive fluorescence [4]. Thus, using appropriate fluorophors, polymers of different fluorescent colour can be obtained.

It is well known that fluorescent 1,8-naphthalimide dyes have a bright colour and possess good dyeability with synthetic polymers [5]. They have found applications in sun energy collectors [6], laser active media [7,8], potential photosensitive biologically active units [9], also as fluorescent markers in biology [10], and in medicine [11,12]. Recently they have been examined in liquid crystals for utilisation in electro-optical devices [13–15]. The introduction of polymeric components into liquid crystals results in enhanced self-support of the display systems [16,17]. The copolymers of 1,8-naphthalimides with vinylcarbazol possess chemiluminiscent properties [18,19].

In previous papers we have reported on the synthesis and the properties of 4-amino-1,8-naphthalimide derivatives as dyes for polymers. The dyes possess an intensive yellow-green fluorescence and very good photostability [20–26]. Due to the presence of a polymerizable group the dyes can undergo polymerisation with some commercial monomers, allowing coloured copolymers with an intensive fluorescence to be obtained [27–30].

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It is worth synthesising other derivatives of 4-alkylamino-*N*-allyl-1,8-naphthalimide which might have a high quantum yield of fluorescence and an ability to polymerise with vinylic monomers. The present work reports on the synthesis of two new 1,8-naphthalimide derivatives with long chain alkylamino groups at the C-4 position of the naphthalimide structure and of their copolymers with styrene. The basic photophysical characteristics of the new monomeric and polymeric dyes were determined in isotropic media.

2. Experimental

2.1. Materials

Commercial styrene (St) was used after purification. Styrene was washed with an aqueous solution of NaOH, dried over CaH_2 and then distilled under reduced pressure in a pure nitrogen atmosphere (99.99%). Dibenzoyl peroxide (DBP) (Fluka), recrystallised from chloroform and methanol was used as initiator of the radical copolymerization reactions used.

2.2. General method for the synthesis of monomeric dyes **1** and **2**

4-Nitro-*N*-allyl-1,8-naphthalic anhydride, synthesised according to the method described recently [23], was reacted in a molar ratio with amines (butylamine or hexylamine) in 60 ml *N*,*N*-dimethylformamide (DMF) for 24 h at room temperature [15]. After that 600 ml of water were added to the solution and the precipitate was then filtered, washed with water and dried in vacuum at 40 °C.

Dyes **1** and **2** were characterised by m.p., TLC (R_f), and elemental analysis, UV/vis, fluorescent, FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

2.2.1. 4-Butylamino-N-allyl-1,8-naphthalimide (**1**)

Yield: 95%; m.p. 138–140 °C, $R_f = 0.37$ (*n*-heptane-acetone 1:1). Elemental analysis, calculated for $C_{19}H_{20}N_2O_2$ (308.1): C 74.00, H 6.49, N 9.08; found: C 74.21, H 6.54, N 9.17. FT–IR (KBr): 3379, 2955, 2931, 2870, 1683, 1640, 1580, 1370, 1247, 979, 936, 821, 773, 758 cm^{-1}. ^{1}H-NMR (DMSO-d_6, 250 MHz) ppm: 0.921 (*t*, 3H, $J = 7.3$ Hz, CH_3); 1.400 (six, 2H, $J = 7.3$ Hz, $C\underline{H}_2CH_3$); 1.661 (quint., 2H, $J = 7.3$ Hz, $CH_2C\underline{H}_2CH_2CH_3$); 3.368 (*t*, 2H, $J = 7.3$ Hz, $NHC\underline{H}_2CH_2$); 4.589 (*d*, 2H, $J = 5.0$ Hz, $NC\underline{H}_2CH=$); 5.045 (dd, 1H, $J = 18.6$ Hz, $=CH_2$ (*trans*); 5.065 (*d*, 1H, $J = 9.0$ Hz, $=CH_2$ (*cis*); 5.896 (*m*, 1H, $-CH=$); 6.730 (*d*, 1H, $J = 8.7$ Hz, ArH-2); 7.638 (*t*, 1H, $J = 7.9$ Hz, ArH-4); 7.749 (*t*, 1H, $J = 5.2$ Hz, NH); 8.218 (*d*, 1H, $J = 8.7$ Hz, ArH-1); 8.390 (*d*, 1H, $J = 7.0$ Hz, ArH-3); 8.657 (*d*, 1H, $J = 8.3$ Hz, ArH-5).

2.2.2. 4-Hexylamino-N-allyl-1,8-naphthalimide (**2**):

Yield: 92%; m.p. 71–72 °C, $R_f = 0.32$ (*n*-heptane-acetone 1:1). Elemental analysis, calculated for $C_{21}H_{24}N_2O_2$ (336.1): C 74.97, H 7.14, N 8.33; C 75.15, H 7.29, N 8.42. FT–IR (KBr): 3389, 2953, 2928, 2856, 1683, 1640, 1579, 1547, 1371, 1246, 978, 928, 829, 773, 758 cm^{-1}. ^{1}H-NMR (DMSO-d_6, 250 MHz) ppm: 0.853 (*t*, 3H, $J = 7.2$ Hz, CH_3); 1.270 (*m*, 6H, $C\underline{H}_2C\underline{H}_2C\underline{H}_2CH_3$); 1.681 (quint, 2H, $J = 7.2$ Hz, $NHCH_2C\underline{H}_2CH_2$); 3.333 (*t*, 2H, $J = 7.2$ Hz, $NHC\underline{H}_2$); 4.601 (*d*, 2H, $J = 5.2$ Hz, $NC\underline{H}_2CH=$); 5.050 (*dd*, 1H, $J = 18.5$ Hz, $=CH_2$ (*trans*); 5.071 (*d*, 1H, $J = 9.0$ Hz, $=CH_2$ (*cis*); 5.892 (*m*, 1H, $-CH=$); 6.754 (*d*, 1H, $J = 8.7$ Hz, ArH-2); 7.657 (*t*, 1H, $J = 7.8$ Hz, ArH-4); 7.767 (*t*, 1H, $J = 5.2$ Hz, NH); 8.237 (*d*, 1H, $J = 8.7$ Hz, ArH-1); 8.417 (*d*, 1H, $J = 6.9$ Hz, ArH-3); 8.672 (*d*, 1H, $J = 7.8$ Hz, ArH-5).

2.3. Copolymerization of monomeric dyes with styrene

The free radical copolymerization of the 1,8-naphthalimide dyes **1** and **2** with styrene was carried out in bulk: 10 g purified styrene, 0.1 g of the dyes and 0.1 g DBP were mixed in an ampoule flushed with dry and pure nitrogen. The ampoule was sealed and heated at 70 °C in a thermostat for 10 h. The solid, transparent copolymers which have an intense yellow-green fluorescence, were dissolved in benzene and precipitated with ethanol, in order to remove the non interacted dyes and styrene monomers. The precipitated copolymers were dried in vacuum at 40 °C to a constant weight.

Thin polymeric films (50 μm) used for all spectral investigations were obtained from 10% solution of poly(St-co-dye) in toluene.

2.4. Methods

2.4.1. Determination of relative molecular weight

The number- and weight-average molecular weights of the copolymers were determined on a GPC Waters 244 apparatus using THF as solvent at a flow rate of 1.0 ml min^{-1} at 45 °C. Both differential refractive index and UV–vis absorption detectors ($\lambda_A = 420$ nm) were used. Polystyrene calibration was used for all molecular mass calculations.

2.4.2. Analysis

UV–vis spectrophotometric investigations of monomeric 1,8-naphthalimide dyes and poly(St-co-dye) copolymers were performed using a Hewlett-Packard 8452 spectrophotometer. UV-vis spectra of both poly(St-co-dye) and of the dyes in toluene and ethanol were recorded. Determination of the amount of covalently bound dyes was investigated using UV–vis spectroscopy in toluene solution. Likewise, unreprecipitated (1 g) and repeatedly reprecipitated (1 g) poly(St-co-dye) were dissolved in toluene (25 ml). UV–vis spectra were taken. The amount of the covalently bound dye was calculated based on the relationship between the reprecipitated polymer absorption and that of the unreprecipitated polymer.

The fluorescence spectra of monomeric 1,8-naphthalimide dyes (toluene and ethanol) and poly(St-co-dye) in toluene solutions and in solid film were taken on a Perkin-Elmer MPF 44.

IR spectra were measured on a Brüker IFS-113v spectrometer, by using a KBr pelette technique (monomeric dyes) and thin pollymeric films (polystyrene and copolymers) at a 2 cm^{-1} resolution.

The ^{1}H- and ^{13}C-NMR spectra of dyes **1** and **2** were recorded on a Brüker spectrometer at 250 and 75 MHz, respectively. Deuteriodimethylsulfoxide and tetramethylsilane were used as a solvent and an internal standard, respectively.

Thin layer chromatography (TLC) analysis of the monomeric dyes and the copolymers were followed on silicagel (Fluka F_{60} 254 20×20; 0.2 mm) using the solvent system n-heptane/acetone (1:1) as eluant.

3. Results and discussion

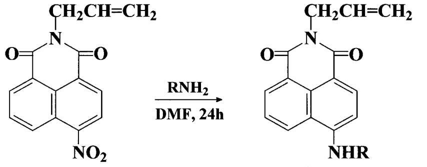
3.1. Synthesis of 4-alkylamino-N-allyl-1,8-naphthalimide dyes

The synthetic route used for the preparation of 4-alkylamino-*N*-allyl-1,8-naphthalimide dyes is presented in Scheme 1.

4-Nitro-*N*-allyl-1,8-naphthalimide, has recently been synthesised by condensation of 4-nitro-1,8-naphthalic anhydride with allylamine in ethanol solution [23]. Dyes **1** and **2** were obtained in good yields by nucleophilic substitution of the nitro group with primary aliphatic amines H_2NR in DMF [15]. In this case, the electron accepting carbonyl group of the naphthalimide molecule favours the nucleophilic substitution reactions of the nitro group with aliphatic amines H_2NR.

3.2. FTIR investigations of the monomeric dyes

The dyes **1** and **2** containing an amino group (−NH) showed absorption bands in the 3379–3389 cm^{-1} region. The bands at 3078–3080 cm^{-1} were assigned to the ν_{CH} vibration. Bands at 1615–1616, 1579–1580 and 1546–1547 cm^{-1}, assigned to the ν_{CC} vibrations, observed in the dyes spectra are characteristic of the aromatic system in the naphthalene ring of the naphthalimide structure. The bands at 773–758 cm^{-1} are characteristic of the deformation vibrations of aromatic ring. The allylic group ($CH_2CH{=}CH_2$) has characteristic bands at 928–936 cm^{-1} for the $=CH_2$ and 978–979 cm^{-1} for the $=CH$ groups. It is well known that imides give an increase in the two frequency bands of the symmetric C=0 (str) groups [31]. The IR spectra of dyes **1** and **2** show intensive absorption bands at 1683 and 1640 cm^{-1}, respectively, which are



where **R**= $-CH_2CH_2CH_2CH_3$ (dye **1**), $-CH_2CH_2CH_2CH_2CH_2CH_3$ (dye **2**)

Scheme 1. Synthesis of monomeric fluorescent 1,8-naphthalimide dyes.

characteristic of the symmetric ν_S and asymmetric ν_{AS} carbonyl vibrations, the latter being separated from each other in the compounds by 43 cm^{-1} for both dyes. The intensive bands at 2955–2931 cm^{-1} in dyes **1** and **2** are characteristic of the vibration of $-CH_2-$ groups.

3.3. ^{13}C-NMR investigations of the monomeric 1,8-naphthalimide dyes

The data from ^{13}C-NMR spectra are presented in Table 1. The number of carbon atoms are presented in Scheme 3.

The total number of peaks for dye **1** (19) and dye **2** (21) corresponds exactly to the different C atoms of the dyes. Each carbon atom produces a different signal in the spectrum. Non proton bearing carbon atoms of the carbonyl group C=O appear at the high field of 162.8–163.7 ppm. In the 120–135 ppm region the peaks are characteristic of the aromatic carbon atoms, while aliphatic carbon atoms have peaks in the 14.0–60.4 ppm region. The signal for ^{1}C with amino substituents at a *para* position is shifted to higher ppm values in comparison to those of ^{8}C having an hydrogen atom at a *para* position [32]. ^{4}C atom possesses a peak at 151 ppm due to its polarization by the N atom of the C–N bond. The peaks at 70.4 ppm ($N-CH_2-$), 104.0 ppm ($-CH=$) and 116.0 ppm ($=CH_2$) are characteristic of the allylic group [33].

Table 1
^{13}C-NMR (75 MHz, DMSO-d_6, ref TMS) assignments of 1,8-naphthalimide dyes **1** and **2** (see text)

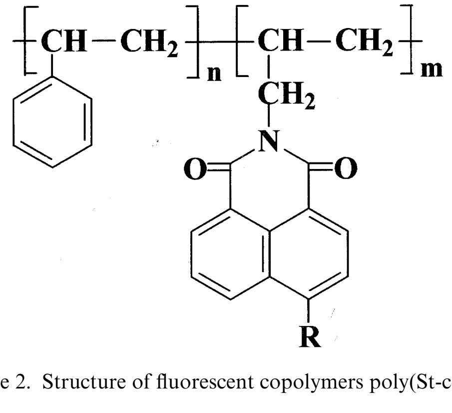
C-number	Dye **1**	Dye **2**
	δC (ppm)	δC (ppm)
1	107.3	105.7
2	133.4	133.4
3	124.5	124.5
4	151.0	151.0
5	131.0	131.0
6	128.5	128.9
7	134.6	134.7
8	129.7	129.7
9	121.8	121.9
10	120.3	120.3
11	163.7	163.7
12	162.8	162.8
13	72.4	72.4
14	104.0	104.0
15	116.1	116.1
16	60.4	60.4
17	30.1	31.3
18	20.0	28.0
19	14.0	14.1
20	–	26.5
21	–	22.3

3.4. Synthesis of copolymers

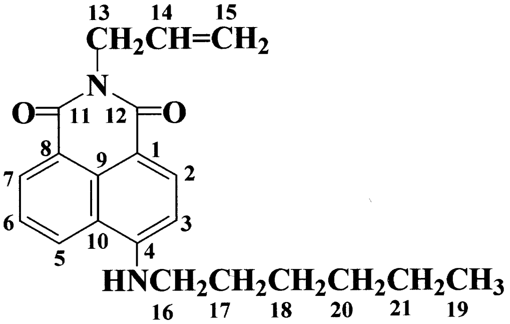
The copolymerization of styrene with dyes **1** and **2** was carried out in the presence of 1% by mass DBP and 1% by mass dye. The copolymerization process was conducted under conditions used with other similar to 1,8-naphthalimide derivatives [16,27]. Transparent coloured polymers with an intensive yellow–green fluorescence were obtained. After a three- to four-fold precipitation, in order to remove the unreacted monomers, the copolymers retained their colour, indicating that the dye was chemically bonded to the polymer chain. The coloured fluorescent poly(St-co-dye) has a structure presented in Scheme 2.

The molecular characteristics of the copolymers obtained are listed in Table 2. The determination of molecular weight and polydispersity confirmed the formation of high molecular weight polymers. The presence of the copolymers is revealed by the close double detection values for the elution time in both chromatograms—absorbance at about 420 nm; the polydispersity Mw/Mn is in the range 1.80–1.84.

The presence of a covalent bond between the monomeric units of styrene and the low molecular



Scheme 2. Structure of fluorescent copolymers poly(St-co-dye).



Scheme 3. Number of carbon atoms of 1,8-naphthalimide.

weight dyes in the copolymers is more directly proved when comparing the IR absorption spectra of the low molecular weight dyes with those of the homo- and copolymers [16,28,34]. Fig. 1 shows the IR spectra of dye **1**, homostyrene and poly(St-co-dye **1**). The comparison of the spectra of homopolystyrene and poly(St-co-dye **1**) has shown a considerable difference in the absorption bands of the polymers in the 1600–1750 cm^{-1} region. In the spectrum of poly(St-co-dye **1**) the absorption band at 1690–1656 cm^{-1} corresponds to the carbonyl groups from dye **1**.

It is worth studying the bonding of dyes to the polymer chain. The amount of dyes **1** and **2** incorporated into the macromolecules determined spectrophotometrically is within 0.90–0.92% (Table 2). Considering that the values are obtained for repeatedly precipitated polymers, where the low molecular weight fractions have been removed during precipitation, the results are rather satisfactory and imply that the dyes are suitable for production of coloured fluorescent copolymers.

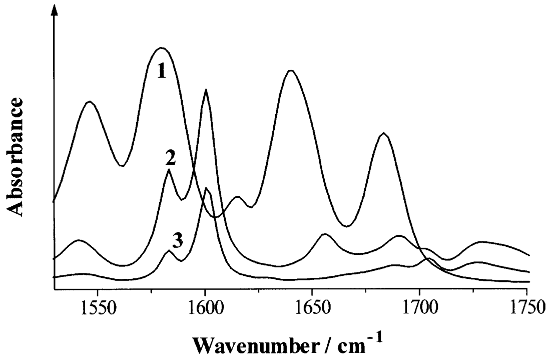


Fig. 1. FT–IR spectra of (1) dye **1**, (2) poly(St-co-dye **1**), (3) pure polystyrene.

Table 2
Molecular characteristics and chemically bonded dye of the copolymers

Copolymers	Mw	Mn	Mw/Mn	Chemically bonded dye (%)
Poly(St-co-dye **1**)	241 000	134 000	1.80	92
Poly(St-co-dye **2**)	212 000	115 000	1.84	90

3.5. Spectral characteristics of monomeric dyes

Absorption and fluorescence spectra of the monomeric dyes were recorded in polar ethanol ($\varepsilon = 24.80$) and non polar toluene ($\varepsilon = 2.38$) solutions; the data are presented in Table 2. The absorption (λ_A) and fluorescent maxima (λ_F), and the extinction coefficient (log ε) of the dyes are shown. Stokes shift (ν_A–ν_F), oscillator strength (*f*) and the quantum fluorescence yield Φ_F are also presented. The polarization of the naphthalimide molecule is governed by the donor–acceptor interactions between its electron-donating substituents at the C-4 position and the electron-accepting carbonyl group, while charge transfer along the chain of conjugated double bonds led to absorption in the visible region for dyes **1** and **2**. The long-wavelength band of the absorption spectrum in the visible region was a band of charge transfer/CT/, due to $\pi \rightarrow \pi^*$ electron transfer on $S_0 \rightarrow S_1$ transition. The dyes exhibit yellow–green colour and intense fluorescence, with absorption maxima $\lambda_A = 438$–440 nm in ethanol and $\lambda_A = 420$–422 nm in toluene solutions. The fluorescence maxima are $\lambda_F = 523$–525 nm in ethanol and $\lambda_F = 500$–502 nm in toluene. In comparison with the protic ethanol, the absorption and fluorescence maxima in toluene are hypsochromically shifted ($\Delta\lambda_A = 18$ nm and $\Delta\lambda_F = 21$–25 nm), as the polarisation of the dye molecule is strongly depended on the solvents' polarity. The Stokes shift is a parameter which indicates the difference in the properties and structure of the dyes between the ground state S_0 and the first exited state S_1. The Stokes shift values are between 3697–3889 cm^{-1} for ethanol and 4271–4351 cm^{-1} for toluene solution, respectively, as common for this class of 1,8-naphthalimide dyes [35–37]. The quantum fluorescence yield Φ_F are determined on the basis of absorption and fluorescence spectra of dyes in ethanol and toluene. As seen from the data in Table 3, it is seen that the dyes had quantum yield values $\Phi_F = 0.70$–0.74 (ethanol) and $\Phi_F = 0.86$–0.88 (toluene). A comparison of these results with those from previous studies on similar 1,8-naphthalimide polymerizable dyes [21] shows the tendency of Φ_F to decrease with the elongation of the alkyl group at the C-4 atom in the chromophoric system. This could be produced by the greater probability of conformation changes to occur with the elongation of the carbon–hydrogen substituent chain at C-4 position. The quantum yield for the dyes increases with the transition from ethanol to the less polar toluene. The difference in Φ_F for dyes **1** and **2** in separate is not large, therefore the Φ_F dependence on the solvent is assigned to a possible solute–solvent interactions.

An important characteristic of the dyes is the oscillator strength (f) which shows the effective number of electrons whose transition from ground to excited state gives the absorption area in the electron spectrum. Values of oscillator strength are calculated using equation (1) [38]:

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

where $\Delta\nu_{1/2}$ is the width of the absorption band (in cm^{-1}) at $1/2\varepsilon_{\max}$.

The value of f varies: 0.238 (dye **1**) and 0.223 (dye **2**) in ethanol, and 0.321 (dye **1**) and 0.312 (dye **2**) in toluene (Table 3). The calculated value for the dyes in ethanol was lower that in toluene, which correlates well with the hypochromic effect of the ethanol (cc. log ε).

Table 3
Photophysical characteristics of 1,8-naphthalimide dyes **1** and **2** in ethanol and toluene solutions

	Ethanol		Toluene	
	Dye **1**	Dye **2**	Dye **1**	Dye **2**
λ_A (nm)	440	438	422	420
log ε	4.16	4.10	4.24	4.19
λ_F (nm)	525	523	500	502
(ν_A–ν_F) (cm^{-1})	3679	3710	3697	3889
f	0.238	0.223	0.321	0.312
Φ_F	0.74	0.70	0.88	0.86

The interaction of the π-donating amino groups in the C-4 position of the dyes molecules and the π-accepting carbonyl group and its effect upon absorption depends on the polarity of solvents. Fig. 2 shows as an example, the dependence of the absorption maximum of the CT band for dye **1** on the empirical parameter of solvent polarity $E_T(30)$ [39]. As seen from the figure, the polarity of the solvents influences significantly the spectral properties of the dyes. Changes in the position of the CT band of dye **1** in various solvents are brought about by the solvatochromic effect of the solvent. As it can be seen, dye **1** has a positive solvatochromism, so does dye **2**. The linear character of the dependence indicates that dipole-dipole interactions prevail in the dye solution.

3.6. Spectral characteristics of copolymers

The copolymers poly(St-co-dye) are coloured yellow–green. The copolymers are soluble in the solvents common for the homopolystyrene. Table 4 presents the data obtained from the basic photophysical characteristics of the side-group copolymers poly(St-co-dye) in toluene. The absorption

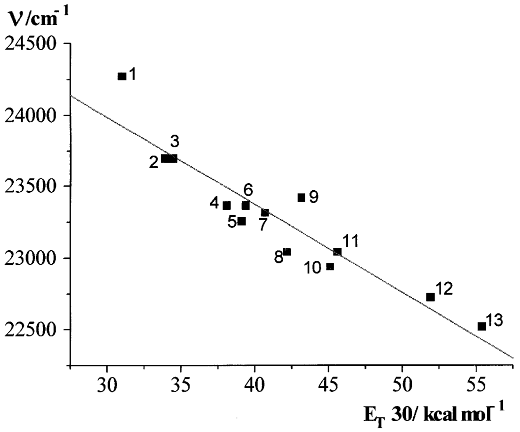


Fig. 2. Dependence of absorption maximum of dye **1** on the empirical parameters of solvent polarity $E_T(30)$. Solvents used: 1, hexane;, 2, toluene; 3, benzene; 4, ethylacetate; 5, chloroform; 6, dichloroethane; 7, dichloromethane; 8, acetone; 9, *N,N*-dimethylformamide; 10, dimethylsulfoxide; 11, acetonitrile; 12, ethanol; 13, methanol.

Table 4
Photophysical characteristics of coloured copolymers in toluene solution

	Poly(St-co-dye **1**)	Poly(St-co-dye **2**)
λ_A nm	420	423
ε (l g^{-1} cm^{-1})	0.052	0.049
λ_F (nm)	501	504
$(\nu_A - \nu_F)$ (cm^{-1})	3849	3799
Φ_F	0.92	0.90

maxima of the copolymers are in the range 420–423 nm. The fluorescence spectra of the copolymers in toluene solution show maxima at $\lambda_F = 501$–504 nm. The absorption and fluorescence maxima of the copolymers are very similar to those of the monomeric dyes **1** and **2** in the same solution indicating further the preservation of the chromophoric system during the copolymerization. The quantum fluorescence yield Φ_F of the copolymers with $\Phi_F = 0.90$–0.92 is higher than those for the monomeric dyes themselves. This is connected with the decrease of emissionless processes and is obviously in relation to the bonding of the chromophore to the polymer chain.

The absorption maxima λ_A of the copolymers in thin polymer films are in 415–416 nm for both copolymers (Table 5). The dyes **1** and **2** exhibit similar absorption properties in toluene solution and in a solid polymeric film, as a result from their similar polarity, with values near to the dielectric constants: ε(toluene) = 2.38, ε (polystyrene) = 2.40–2.65 [40]. The fluorescence maxima of thin solid film are in the 498–500 nm region. However, the fluorescence spectra of the solid polymer films differ significantly from those in toluene solution being bathochromically shifted, because of the rigidity of the structure. Obviously the results do not show evidence any structural changes in the chromophoric system owing to the polystyrene matrix and/or to the polymerization process such that can alter their spectral properties.

Table 5
Absorption λ_A and fluorescence λ_F maxima and Stokes shift $(\nu_A - \nu_F)$ of poly(St-co-dye) in solid state

Copolymers	λ_A (nm)	λ_F (nm)	$(\nu_A - \nu_F)$ (cm^{-1})
Poly(St-co-dye **1**)	416	498	3978
Poly(St-co-dye **2**)	415	498	4016

4. Conclusions

4-Alkylamino-*N*-allyl-1,8-naphthalimide derivatives are obtained in high yields by a two-step synthesis from 4-nitro-1,8-naphthalic anhydride. The final naphthalimide dyes absorb in the visible region exhibiting yellow-green fluorescence with a high quantum yield. The dyes under study are being investigated for application in dyeing of polymeric materials to obtain coloured and fluorescent polystyrene copolymers. On the basis of the present investigations it can be assumed that the monomeric 1,8-naphthalimide dyes investigated are suitable for obtaining coloured fluorescent polystyrene.

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