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Journal of Photochemistry and Photobiology A: Chemistry 162 (2004) 207–212
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Novel adducts of a hindered amine and a blue-emitting fluorophore for "one-step" fluorescent brightening and stabilisation of polymer materials

Vladimir B. Bojinov*

Department of Organic Synthesis, University of Chemical Technology and Metallurgy, 8 Kliment Ohridsky Str., 1756 Sofia, Bulgaria

Received 4 July 2003; received in revised form 4 July 2003; accepted 29 July 2003

Abstract

Two new monomeric 1,8-naphthalimide blue-emitting fluorophores, containing hindered amine stabiliser fragment have been synthesised for the first time using phase-transfer catalysis conditions. Their ability for simultaneously fluorescent brightening and stabilisation of polyacrylonitrile has been demonstrated. The chemical bonding of the synthesised 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 polymerisation did not affect considerably the co-polymers' molecular weight. A significant stabilising effect against photodegradation was determined.

Keywords: Polymerisable adducts; 1,8-Naphthalimide blue-emitting fluorophores; 2,2,6,6-Tetramethylpiperidines; Phase-transfer catalysis; Co-polymerisation; Photostability

1. Introduction

During the last few years, a large number of light-emitting polymers have been investigated intensively [1,2]. Polymers with aromatic or heteroaromatic fluorophores absorb light with wavelength in the range from 300 to 500 nm due to π–π^* transition and re-emit the light as fluorescence with different colour.

Naphthalimide derivatives usually exhibit strong fluorescent emission on irradiation and are well known to act as photo-induced electron-transfer sensors [3], fluorescence switchers [4], liquid crystal displays [5] or electroluminescent materials [6]. Their fluorescence emission can be widely tuned (from blue through yellow to green) with amino- and alkoxy-groups at the 4-position of naphthalimide [7]. 4-Alkoxy-1,8-naphthalimides are a new type of electron-transporting emitting materials. They act as an additional light source by transforming the absorbed UV light of terrestrial solar irradiation, below about 400 nm, re-emitting the light as a violet–blue fluorescence in the visible region [8]. In the recent years, 4-alkoxy-1,8-naphthalimide derivatives have aroused the scientific interest because of their potential use as fluorophores for synthetic blue fluorescent polymers [9]. Due to the presence of a polymerisable group, they can polymerise with some commercial monomers, allowing to obtain co-polymers with an intensive blue fluorescence [9c,10].

On the other hand, as a possible way to improve the polymer photostability, a number of different stabilisers have successfully been used [11]. Among them, hindered amines such as 2,2,6,6-tetramethylpiperidine derivatives are of a great interest due to their high photostabilising efficiency [12]. They inhibit the process of autoxidation by transformation of the parent amines to *N*-oxyl radicals, either by reaction with peroxyl radicals or occasionally by reaction with singlet oxygen, which stop oxidative degradation by coupling of alkyl radicals [13].

A combination of 2,2,6,6-tetramethylpiperidine and 4-alkoxy-1,8-naphthalimide fragments in one molecule could result in a new type of fluorescent brighteners capable of photostabilising the polymer materials. Here, the synthesis of two new polymerisable adducts of a hindered amine and a blue-emitting fluorophore, 6-allyloxy-2-(2,2,6,6-tetramethylpiperidin-4-yl)-benzo[*de*]isoquinoline-1,3-dione **5** (Scheme 1) and 2-allyl-6-(2,2,6,6-tetramethylpiperidin-4-yloxy)-benzo[*de*]isoquinoline-1,3-dione **8** (Scheme 2), and their potential for simultaneously fluorescent brightening and photostabilisation of polyacrylonitrile (PAN) are reported.

* Tel.: +359-2-6254359.
E-mail address: vlbojin@uctm.edu (V.B. Bojinov).

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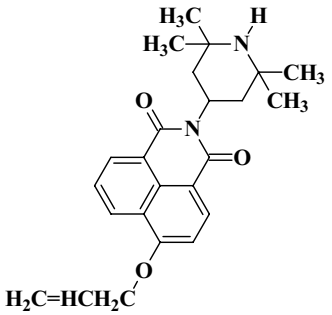
doi:10.1016/S1010-6030(03)00354-X



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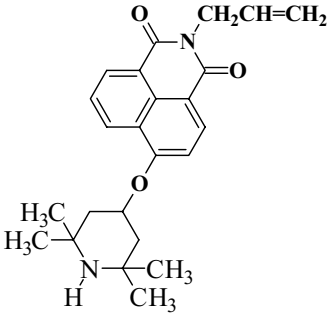
Scheme 1.



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Scheme 2.

2. Experimental

2.1. Materials

The 4-bromo-1,8-naphthalic anhydride **1**, 2,2,6,6-tetramethylpiperidin-4-ylamine **2**, allyl alcohol **4**, 2,2,6,6-tetramethylpiperidin-4-ol **7**, allylamine and 18-crown-6 (Fluka Products), p.a. grade, were used without purification. Commercial acrylonitrile (AN) was distilled before use. Dibenzoylperoxide (DBP, Fluka, 99.6%) re-crystallised from chloroform was used as an initiator of the free radical co-polymerisation. *N*,*N*-dimethylformamide (DMF, Merck) for synthesis and of a spectroscopy grade was used.

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 measurements were carried out in $CDCl_3$ solution at ambient temperature. The electronic and fluorescence spectra were recorded on a Hewlett-Packard 8452A spectrophotometer with 2 nm resolution and on a Perkin-Elmer MPF 44 spectrophotometer, respectively, at room temperature in DMF. 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 and chloroform/methanol = 9:1. The quantum yield of fluorescence was determined on the basis of the absorption and fluorescence spectra at a concentration of 10^{-6} mol l^{-1}, using quinine bisulfate ($\Phi_0 = 0.55$), as a standard [14]. Elemental analysis data were obtained on a Perkin-Elmer 240 automatic analyser. The melting points were determined by means of a Kofler melting point microscope.

2.3. Synthesis of monomers

2.3.1. Synthesis of 6-bromo-2-(2,2,6,6-tetramethylpiperidin-4-yl)-benzo[de]isoquinoline-1,3-dione (3)

To a suspension of 4-bromo-1,8-naphthalenedicarboxylic acid anhydride **1** (8.31 g, 30 mmol) in 100 ml of absolute ethanol, 4.68 g of 2,2,6,6-tetramethylpiperidin-4-ylamine **2** ($d = 0.91$, 30 mmol) were added dropwise under stirring at ambient temperature over a period of 30 min. The resulting mixture was stirred at 70 °C for 4 h (TLC control in a solvent system *n*-heptane/acetone = 1:1). The crude product that precipitated on cooling with addition of water was treated with 50 ml of 5% aqueous sodium hydroxide to give after filtration, washing with water and drying 11.76 g of 6-bromo-2-(2,2,6,6-tetramethylpiperidin-4-yl)-benzo[*de*] isoquinoline-1,3-dione (**3**) as pale yellow crystals.

FT-IR (KBr) (cm^{-1}): 3238 (νNH); 3074 (νArCH); 2924 ($\nu^{as}CH_3$); 2874 ($\nu^{s}CH_3$); 1696 (ν^{as}C=O); 1654 (ν^{s}C=O); 1590 (νArC=C); 1452 ($\delta^{as}CH_3$); 1364 ($\delta^{s}CH_3$); 1346 (νC–N–C); 778 (δArCH).

^1H NMR (250.13 MHz, $CDCl_3$) (ppm): 8.62 (dd, 1H, J = 7.3 and 1.1 Hz, benzo[*de*]isoquinoline 7-H); 8.53 (dd, 1H, J = 8.5 and 1.1 Hz, benzo[*de*]isoquinoline 9-H); 8.36 (d, 1H, J = 7.9 Hz, benzo[*de*]isoquinoline 4-H); 8.02 (d, 1H, J = 7.9 Hz, benzo[*de*]isoquinoline 5-H); 7.81 (dd, 1H, J = 8.5 and 7.3 Hz, benzo[*de*]isoquinoline 8-H); 5.68 (m, 1H, tetramethylpiperidine CH); 2.52 (t, 2H, J = 12.4 Hz, tetramethylpiperidine CH_2); 1.83 (br.s, 1H, tetramethylpiperidine NH); 1.68 (dd, 2H, J = 12.6 and 2.9 Hz, tetramethylpiperidine CH_2); 1.41 (s, 6H, tetramethylpiperidine 2 × CH_3); 1.28 (s, 6H, tetramethylpiperidine 2 × CH_3).

Elemental analysis: Calculated for $C_{21}H_{23}BrN_2O_2$ (MW: 415.32) C 60.73, H 5.58, N 6.74%; Found C 61.08, H 5.49, N 6.82%.

2.3.2. Synthesis of 6-allyloxy-2-(2,2,6,6-tetramethylpiperidin-4-yl)-benzo[de]isoquinoline-1,3-dione (5)

A solution of 6-bromo-2-(2,2,6,6-tetramethylpiperidin-4-yl)-benzo[*de*]isoquinoline-1,3-dione **3** (4.15 g, 10 mmol) in 50 ml of toluene was added to a mixture of 0.70 g of allyl alcohol ($d = 0.85$, 12 mmol), 0.16 g of 18-crown-6 (0.6 mmol, 5 mol% to the allyl alcohol) and 0.79 g (14 mmol) of finely ground potassium hydroxide at ambient temperature. The resulting mixture was vigorously stirred and heated to 90 °C for 3 h, then cooling to room temperature. The solid

phase was filtered off, and the toluene solution was washed with water and dried over anhydrous sodium sulfate. After evaporation of the toluene under reduced pressure the crude residual was re-crystallised from *n*-hexane to give 3.57 g of 6-allyloxy-2-(2,2,6,6-tetramethylpiperidin-4-yl)-benzo-[*de*]isoquinoline-1,3-dione (**5**) as pale beige crystals.

FT-IR (KBr) (cm^{-1}): 3230 (νNH); 3062 (νArCH); 2922 ($\nu^{as}CH_3$); 2880 ($\nu^{s}CH_3$); 1698 ($\nu^{as}C{=}O$); 1656 ($\nu^{s}C{=}O$); 1618 (νAllylC=C); 1594 (νArC=C); 1458 ($\delta^{as}CH_3$); 1372 ($\delta^{s}CH_3$); 1354 (νC–N–C); 1266 (νC–O–C); 996 ($\delta CH_2{=}$); 932 (δCH=); 780 (δArCH).

^{1}H NMR (250.13 MHz, $CDCl_3$) (ppm): 8.58 (m, 2H, benzo[*de*]isoquinoline 7-H and 9-H); 8.49 (d, 1H, J = 8.3 Hz, benzo[*de*]isoquinoline 4-H); 7.70 (dd, 1H, J = 8.2 and 7.5 Hz, benzo[*de*]isoquinoline 8-H); 7.04 (d, 1H, J = 8.3 Hz, benzo[*de*]isoquinoline 5-H); 6.16 (m, 1H, allyl CH=); 5.67 (m, 1H, tetramethylpiperidine CH); 5.49 (m, 2H, allyl $CH_2{=}$); 4.84 (d, 2H, J = 5.2 Hz, allyl OCH_2); 2.49 (t, 2H, J = 12.4 Hz, tetramethylpiperidine CH_2); 1.77 (br.s, 1H, tetramethylpiperidine NH); 1.65 (dd, 2H, J = 12.4 and 3.0 Hz, tetramethylpiperidine CH_2); 1.37 (s, 6H, tetramethylpiperidine 2 × CH_3); 1.23 (s, 6H, tetramethylpiperidine 2 × CH_3).

Elemental analysis: Calculated for $C_{24}H_{28}N_2O_3$ (MW: 392.49) C 73.44, H 7.19, N 7.14%; Found C 73.72, H 7.26, N 7.06%.

2.3.3. Synthesis of 2-allyl-6-(2,2,6,6-tetramethylpiperidin-4-yloxy)-benzo[de] isoquinoline-1,3-dione (8)

A solution of 2-allyl-6-bromo-benzo[*de*]isoquinoline-1,3-dione **6** (3.16 g, 10 mmol) in 30 ml of toluene was added to a mixture of 1.89 g of 2,2,6,6-tetramethylpiperidin-4-ol **7** (12 mmol), 0.79 g (14 mmol) of finely ground potassium hydroxide, 0.16 g of 18-crown-6 (0.6 mmol, 5 mol% to the 2,2,6,6-tetramethylpiperidin-4-ol) and 50 ml of toluene at 40 °C. The resulting mixture was vigorously stirred and heated to reflux for 3 h, then cooling to room temperature. The solid phase was filtered off, and the toluene was evaporated in vacuum. The crude product was dissolved in a mixture solvent of minim 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-crystallisation from ethanol–water (50:50 vol.%) afforded 3.45 g of 2-allyl-6-(2,2,6,6-tetramethylpiperidin-4-yloxy)-benzo[*de*] isoquinoline-1,3-dione (**8**) as white crystals.

FT-IR (KBr) (cm^{-1}): 3242 (νNH); 3066 (νArCH); 2956 ($\nu^{as}CH_3$); 2894 ($\nu^{s}CH_3$); 1704 ($\nu^{as}C{=}O$); 1668 ($\nu^{s}C{=}O$); 1614 (νAllylC=C); 1598 (νArC=C); 1464 ($\delta^{as}CH_3$); 1382 ($\delta^{s}CH_3$); 1360 (νC–N–C); 1248 (νC–O–C); 998 ($\delta CH_2{=}$); 928 (δCH=); 788 (δArCH).

^{1}H NMR (250.13 MHz, $CDCl_3$) (ppm): 8.61 (m, 2H, benzo[*de*]isoquinoline 7-H and 9-H); 8.56 (d, 1H, J = 8.4 Hz, benzo[*de*]isoquinoline 4-H); 7.69 (dd, 1H, J = 8.4 and 7.3 Hz, benzo[*de*]isoquinoline 8-H); 7.05 (d, 1H, J = 8.4 Hz, benzo[*de*]isoquinoline 5-H); 6.01 (m, 1H, allyl CH=); 5.25 (m, 2H, allyl $CH_2{=}$); 5.09 (m, 1H, tetramethylpiperidine CH); 4.80 (dt, 2H, J = 5.7 and 1.3 Hz, allyl OCH_2); 2.24 (dd, 2H, J = 12.5 and 2.4 Hz, tetramethylpiperidine CH_2); 1.53 (br.s, 1H, tetramethylpiperidine NH); 1.46 (d, 2H, J = 12.5 Hz, tetramethylpiperidine CH_2); 1.38 (s, 6H, tetramethylpiperidine 2 × CH_3); 1.26 (s, 6H, tetramethylpiperidine 2 × CH_3).

Elemental analysis: Calculated for $C_{24}H_{28}N_2O_3$ (MW: 392.49) C 73.44, H 7.19, N 7.14%; Found C 73.22, H 7.11, N 7.21%.

2.4. Synthesis of polymers

The radical co-polymerisation of AN with the compounds **5** and **8** was carried out in vials, purged with pure nitrogen before use. The co-polymerisation was conducted under conditions used with other similar 1,8-naphthalmide derivatives [5a–c,9a]. The initial concentration of DBP was 1 and 0.5 wt.% of the monomer compounds **5** and **8** with respect to the AN monomer. The vials were treated in a thermostat for 12 h at 70 °C. The side-group co-polymers thus obtained were re-precipitated several times with methanol from DMF in order to remove the non-interacted monomers. The co-polymers poly(AN-*co*-**5**,**8**) were dried to a constant weight in vacuum at 40 °C. All spectrophotometric measurements were carried out with precipitated polymers.

2.5. Photodestruction of co-polymers

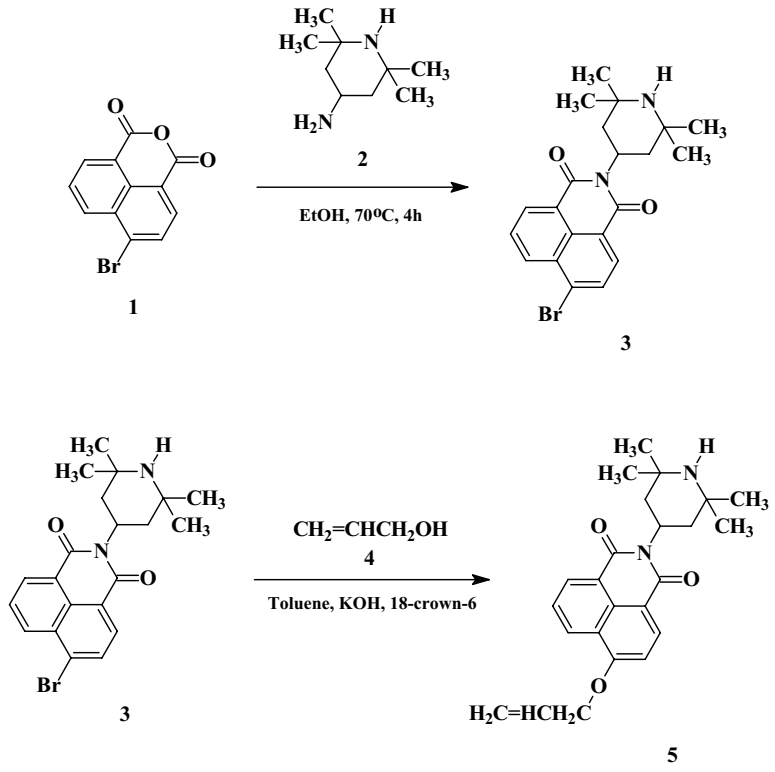
A solar simulator (Suntest CPS+, HERAEUS), equipped with a 1.5 kW xenon arc lamp, protected with an adequate filter to simulate the solar spectrum between 290 and 800 nm, was used and the experiments were carried out in ordinary atmosphere at 20 °C. The irradiation of the PAN and poly(AN-*co*-**5**,**8**) were performed in DMF solution at a concentration of 1.5 g l^{-1}.

2.6. Determination of polymer molecular weights

The molecular weights of PAN and poly(AN-*co*-**5**,**8**) were determined by measuring the limiting viscosity number [η] in DMF solution, using an Ubbelohde viscosimeter at 25 °C. Mark-Houwink equation: $[\eta] = KM_v^a$ was used for determination of the average viscosimetric molecular weight (M_v). The respective constants for PAN are $K = 1.75 \times 10^{-3}$ and $a = 0.66$ [15].

3. Results and discussion

The aim of the present study was to synthesise 1,8-naphthalimide fluorescent brighteners, containing a 2,2,6,6-tetramethylpiperidine stabiliser fragment and a polymerisable allyl group for “one-step” chemically brightening and stabilisation of PAN. It was of interest to obtain two combined compounds in which the allyl group is situated at a



Scheme 3.

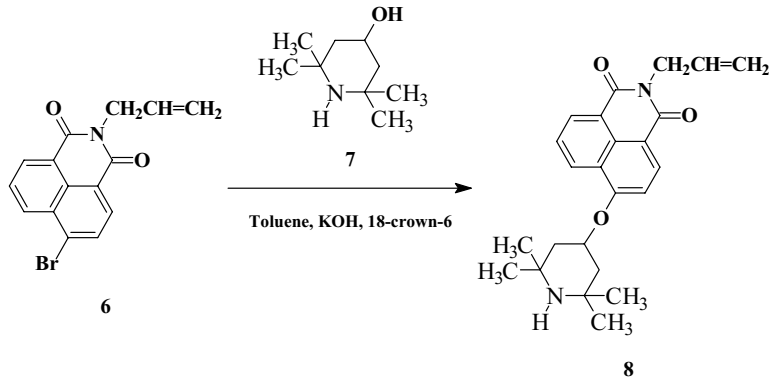
different position (at the *N*-imide atom or at the C-6 position in the benzo[*de*]isoquinoline-1,3-dione ring) with a view to investigate the position effect of the allyl group upon the monomers ability for a radical co-polymerisation with AN.

3.1. Synthesis

The target 6-allyloxy-2-(2,2,6,6-tetramethylpiperidin-4-yl)-benzo[*de*]isoquinoline-1,3-dione **5** was synthesised in just two steps as outlined in Scheme 3.

First, the intermediate 6-bromo-2-(2,2,6,6-tetramethylpiperidin-4-yl)-benzo[*de*]isoquinoline-1,3-dione **3** was prepared by condensation of the commercially available 4-bromo-1,8-naphthalic anhydride **1** and 2,2,6,6-tetramethylpiperidin-4-ylamine **2**. In order to obtain the blue-emitting fluorescent compound **5** and functionalise it with polymerisable group, the intermediate **3** was reacted with allyl alcohol **4** under phase-transfer catalysis (PTC) conditions [16]. By selection of the favourable reaction conditions, in a solid–liquid two-phase system in the presence of 18-crown-6 as a phase-transfer catalyst, the desired compound **5** was obtained in high yield (Table 1).

The synthesis of 2-allyl-6-(2,2,6,6-tetramethylpiperidin-4-yloxy)-benzo[*de*]isoquinoline-1,3-dione **8** is displayed in Scheme 4.



Scheme 4.

Table 1
Yields, melting points and TLC R_f values for compounds **3**, **5** and **8**

Compound	Yield (%)	mp (°C)	R_f
3	94.5	204–206	0.38[a]
5	91	178–180	0.34[b]
8	82	165–167	0.32[b]

[a] TLC solvent system *n*-heptane/acetone = 1:1.
[b] TLC solvent system chloroform/methanol = 9:1.

The starting 2-allyl-6-bromo-benzo[*de*]isoquinoline-1,3-dione **6** was prepared by condensation of 4-bromo-1,8-naphthalic anhydride **1** with the commercially available allylamine according to the reported procedure [17]. The target compound **8** was synthesised by a nucleophilic substitution of the bromine atom in the intermediate **6** with 2,2,6,6-tetramethylpiperidin-4-ol **7** under the above described phase-transfer catalysis conditions in a good yield (Table 1).

The synthesised intermediate **3** as well as the new combined compounds **5** and **8** were characterised by their melting point, TLC R_f value (Table 1), absorption and fluorescence maxima, Stokes shift ($\nu_A - \nu_F$) and quantum yield of fluorescence (Φ_F) [14a] (Table 2) and identified by elemental analysis data and FT-IR and ^{1}H NMR spectra.

Data presented in Table 2 show that the different substituents at the *N*-imide and C-6 atoms have a small effect on both the absorption and the fluorescence maxima. Stokes shift values are common for this class of 1,8-naphthalimide derivatives [14b], while the Φ_F value of the compound **8** is higher than that of compound **5**, which is surely connected with the electron-donating nature of the substituent in a C-6 position.

3.2. Polymerisation

The applicability of the new compounds for "one-step" fluorescent brightening and stabilisation of polymers was examined on the basis of their ability to co-polymerise with AN. The free-radical polymerisation of AN was investigated in the presence of 0.5 wt.% of the corresponding monomer (**5** or **8**). The polymer yields obtained were 79 wt.% for poly(AN-*co*-5), 81 wt.% for poly(AN-*co*-8) and 87 wt.% for PAN (Table 3). It can be seen that monomer compounds **5** and **8** did not affect significantly the process of the co-polymerisation.

The presence of a covalent bond between the monomeric compound **5** or **8** and the polymer chain has been proved by a TLC technique. The unprecipitated co-polymers (they also comprise some amount of unreacted monomers), precipitated co-polymers, monomeric compounds **5** and **8**, and mixtures of a homopolymer with the monomers **5** and **8** were studied by TLC. After the chromatography development, it was established that the monomers **5** and **8** 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 compounds **5** and **8** to the polymer chain.

Table 2
Photophysical characteristics of compounds **5** and **8**

Compound	λ_A (nm)	$\log \varepsilon$	λ_F	$\nu_A - \nu_F$	Φ_F
5	366	4.16	446	4752	0.51
8	364	4.22	440	4745	0.62

Table 3
Spectrophotometric data for co-polymers of AN with monomeric compounds **5** and **8**

Polymer	λ_A (nm)	Yield (wt.%)	Chemically bonded **5** and **8** (wt.%)
PAN		87	
poly(AN-*co*-**5**)	370	79	0.42
poly(AN-*co*-**8**)	366	81	0.40

The UV-Vis absorption spectra of the co-polymers showed similar absorption maxima as those of the monomers **5** and **8** (Table 3). This is an indication that no changes occurred in their chromophoric systems, neither during the polymerisation nor as a result of their incorporation to the polymer chain. That is why, the method of the standard curve was used for spectrophotometric determination of the content of a chemically bound monomer in the polymer (Table 3).

3.3. Photostability of PAN and poly(AN-co-5,8)

In order to investigate the influence of the monomers **5** and **8** on the photostability of the co-polymers, the latter were analysed viscosimetrically [15a] before and after 10 h of irradiation. Because of the low percentage of **5** and **8** into the polymer chain (about 0.4 wt.%) towards AN, the values *K* and *a* for homopolyacrylonitrile were used in the Mark-Houwink equation [15b]. The average viscosimetric molecular weights M_v determined for poly(AN-*co*-**5**) and poly(AN-*co*-**8**) showed (Table 4) that compounds **5** and **8** did not affect significantly the co-polymers' molecular weight.

Table 4
Molecular characteristics of PAN and AN co-polymers before and after irradiation

Polymer	Before irradiation		After irradiation		$S = M_{vo}/M_v - 1$
	$[\eta]$ ($cm^{-1}\,g^{-1}$)	M_{vo}	$[\eta]$ ($cm^{-1}\,g^{-1}$)	M_v	
PAN	2.01	43300	1.84	37900	0.14
poly(AN-*co*-**5**)	1.90	39800	1.88	39100	0.02
poly(AN-*co*-**8**)	1.92	40400	1.91	40100	0.01

The data obtained for the chain breaks per molecule (*S*) [18] demonstrate the very good stabilising effect of the new compounds (Table 4).

4. Conclusions

As a result of this investigation, it can be assumed that the new adducts **5** and **8**, a combination of a 2,2,6,6-tetramethylpiperidine stabiliser and a polymerisable group in the molecule of the 1,8-naphthalimide fluorescent brightener were successfully synthesised using phase-transfer catalysis conditions. The new compounds were suitable for preparing polyacrylonitrile co-polymers with intensive blue fluorescence and high photostability. In terms of the electron donor–acceptor interaction, which govern the polarisation of the 1,8-naphthalimide molecule, the results imply that the electron-donating ability of the 4-alkoxy derivative **8** is somewhat higher than that of the 4-allyloxy derivative **5**.

Acknowledgements

The author thanks the Science Foundation at the University of Chemical Technology and Metallurgy for the financial support of these investigations.

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