

Synthesis, Spectral Properties, and Application of 1,8-Naphthalimide Fluorophores for Modified Polymers

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ABSTRACT: The presence of the epoxy group in the structure of 1,8-naphthalimide fluorophores opens up possibilities to prepare compounds with new valued properties through covalent bonding to both polyamide and epoxy oligomers. Two new 4-(1-amino-2,3-epoxypropyl)-9-substituted-1,8-naphthalimides were synthesized, and their absorption and fluorescence characteristics were determined. The introduction of the substituent contributes to both the yellow color and strong fluorescence of the compounds, the quantum yield being about 0.9. The possibility for structural coloration of polyamide textile materials and epoxy oligomers has been investigated. The modified polymers are with intense green fluorescence, possessing a strong resistance to various physicochemical treatments and light. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1863–1869, 2001

Key words: 1,8-naphthalimide derivatives; FTIR spectroscopy; NMR; fluorescence; photophysical properties; polyamide; epoxy oligomers

INTRODUCTION

The introduction of epoxy group into molecules of fluorophores leads to the preparation of substances with valuable properties that can be bound to epoxy oligomers and polyamides. This offers the possibility to obtain structurally colored high molecular compounds with strong resistance to various physical-chemical treatments. It is well known that some anthraquinone, benzothrone, and azo-chromophores, containing an epoxy group, are used for coloration of epoxy resins,^{1,2} polyamide,³ and wool.⁴ In previous publications we reported on dispersion coloration of both polyamide textile materials and diene epoxy resins.^{5–7}

The present study deals with the synthesis of novel 1,8-naphthalimide fluorophores containing an active epoxy group. The spectral characteristics and the possibility of these substances to color epoxy oligomers as well as polyamide textile materials have been investigated. The synthesis of the fluorophores was carried out according to Scheme 1.

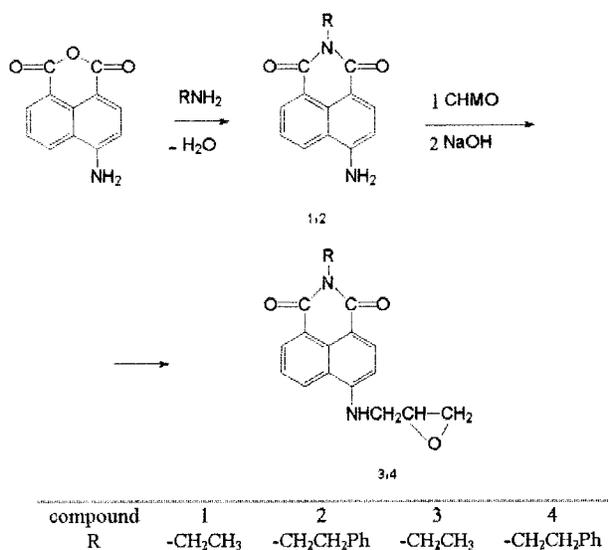
EXPERIMENTAL

General

Melting points were determined on a Büchi apparatus. FTIR spectra were taken at 2 cm⁻¹ resolution on a Perkin-Elmer 1600 FTIR Spectrophotometer, using KBr pellets. The calculation of the mathematical derivatives of a spectral band is an incorporated function of the apparatus. Ultraviolet

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Scheme 1

let visible ($5 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$ in ethanol) and emission ($5 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$ in ethanol; excitation at λ_{max} of the absorption band) spectra were taken on a UV/Vis Spectrophotometer Model 554 (Perkin-Elmer) and Jobin-Yvon JY3D Spectrofluorimeter equipped with a low-pressure mercury lamp. $^1\text{H-NMR}$ spectra (in CDCl_3 and DMSO-d_6 , TMS) were recorded with a BAUKER 250 MHz instrument. The measurement of the color of the dyed textile materials was performed using the spectrophotometer Texflach 3881 ACS/Datacolor previously calibrated for fluorescent materials.

Synthesis of 4-(1-amino-2,3-epoxypropyl)-9-ethyl-1,8-naphthalimide, 3

4-Amino-1,8-naphthalanhydride [2.1 g (0.01 M)] were dissolved in 40 mL of 2-methoxyethanol. To the prepared solution 0.7 mL 70% aqueous ethylamine at 90–100°C with continuous stirring were added. At this temperature the reaction mixture was stirred for 3 h. After termination of the reaction the mixture was cooled and poured into water. The formed residue was filtered and dried. The obtained 4-amino-9-ethyl-1,8-naphthalimide (1) was recrystallized from chlorobenzene.

In a three-necked flask of 250 mL, equipped with a stirrer, refluxer, and separating funnel, 2.4 g (0.04 M) 1 were dissolved in 50 mL 100% acetic acid. To the suspension with continuous stirring at 85–90°C at equal portions in an interval of 1 h, 3.5 mL of chloromethoxyran were

added. After heating at the same temperature for 4 h, the reaction mixture was cooled and poured into 300 mL of 20% aqueous NaOH. The residue was filtered and dried at 50°C under reduced pressure. The product 3 was recrystallized from chlorobenzene. In an analogous way from 4-amino-9-(2-phenylethyl)-1,8-naphthalimide 2 was prepared 4-(1-amino-2,3-epoxypropyl)-9-(2-phenylethyl)-1,8-naphthalimide 4.

Coloration of Polyamide-6 with 1–4

The corresponding fluorophore (0.5 wt % with respect to the polyamide textile material) was suspended in 5 mL 2% aqueous solution of nonionogen PAV (Verol C10), then an aqueous solution of sodium carbonate ($5 \text{ g} \cdot \text{L}^{-1}$) up to 1 : 50 bath module was added. The work solution was heated to 40°C then the previously moisturized polyamide material was placed in water. The heating rate of the bath was maintained at $1^\circ\text{C}/\text{min}^{-1}$ until boiling. Under these conditions the duration of the process was 1.5 h, followed by cooling up to 80°C. The sample was taken out, boiled for 1 h in Verol C10 solution ($1 \text{ g} \cdot \text{l}^{-1}$), rinsed repeatedly with both hot and cool water, then dried.

The presence of the covalent bond was proved as the colored textile material was treated 30 min in boiling ethanol. Colorimetrically, using a standard calibration curve, it was determined that 85–98% of the initial amount of the fluorophore was incorporated into the polyamide-6 (see Table VI).

Coloration of Epoxy Oligomers

Method 1

To 7.473 g diethylenetriamine (DETA) were added 0.053 g fluorophore; then, upon stirring, a homogeneous solution was obtained. This was added as a hardener to 100 g epoxy oligomer. After stirring, the mixture was poured into a matrix of silicon rubber to make the specimens. At 25°C the time of gelation is about an hour, and the time of hardening is 12 h. The specimens were taken out of the matrix after 24 h.

Method 2

Fluorophore (0.057 g) were dissolved in 7 mL acetone, and the prepared solution was added to 100 g epoxy oligomer. After stirring to a homogeneous solution, 7.53 g DETA were added. The time of gelation and hardening is as in the first method.

Table I Physical Constants, Yield, and Elemental Analysis Data of 1–4

No.	m.p. (°C)	Yield (%)	Formula Mol. Mass	Analysis (%) Calc./Found		
				C	H	N
1	264–266	91	C ₁₄ H ₁₂ N ₂ O ₂ 240	70.00	5.00	11.67
				70.15	5.18	11.72
2	207–209	94	C ₂₀ H ₁₅ N ₂ O ₂ 316	75.95	5.63	8.86
				76.05	5.52	8.75
3	106–108	75	C ₁₇ H ₁₅ N ₂ O ₃ 344	68.92	5.41	9.46
				69.02	5.47	9.51
4	92–95	81	C ₂₃ H ₂₀ N ₂ O ₃ 372	74.19	5.38	7.53
				74.24	5.43	7.58

RESULTS AND DISCUSSION

Synthesis of 4-(Amino-2,3-epoxypropyl)-9-substituted-1,8-naphthalimides

As initial product for the synthesis of 4-(1-amino-2,3-epoxypropyl)-9-substituted-1,8-naphthalimides was used 4-amino-1,8-naphthalanhydride.

At the first stage, a reaction of amination of 4-amino-1,8-naphthalanhydride with equimolar amounts of amine in the medium of 2-methoxyethanol at 90–100°C for 3 h takes place, resulting in compounds **1** and **2**. The second stage includes epoxydation of 4-amino-9-substituted-1,8-naphthalimides with chloromethyloxirane (**CHMO**) in acetic acid at 80°C. After determining the end of the reaction with thin-layer chromatography (TLC), the reaction mixture was poured into water, then alkalized with NaOH to pH 8,

which gave rise to a residue of the substances **3** and **4**.

The newly synthesized compounds are water insoluble, but well soluble in alcohols, acetone, chloroform, dioxane, dimethylformamide, etc. Their structures were determined by means of elemental analysis, FTIR and ¹H-NMR spectroscopy.

Structural Analysis

The IR spectral data are presented in Table II. The values of ν_{NH} for the primary and secondary amine groups are in the range of 3450–3251 cm⁻¹ as three, two, and one band, respectively. It is very well known that an interaction of vibrations of the C=O groups exists in the imide groups. Two bands are observed in the IR spectra corre-

Table II FTIR Absorbance Data (cm⁻¹) for Compounds 1–4

No	ν_{NH}	ν_{CH} Arom.	ν_{CH} Aliphatic	$\nu_{\text{C=O}}^{\text{s}}$	$\nu_{\text{C=O}}^{\text{as}}$	$\nu_{\text{C-C}}$ Arom.	$\nu_{\text{C-N}}$ Imide	$\nu_{\text{COC}}^{\text{as}}$ Epoxy
1	3450	3066	2976	1686*	1651*	1613	1372	
	3358		2935	1676	1632	1569		
	3251		2874		1526			
2	3354	3064	2957	1694 ^a	1650*	1614	1379	
	3244		2935	1685	1638	1576		
			2963		1496			
3	3361	3084	2959	1694 ^a	1651	1612	1384	1256
		3060	2931	1685	1637	1574		
		3025	2859		1546			
4	3361	3085	2957	1694 ^a	1640	1614	1380	1256
		3056	2927	1684	1632	1569		
		3026	2859		1526			

^a $\nu_{\text{C=O}}$ vibrations are obtained by calculating of mathematic derivatives. ν^{s} and ν^{as} are separated with 44–54 cm⁻¹.

Table III ¹H-NMR Chemical Shifts δ (in ppm) for Compounds 1-4

No.	H-7	H-5	H-2	H-6	H-3	R ⁴	R ⁹
1 ^a	8.61 d, 1H $J_{6,7} = 8.4$ $J_{5,7} = 0.9$	8.42 d, 1H $J_{5,6} = 7.3$ $J_{5,7} = 0.9$	8.19 d, 1H $J = 8.4$	7.65 t, 1H $J_{6,7} = 8.4$ $J_{5,6} = 7.3$	6.85 d, 1H $J = 8.4$	7.43 br.s, 2H -NH ₂	1.18 t, 3H 4.05 q, 2H
1 ¹	8.58 d, 1H $J = 7.3$	8.37 d, 1H $J = 8.0$	8.1 d, 1H $J = 8.1$	7.60 t, 1H $J_{6,7} = 8.0$ $J_{5,6} = 8.3$	6.82 d, 1H $J = 8.2$	7.52 br.s, 1H -NH-	1.25 t, 3H 4.24 q, 2H
1 ²	8.46 d, 1H $J = 7.0$	8.3 d, 1H $J = 8.2$	8.05 d, 1H $J = 8.4$	7.52 t, 1H $J_{6,7} = 7.8$ $J_{5,6} = 8.4$	6.72 d, 1H $J = 8.4$	5.58 s, 1H -OH	
2 ^a	8.59 d, 1H $J_{6,7} = 7.5$ $J_{5,7} = 0.9$	8.41 d, 1H $J_{5,6} = 6.4$ $J_{5,7} = 0.9$	8.18 d, 1H $J = 8.4$	7.63 t, 1H $J_{6,7} = 7.5$ $J_{5,6} = 6.4$	6.83 d, 1H $J = 8.4$	7.43 br.s, 2H -NH ₂	2.88 q, 2H 4.21 q, 2H 7.30-7.27 m, 5H
2 ¹	8.57 d, 1H $J = 7.2$	8.38 d, 1H $J = 8.1$	8.09 d, 1H $J = 8.2$	7.62 t, 1H $J_{6,7} = 7.2$ $J_{5,6} = 8.1$	6.86 d, 1H $J = 8.2$	7.40 br.s, 1H -NH-	3.04-2.96 m, 2H 4.40-4.32 m, 2H
2 ²	8.4 d, 1H $J = 7.0$	8.3 d, 1H $J = 8.3$	8.0 d, 1H $J = 8.4$	7.53 t, 1H $J_{6,7} = 7.0$ $J_{5,6} = 8.3$	6.68 d, 1H $J = 8.4$	5.00 s, 1H -OH	7.39-7.24 m, 5H
3 ^a	8.55 d, 1H $J_{6,7} = 7.9$ $J_{5,7} = 0.9$	8.39 d, 1H $J_{5,6} = 7.4$ $J_{5,7} = 0.9$	8.17 d, 1H $J = 8.4$	7.63 t, 1H $J_{6,7} = 7.9$ $J_{5,6} = 7.1$	6.84 d, 1H $J = 8.4$	3.68 d, 2H 3.43 m, 1H 3.60 m, 2H 5.87 s, 1H	2.88 m, 3H 4.25 m, 2H
3 ¹	8.57 d, 1H $J = 7.2$	8.36 d, 1H $J = 8.1$	8.10 d, 1H $J = 8.2$	7.60 t, 1H $J_{6,7} = 7.1$ $J_{5,6} = 8.2$	6.82 d, 1H $J = 8.3$	3.73 d, 2H 3.47	2.98 m, 3H 4.30
3 ²	8.48 d, 1H $J = 7.0$	8.29 d, 1H $J = 8.5$	8.05 d, 1H $J = 8.5$	7.56 t, 1H $J_{6,7} = 7.3$ $J_{5,6} = 8.5$	6.64 d, 1H $J = 8.5$	m, 1H 3.67 m, 2H 7.49 s, 1H 5.88 s, 1H	m, 2H
4 ^a	8.58 d, 1H $J_{6,7} = 7.4$ $J_{5,7} = 0.9$	8.40 d, 1H $J_{5,6} = 6.6$ $J_{5,7} = 0.9$	8.16 d, 1H $J = 8.4$	7.60 t, 1H $J_{6,7} = 7.7$ $J_{5,6} = 6.5$	6.84 d, 1H $J = 8.3$	3.65 d, 2H 3.56 m, 1H 3.68 m, 2H 5.69 s, 1H	2.89 m, 2H 4.27 m, 2H 7.34-7.26 m, 5H
4 ¹	8.52 d, 1H $J = 7.8$	8.33 d, 1H $J = 8.3$	8.00 d, 1H $J = 8.2$	7.56 t, 1H $J_{6,7} = 7.8$ $J_{5,6} = 8.3$	6.81 d, 1H $J = 8.2$	3.72 d, 2H 3.65 m, 1H 3.77 m, 2H	3.00 m, 2H 4.34
4 ²	8.47 d, 1H $J = 7.1$	8.28 d, 1H $J = 8.4$	8.04 d, 1H $J = 8.4$	7.45 t, 1H $J_{6,7} = 7.2$ $J_{5,6} = 8.4$	6.60 d, 1H $J = 8.4$	7.42 s, 1H 5.88 s, 1H	m, 2H 7.37-7.20 m, 5H

^a DMSO-d₆ and ^{1,2}CDCl₃—tautomeric forms T₁ and T₂.

sponding to ν^s and ν^{as} (at 1780–1720 cm⁻¹ and 1710–1670 cm⁻¹), separated from each other at 60 cm⁻¹. The more intense band in this case is

that of $\nu_{C=O}^s$.⁸ The presence of a strong p-electron-donor substituent (R⁴) in the investigated compounds is the reason for ED-EA interaction be-

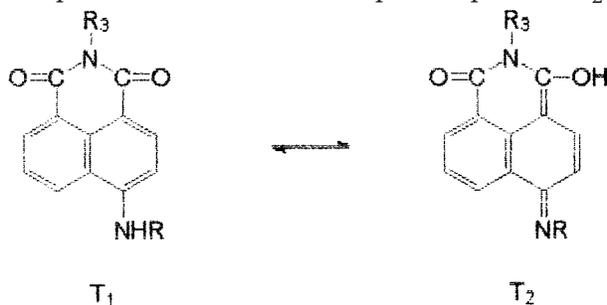
Table IV Spectral Data for the Compounds 1-4

No.	λ_A^{\max} nm	$\log \epsilon$	λ_F^{\max} nm	$\Delta\nu$ cm^{-1}	λ_{S1} nm	E_{S1} $\text{kJ}\cdot\text{mol}^{-1}$	ϕ_F
1	430	4.161	522	4096	488	245.3	0.63
2	430	4.107	523	4135	482	248.5	0.81
3	430	4.190	523	4135	486	246.5	0.73
4	430	4.134	527	4280	480	249.4	0.99

where: λ_A^{\max} is the wavelength of absorption; $\log \epsilon$ is the molar extinction coefficient; λ_F^{\max} is the wavelength of the fluorescence; $\Delta\nu$ is the Stokes shift; λ_{S1} is the wavelength of the excited state S_1 ; E_{S1} is the energy of excited state S_1 ; ϕ_F is relative quantum yield toward Rodamine 6G.

tween the amine group and the C=O group. This interaction polarizes the C=O bond additionally, and the bands of the $\nu_{C=O}$ vibrations were split. In the spectra of most of the compounds the bands of ν^s and ν^{as} are observed as doublets. Absorbance bands of the $\nu_{C=O}$ vibrations are in the range of 1694–1632 cm^{-1} . The second and fourth derivatives of recovered bands were recorded when the $\nu_{C=O}$ vibrations were masked.

In the IR spectra of the investigated compounds in the solid state (KBr) the splitting of the spectral bands of $\nu_{C=O}$ can be a result of interaction between one or the same vibrations of different molecules. To prove that the obtained doublets of ν^s and ν^{as} (in KBr) are due to ED-EA interaction, we investigated the behavior of 1,8-naphthalimides in solvents with growing polarity: PhCH₃, CHCl₃, CH₃CN, and DMSO.^{9,10} It is established that in polar solvents the ED-EA interaction becomes stronger, which leads to splitting of the bands. Upon going from CHCl₃ to more polar solvents, such as CH₃CN and DMSO, the intensity of the absorption band of $\nu_{C=O}^{as}$ increases, while that of $\nu_{C=O}^s$ decreases, and in DMSO, the band practically disappears. A band characteristic of ν_{OH} vibrations is observed in the IR spectra in CHCl₃ and CH₃CN. The identification of the OH group by the corresponding band is conclusive, because in the IR spectra of the organic compounds only the O—H bond has a vibration above 3550 cm^{-1} . The observed band at 3619 cm^{-1} can be referred only to the OH group. That experimental fact proves the existence of the prototropic form T_2 .



There exists an equilibrium mixture of two tautomeric forms— T_1 and T_2 . In an unpolar solvent such PhCH₃, the equilibrium is shifted to the prototropic form T_1 . Such is the case when the polarity of the solvent increases.¹⁰

The experimental data of the chemical shift (δ) and the calculated coupling constants (J) were used for identification of the naphthalene protons. For the investigated compounds, doubling of the signals of the aromatic protons was observed, which strongly depends on the solvent used.

In CDCl₃, the doubling of more signals is in a ratio of around 2 : 1 (Table III). This can be related to the tautomeric forms T_1 and T_2 . Such doubling of the signals in the more polar solvent as DMSO-d₆ was not observed.

The results of absorption and fluorescence spectra of the compounds in EtOH are presented in Table IV and Figure 1.

It is clear that for compounds **3** and **4**, with an epoxy group in the structure, that observed higher values of $\log \epsilon$ are observed, with a weak bathochromic shift to 4 nm for λ_F and an increase of ϕ_F from 0.63 to 0.73 and from 0.81 to 0.99, respectively. The intensive fluorescence in EtOH for the same compounds confirms the possibility

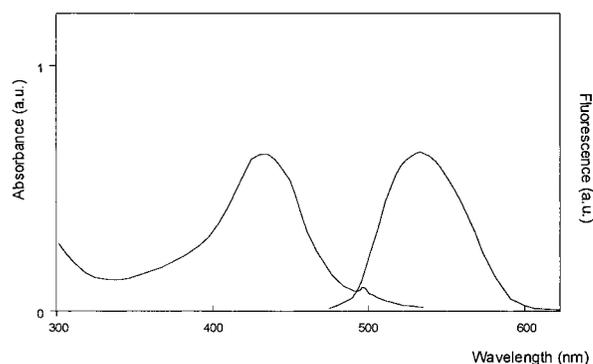


Figure 1 Absorption and emission ($\lambda_{ex} = 430 \text{ nm}$) spectra of compound **3** in ethanol ($5 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$).

Table V Color Characteristics of Polyamide-6 Treated with Fluorophores 1-4^a CIELab Coordinates

No.	CIELab Coordinates				
	L ^a	a ^a	b ^a	C ^a	H ^a
1	93.675	-11.257	72.542	72.341	103.247
2	91.038	-11.322	64.690	65.673	99.927
3	89.568	-2.324	88.699	88.729	99.059
4	88.261	8.175	101.612	101.940	91.073

^a Dyeings at 0.5 wt % fluorophore.

for prototropy. The tautomeric form fixes the molecule and makes difficult the dissipation of the energy to other levels. Our investigations show that in the solid state all compounds have more intensive fluorescence than in EtOH.¹⁰

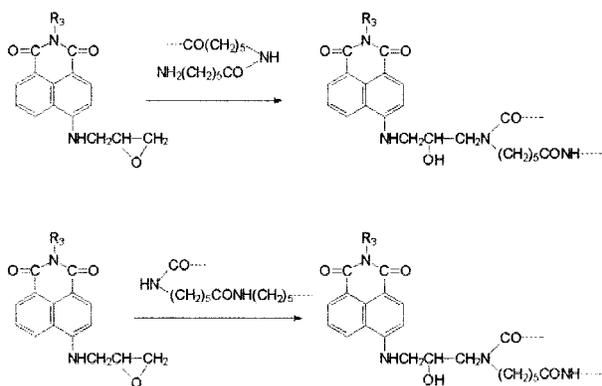
Color Assessment

The compounds were used for coloration of polyamide textile materials such as fluorophores.

The initial concentration of the fluorophores (0.25–1.00 wt % with an increasing factor of 2) was investigated. It is observed that concentration of 0.5 wt % is enough to achieve a deep color with intensive green fluorescence. The color characteristics of the materials are presented in Table V.

In the technological process of coloring, the polyamide reacts with the chromophors with opening of the epoxy ring, followed by interaction with end NH₂ or NH groups of the polyamide molecule shown by Scheme 2.³

It was interesting to investigate the stability of the colored samples toward some physico-chemi-

**Scheme 2****Table VI** Color Data of Polyamide-6 Treated with Fluorophores 1-4^a

No.	Fastness of				Connected Fluorophore (%)
	Light	Washing (60°C)	Alkalinity	Rubbing	
1	4-5	4	3-4	4	85
2	4-5	4	3-4	4	87
3	5	6	6	6	97
4	5	6	6	6	98

^a Fastness of light, washing, alkalinity, and rubbing was determined according to test methods using the standards: ISO 105-B01, ISO 105-C06, BDS 4678-92, and ISO 105-X12.

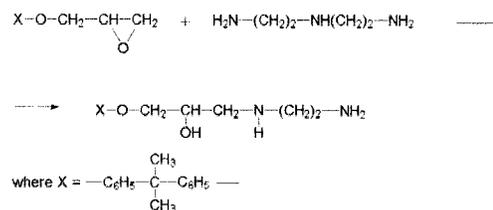
cal influences and light. It is known that the covalent bond between the chromophor and textile material does not exercise influence on the light sensitivity of the samples, while the chemical structure of the compounds, their position in the polymer, physical and chemical structure of the polymer, conditions of irradiation, and other factors are very important.^{11,12}

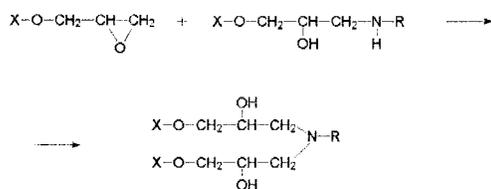
In Table VI are presented the observed parameters for the stability to light, alkalies, washing at 60°C, rubbing, and percentage of bound fluorophores.

The use of the investigated active fluorophores **3** and **4** lead to the preparation of color polyamide textile samples with high stability to physico-chemical treatment, one to two grades higher than that, obtained by disperse coloring with 1,8-naphthalimide fluorophores.⁵

Dyeing of Epoxy Oligomers

The structural coloration of epoxy oligomers with 4-(1-amino-2,3-epoxypropyl)-9-ethyl and 9-(2-phenylethyl)-1,8-naphthalimide fluorophores (**3** and **4**) was studied. The epoxy oligomer was of molecular mass 444–500, percentage of the epoxy groups 17.2–19.4%, density at 25°C 1.13–1.16 g · cm⁻³, and viscosity (Höller) 1300–1800 mPa · s.

**Scheme 3**



Scheme 4

The increase of the molecular mass and the formation of crosslinks is a result of inclusion of effective solvents—hardeners into the oligomer. The change of the size of the molecules is connected with the change of the physico-chemical, mechanical and electrical properties of the epoxy oligomer. Depending on the sort and the quantity of the hardener, thermoreactive products with high chemical stability, mechanical strength, and good electroinsulation properties can be prepared.¹³

DETA is used as hardener of low molecular epoxy oligomer. It reacts with epoxy groups shown in Scheme 3.

Increasing the number of epoxy groups may lead to their interaction with hydrogen atoms from secondary amine groups (Scheme 4).

Six concentration of compounds **3** and **4** were investigated—0.005, 0.01, 0.05, 0.1, 0.15, 0.2, and 0.3%. It was found that 0.1 wt % of fluorophore is enough for obtaining intensive color. The proof of the full hardening of the epoxy oligomer is connected with the disappearance of the absorption band at 1256 cm^{-1} , which is characteristic of the vibrations of epoxy group.¹⁴ The obtained color samples are transparent, with yellow color and intensive green fluorescence. They are stable with treatment of organic solvents for 48 h. The absorption spectra in the visible range of the colored epoxy oligomers show the presence of absorption maximum at 430 nm. This proves that during the process of coloring the chromophor system does not change.

CONCLUSIONS

Two new 1,8-naphthalimide fluorophores containing epoxy groups were synthesized, and their

spectral and fluorescent properties were investigated. The experimental results convincingly confirm the possibility for tautomerism of compounds containing a labile hydrogen atom at the 4-position in the naphthalene ring. The compounds display a broad absorption band in the visible spectral region and a fluorescence in the green region (523–527 nm) and a purity of color.

The new 1,8-naphthalimide fluorophores are suitable for structural coloration of polyamide-6 and epoxy oligomers. The modified polyamide-6 and epoxy oligomers are with intense green fluorescence, good color characteristics, and resistance to physico-chemical effects.

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