

Photophysical and photochemical properties of blue fluorescent polystyrene

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Abstract

Two blue fluorescent 1,8-naphthalimide derivatives (fluorescent brighteners) having an allyloxy group have been investigated as modifiers for polystyrene. It has been found that the monomeric fluorescent brighteners take part in the radical polymerization and are covalently bound to the polymer chain yielding fluorescent side-groups in the polystyrene. The basic photophysical characteristics and photostability of monomeric and polymeric fluorescent compounds are discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Some spectral properties of the fluorescent polymers indicate their potential application in the high technologies [1]. The class of fluorescent brighteners (FBs) are of interest as prospective polymer modifiers to produce fluorescent polymers. FBs act as an additional light source by transforming the absorbed UV light of terrestrial solar radiation, and reemitting the light as fluorescence, in the violet–blue visible region. An important group of FBs is based on 1,8-naphthalimide derivatives which are effective compounds for attaining a high degree of whiteness [2].

During our investigation of new polymerizable fluorophores we have found some 1,8-naphthalimides to be suitable for structural modifications of synthetic polymers, especially polystyrene, polymethylmethacrylate and polyacrylonitrile [3–8]. The investigations have shown that these copolymers exhibit a highly intensive and stable fluorescence.

In this paper we report on the ability of two 4-methoxy-1,8-naphthalimide derivatives to copolymerize with styrene in the bulk thus obtaining blue fluorescent side-group copolymers. Basic photophysical properties of the monomeric and polymeric FBs are determined. It has

also been worth investigating the photostability of the FBs and their copolymers.

2. Experimental part

2.1. Materials

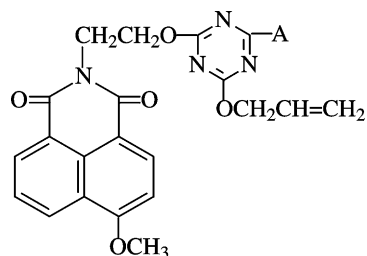
Commercial styrene (St) was used after purification. Styrene was washed with an aqueous solution of NaOH, dried over CaH₂ and then distilled under reduced pressure in pure nitrogen (of 99.99%) atmosphere. Dibenzoylperoxide (DBP) (Fluka) was used as initiator of the radical copolymerization. The monomeric FBs used in the copolymerization process were of the structure shown in Scheme 1 with A: –N(CH₃)₂ (1) and morpholino (2). Their synthesis has been described previously [9].

2.2. Synthesis of fluorescent copolymers

The radical copolymerization of St with the unsaturated FBs 1 and 2 was carried out in ampoules, previously purged with pure dry nitrogen. The process of copolymerization was conducted under conditions used for other similar monomers [3–5], at 80°C for 10 h, in the presence of 1.0% (w/w) FB and 1.0% (w/w) DBP under nitrogen. The side-group copolymers thus obtained were precipitated several times with ethanol from their solutions in toluene. The precipitated

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Scheme 1.

copolymers were repeatedly washed with ethanol, recovered by filtration and dried in a vacuum to constant weight.

2.3. Analysis

Spectrophotometric investigations were performed on a Hewlett Packard 8452A spectrophotometer with a 2 nm resolution at room temperature. Fluorescence spectra were taken on a Perkin-Elmer MPF 44. The absorption and fluorescence characteristics of fluorescent copolymers were studied in solid film 60 μm thick and in toluene solution at room temperature. For excitation of fluorescence measurement, monochromatic light of $\lambda = 360 \text{ nm}$ was used.

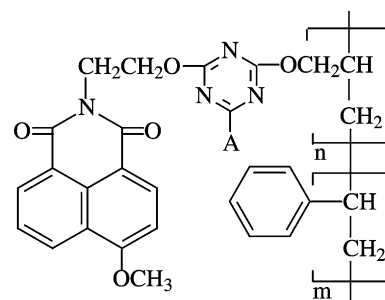
2.4. Photodestruction of the FBs and copolymers

The solutions of the monomeric and the polymeric FBs were irradiated with monochromatic light ($\lambda = 366 \text{ nm}$). The changes in the FB concentration was followed spectrophotometrically by the changes in the λ_A maxima [10]. Photodegradation of low molecular weight FBs 1 and 2 was performed at concentration $1 \times 10^{-5} \text{ mol l}^{-1}$. Both the copolymers (at 5 g l^{-1} concentration) and the low molecular weight FBs were studied in toluene solution. The copolymers Poly(St-co-FB) were also irradiated in a solid film 60 μm thick.

3. Results and discussion

3.1. Polymerization investigations

The bulk copolymerization of styrene with the FBs (1 wt.%) was investigated. The yields for the Poly(St-co-FB) were 80 and 87 wt.% for the pure polystyrene. Transparent



Scheme 2. Structure of fluorescent copolymers Poly(St-co-FB).

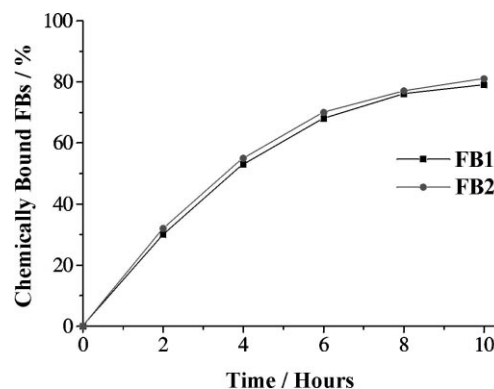


Fig. 1. Dependence of the chemically bonded 1,8-naphthalimide FBs 1 and 2 on the time of polymerization.

fluorescent copolymers having an intense blue emission with the structure presented in Scheme 2 were obtained.

The molecular characteristics of the copolymers obtained are listed in Table 1. The molecular weight and polydispersity determined confirm the formation of high molecular weight polymers: $M_w = 0.83\text{--}0.85 \times 10^5$ and $M_n = 1.61\text{--}1.68 \times 10^5$. Their polydispersity M_w/M_n is in the range 1.94–1.98.

It is worth studying the bonding of FBs to the polymer chain. Fig. 1 shows the kinetics of this bonding. As seen, FBs 1 and 2 have strongly reacted with the St monomers. The amount of FBs 1 and 2 incorporated into the macromolecules determined spectrophotometrically is within 0.79–0.81%.

3.2. Photophysical properties of monomeric FBs

Table 2 presents the spectral characteristics of the low molar weight FBs 1 and 2 measured in toluene solution:

Table 1
Molecular characteristics of polystyrene copolymers (see text)

Polymers	Before irradiation			After irradiation			
	$(M_w)_0 10^{-5}$	$(M_n)_0 10^{-5}$	$(M_w)_0/(M_n)_0$	$M_w 10^{-5}$	$M_n 10^{-5}$	M_w/M_n	A
Polystyrene	1.77	0.94	1.89	1.50	0.54	2.78	0.74
Poly(St-co-FB1)	1.61	0.83	1.94	1.57	0.72	2.16	0.15
Poly(St-co-FB2)	1.68	0.85	1.98	1.60	0.75	2.12	0.13

Table 2
Photophysical characteristics of the FBs 1 and 2 in toluene (see text)

	FB1	FB2
λ_A (nm)	356	358
$\log \varepsilon$	4.36	4.40
λ_F (nm)	435	436
$\nu_A - \nu_F$ (cm ⁻¹)	5101	4997
f	0.327	0.349
Φ_F	0.83	0.85

the absorption (λ_A) and fluorescence (λ_F) maxima, the extinction coefficients ($\log \varepsilon$) and the Stokes shifts ($\nu_A - \nu_F$). The long-wavelength band of the absorption spectrum in the UV region was a band of charge transfer (CT), due to $\pi \rightarrow \pi^*$ electron transfer on $S_0 \rightarrow S_1$ transition. In toluene solution, the FBs are colorless and have an intense fluorescence, with absorption maxima in the near UV-region at $\lambda_A = 356$ – 358 nm. Fluorescence emission was observed in the region 350–500 nm with a well pronounced maxima λ_F at 435–436 nm. The substituents *A* in the triazine ring have negligible effect upon λ_A , and λ_F values.

The Stokes shift is a parameter which indicates the differences in the properties and structure of the FBs between the ground state S_0 and the first excited state S_1 . The Stokes shift was found by Eq. (1):

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

The calculated values of Stokes shift in toluene solution are between 5101 and 4997 cm⁻¹. The significant Stokes shift is due to the energy losses during the transition into the excited state. This is evidence of notable steric changes, which the molecules undergo during the transition from basic to excited state.

The oscillator strength f , which shows the effective number of electrons whose transition from ground to excited state gives the absorption area in electron spectrum, was calculated by Eq. (2):

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

Here $\Delta\nu_{1/2}$ is the width of the absorption band (in cm⁻¹) at $\frac{1}{2}\varepsilon_{\max}$ [11]. The f values found for FBs 1 and 2 are in the region 0.327–0.349.

The ability of the molecules to emit the absorbed light energy is characterized quantitatively by the fluorescence quantum yield Φ_F . It was determined on the basis of the

absorption and fluorescence spectra of the FBs dissolved in toluene. The results for Φ_F are in the region 0.83–0.85. The difference in Φ_F for FBs 1 and 2 is not large.

3.3. Photophysical properties of polymeric FBs

The copolymers Poly(St-co-FB) are colorless with intense blue fluorescence. The copolymers are soluble in the solvents common for the homopolystyrene. Table 3 presents the data obtained from the basic photophysical characteristics of the side-group copolymers Poly(St-co-FB) in toluene. The absorption maxima of the copolymers are in the range 358–360 nm. The fluorescence spectra of the copolymers in toluene solution show maxima at $\lambda_F = 434$ – 435 nm. The absorption and fluorescence maxima of the copolymers are very similar to those of the monomeric FBs 1 and 2 in the same solution. That means their chromophoric system is preserved during the copolymerization. The quantum fluorescence yield in toluene Φ_F of the copolymers with $\Phi_F = 0.89$ – 0.91 is higher than those for the monomeric FBs themselves (Table 2). This is connected with the decrease of non-radiative processes and is obviously in relation to the bonding and conformation of the fluorophors into the polymer chain.

The absorption maxima λ_A of the copolymers in the solid state are at 362 nm for both copolymers (Table 3). The FBs 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 [12]. The fluorescence maxima of thin solid films are at 425 and 428 nm. However, the fluorescence spectra of the solid polymer films differ significantly from those in toluene solution being bathochromically shifted ($\Delta\lambda_F = 6$ – 10 nm), because of the rigidity of the structure. Obviously the results do not show any evidence for structural changes in the chromophoric system owing to the polystyrene matrix.

3.4. Investigation of the photostability of the monomeric FBs in solution and in polymeric matrix

With regard to the practical usage of the 1,8-naphthalimide FBs and their copolymers Poly(St-co-FB), it is worth studying their photostability.

The mechanism of photodegradation of the monomeric and polymeric FBs was clarified by irradiating their solutions in toluene in the presence of singlet oxygen inhibitors

Table 3
Spectral characteristics of the fluorescent copolymers recorded in solution and on thin films (see text)

Polymer	Solution of toluene				Solid film		
	λ_A (nm)	λ_F (nm)	$\nu_A - \nu_F$ (cm ⁻¹)	Φ_F	λ_A (nm)	λ_F (nm)	$\nu_A - \nu_F$ (cm ⁻¹)
Polystyrene	–	–	–	–	286	–	–
Poly(St-co-FB1)	358	435	4944	0.89	362	425	4094
Poly(St-co-FB2)	360	434	4736	0.91	362	428	4252

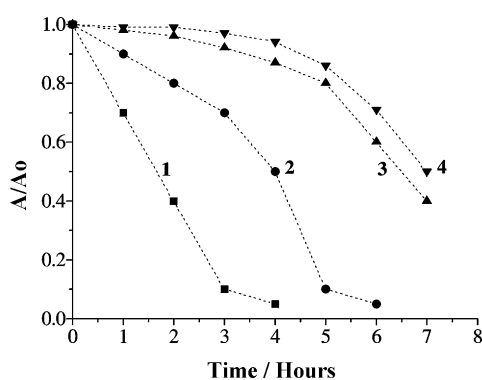


Fig. 2. Photodestruction of FB1 in the presence of (1) acetone, (2) alone, (3) DABCO, and (4) Poly(St-co-FB1) in toluene solution.

,4-diazabicyclo[2.2.2]octane (DABCO) as well as in the presence of acetone as a radical initiator. Fig. 2 plots the kinetics of photodegradation of the model FB 1. As seen, the fastest photodegradation of the FB is in the presence of acetone. In this case the FB solution loses its absorption maximum within 3 h as a result from the photodegradation of its chromophoric system. In the presence of DABCO the effect is less pronounced if compared to that in the neat toluene solution. After 5 h a more significant decrease in the FB concentration is observed. The components temporarily stabilize the degradation of the chromophoric system. The results obtained show that FB photodegradation results most probably from a radical mechanism. The observations were similar when studying the photodegradation of such chromophoric systems in ethanol and *N,N*-dimethylformamide. They exhibited very good photostability [8,10,13]. As seen, the photostabilization of the FB is more pronounced in the case of Poly(St-co-FB1) which might be due to an electron transfer from the polymer molecule to the main polymer chain during the transfer from excited to ground state: $S_1 \rightarrow S_0$ [14]. Similar spectral dependences are observed for Poly(St-co-FB2).

3.5. Photostability of the copolymers

The effect of monomeric FBs 1 and 2 upon the photodestruction of polystyrene was investigated. The photostability of the FBs was studied by GPC with prior UV light irradiation ($\lambda = 366$ nm for 10 h) of their copolymers with styrene. The molecular weights *M_w* and *M_n* of the products were determined before and after the irradiation of the copolymers against the data for polystyrene.

The number of chain breaks per molecule *A* is given by Eq. (3) [15]:

$$A = \frac{(Mn)_0}{(Mn)} - 1 \quad (3)$$

where $(Mn)_0$ and (Mn) are the number-average molecular weights before and after irradiation, respectively. The results are listed in Table 1. As seen, Poly(St-co-FB) does not change significantly its polydispersity and molecular weight distribution while the values for *M_w* and *M_n* for polystyrene decrease strongly. For the FBs the results show that the stabilizing effect is bigger for FB2. The photostabilizing effect could be explained by the absorption of UV light which is reemitted as long wave visible light during fluorescent emission. As a result, the degrading effect of high energy UV light upon the polymer molecules is strongly absorbed.

4. Conclusions

In this paper we have presented the results from the radical copolymerization of styrene with fluorescent 1,8-naphthalimide derivatives. The monomeric and polymeric compounds obtained emit intensive blue fluorescence. The results achieved show that the monomeric 1,8-naphthalimide derivatives investigated are suitable for preparing polystyrene with intensive blue fluorescence emission and good photostability.

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