

# Copolymerization and photostabilization of methylmethacrylate with 1,8-naphthalimide fluorescent brighteners

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Received 11 February 2001; received in revised form 15 May 2001; accepted 22 May 2001

## Abstract

The copolymerization of methylmethacrylate (MMA) with 1,8-naphthalimide fluorescent brighteners (fluorophores) yielding transparent blue fluorescent side-group copolymers has been investigated. It has been found that more than 0.92% of the fluorophores are chemically bonded to the polymer chain. Changes occurring in the chromophoric systems of the fluorophores during copolymerization have not been detected. The effect of polymer modification has been proved by an appropriate spectrophotometric method. The influence of the studied monomeric 1,8-naphthalimide fluorescent brighteners upon the photostability of the structurally bleached polymethylmethacrylate has been determined. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Polymerizable 1,8-naphthalimide; Fluorescent side-group copolymers; Polymethylmethacrylate; Photostabilization

## 1. Introduction

The copolymerization of monomeric fluorophores with some traditional monomers has been investigated intensively. Side-chain fluorescent copolymers thus obtained are of theoretical and practical interest due to the emission fluorescence [1,2].

Many authors reported on the synthesis of fluorescent polymerizable fluorophores [3–9], and on their ability to copolymerize with styrene, methylmethacrylate (MMA) or acrylonitrile, forming copolymers with an intensive fluorescence [10–16]. The fluorescent copolymers obtained are resistant to wet treatment and organic solvents, because the monomeric fluorescent units are covalently bonded to the polymer chain. Similar fluorescent copolymers have been recently reported to have a novel use as luminophores in liquid crystal systems for displays [17–19]. Some of the fluorescent copolymers with side-chain fluorophores possess chemiluminescent properties [20,21].

It is well known that the photostability of polymers is of great importance for their practical applications. Various photostabilizers for polymeric materials are used [22]. An improvement in their environmental behavior is achieved both by the covalent bonding to the polymer molecules which provides stability towards solvents and by the mi-

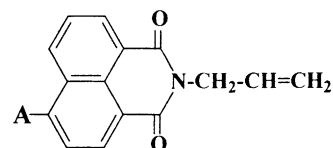
gration stabilizing effect [23,24]. Recently the photostabilizing efficiency of some 1,8-naphthalimide chromophores in polymer matrices has been investigated [25,26]. On the other hand the “one-step” coloration and stabilization of polymers has been reported as well [27].

In this article we report on the ability of two polymerizable 1,8-naphthalimide fluorescent brighteners (FB) to copolymerize with MMA in bulk as well as on the basic photophysical characteristics of monomeric and polymeric fluorescent brighteners obtained by the above reaction. The photostability of the FBs and their copolymers with MMA has been investigated too.

## 2. Experimental

### 2.1. Materials

The monomeric fluorescent 1,8-naphthalimide fluorescent brighteners used in the copolymerization process have the structure



where **A** are:  $-\text{OCH}_3$  (1), and  $-\text{OCH}_2\text{CH}_3$  (2).

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Their synthesis has been described previously [28]. The choice of this class of fluorescent brighteners has been made on the basis of their good photophysical and bleaching properties [28,29].

Commercial MMA was used after distillation under reduced pressure in nitrogen atmosphere. Dibenzoylperoxide (DBP) (Fluka) recrystallized from chloroform was used as an initiator of the free radical copolymerization.

## 2.2. Synthesis and characterization of fluorescent copolymers

The radical copolymerization of the 1,8-naphthalimide fluorescent brighteners **1** and **2** with MMA was carried out in ampoules, previously purged with pure dry nitrogen. The process of copolymerization was conducted under conditions used with other similar monomers [14,18] at 70°C for 10 h, in the presence of 1.0 wt.% fluorescent brighteners and 1.0 wt.% DBP under nitrogen. The side-chain fluorescent blue copolymers thus obtained were several times reprecipitated with ethanol from chloroform. The precipitated copolymers were repeatedly washed with ethanol, recovered by filtration and dried in vacuum to constant weight. All spectrophotometric measurements were carried out with precipitated polymers.

## 2.3. Determination of molecular weight

The molecular weights were determined on a GPC Waters 244 apparatus equipped with a combination of 100 and 1000 Å, linear Ultrastaygel columns; the solvent was THF at a flow rate of 1.0 ml min<sup>-1</sup> at 45°C. Both a differential refractive index and an UV absorption detector ( $\lambda_A = 360$  nm) were used. Polystyrene calibration was used for all molecular weight calculations.

## 2.4. Analysis

UV–VIS spectra of both the poly(MMA-co-FB) and fluorescent brighteners in chloroform, and in solid polymeric films were recorded. The polymeric films used in the study were sufficiently thin (50  $\mu$ m) to absorb in the range of validity of the Lambert–Beer law. Likewise, non-reprecipitated (1 g) and repeatedly reprecipitated (1 g). Poly(MMA-co-FB) were dissolved in chloroform (25 ml). UV–VIS spectra were taken and depending on the relation of the absorption of the reprecipitated polymer to that of the non-reprecipitated one, the percent content of the covalently bond FB was calculated.

Fluorescence spectra of the monomeric FBs and copolymers in chloroform solutions as well as in thin polymer films were taken on a Perkin-Elmer MPF 44.

The quantitative color characterization of the copolymers was made on the basis of the respective colorimetric parameters obtained and calculated by a Texflach ACS/DATACOLOR color measurement system.

## 2.5. Photodestruction of the FBs and copolymers

The solutions of the monomeric FBs and the copolymers were irradiated with TQ 150 Original Hanau high pressure 150 W mercury lamp, with filter for monochromatic light ( $\lambda = 366$  nm), provided with a quartz tube. The solid copolymeric films were in 20 cm distance. The changes in concentration were followed spectrophotometrically by the changes in the absorption maximum  $\lambda_A$ . Photodestruction of low molecular weight 1,8-naphthalimide FBs was carried by irradiation of the ethanol solution of the dyes at concentration 1.10<sup>-5</sup> mol l<sup>-1</sup>. The photodestruction of the polymers was followed by measuring the changes in the molecular weight using GPC. The copolymeric films of poly(MMA-co-FB) were 50  $\mu$ m thick.

## 3. Results and discussion

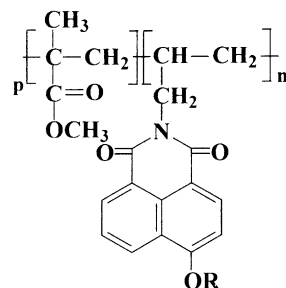
### 3.1. Polymerization investigations

Free radical polymerization of MMA in the presence of 1 wt.% of the FBs has been investigated. The copolymerization process was conducted under conditions used with other similar 1,8-naphthalimide derivatives [14,18]. Transparent fluorescent blue copolymers with the structure presented in Scheme 1 have been obtained.

The yields for poly(MMA-co-FB) were 83 wt.% (FB1) 82 wt.% (FB2) and 79 wt.% for the homopolymethylmethacrylate.

The presence of a covalent bond between the monomeric FB units and polymer chain has been proved by UV–VIS spectroscopic methods and by GPC techniques. Noteworthy is the effect of the FBs upon the molecular weight of the copolymers.

The molecular characteristics of the copolymers obtained by GPC are listed in Table 1. The molecular weight and molecular weight distribution confirm the formation of high molecular weight polymers. The molecular weights found are in the range  $M_w = 1.36$  to  $1.52 \times 10^5$  and  $M_n = 0.67$  to  $0.95 \times 10^5$  for polymethylmethacrylate copolymers. The double detection shows close values for the elution time in both chromatograms indicating the presence of copolymers



Scheme 1.

Table 1  
Molecular characteristics of polymethylmethacrylate copolymers

Polymers	Before irradiation			After irradiation			A
	$(M_w)_0 \cdot 10^{-5}$	$(M_n)_0 \cdot 10^{-5}$	$(M_w)_0/(M_n)_0$	$M_w \cdot 10^{-5}$	$M_n \cdot 10^{-5}$	$M_w/M_n$	
Poly(MMA-co-FB1)	1.41	0.67	2.1	1.30	0.50	2.6	0.34
Poly(MMA-co-FB2)	1.39	0.68	2.0	1.31	0.50	2.6	0.36
PMMA	1.52	0.95	1.6	1.31	0.45	2.9	1.11

which absorb at about 360 nm. The polydispersity  $M_w/M_n$  is in the region 1.6–2.1 (Table 1).

The UV–VIS absorption spectra of the precipitated polymers had similar absorption maxima as the monomeric FBs, showing that the basic chromophore of the FBs does not change, neither during the polymerization, nor as a result from its bonding to the polymer chain. Fig. 1 shows the kinetics of FBs bonding to the polymer macromolecules. As seen in Fig. 1 the FBs did react with the methylmethacrylate monomers. Both FBs have almost the same activity with the monomers due to their similar chromophoric systems. It has been found that over 92–93% of the initially introduced FB (1%), are chemically bonded. Considering that the values are obtained for repeatedly precipitated polymers where low molecular fractions have been removed during precipitation, the results are rather satisfactory and imply that the FBs are suitable for production of blue fluorescent polymethylmethacrylate copolymers.

### 3.2. Color measurement

The assessment of the fluorescent polymethylmethacrylate copolymers has been made in terms of tristimulus colorimetry. The color range achieved has been characterized quantitatively and according to the three main CIELab parameters ( $L^*$ ,  $a^*$  and  $b^*$ ) and the chromaticity coordinates ( $x$ ,  $y$  and  $Y\%$ ). The color space defined as CIELab space is determined by planar axes. These are axes  $a^*$  and  $b^*$ , i.e. the axes of undefined length in which the intersection is under the right angle and which can have positive and negative

values. CIELab values are determined from the Eqs. (1)–(3)

$$L^* = 116 \left( \frac{Y}{Y_0} \right)^{1/3} - 16 \quad (1)$$

$$a^* = 500 \left[ \left( \frac{X}{X_0} \right)^{1/3} - \left( \frac{Y}{Y_0} \right)^{1/3} \right] \quad (2)$$

$$b^* = 200 \left[ \left( \frac{Y}{Y_0} \right)^{1/3} - \left( \frac{Z}{Z_0} \right)^{1/3} \right] \quad (3)$$

where  $X_0$ ,  $Y_0$ ,  $Z_0$  are the tristimulus values of specified achromatic light used in illumination,  $X$ ,  $Y$ ,  $Z$  are the values defined for the fluorescent polymers. The values of  $Y_0$  is normalized so that  $Y_0 = 100$ .

In Table 2 are presented the values of the chromaticity coordinates ( $x$ ,  $y$  and  $Y\%$ ) and the position of the color in the CIELab color solid ( $L^*$ ,  $a^*$ ,  $b^*$ ).

Fig. 2 shows the reflectance and fluorescence of poly(MMA-co-FB) and pure PMMA polymers. As seen then copolymers re-emit the light absorbed as blue fluorescence that complement the yellowness and adds a bluish hue to the polymeric substrate.

### 3.3. Photophysical characteristics of monomeric and polymeric fluorescent brighteners

The UV–VIS absorption properties of the FBs under study are basically related to the polarization of the naphthalimide molecule on irradiation, resulting from the electron

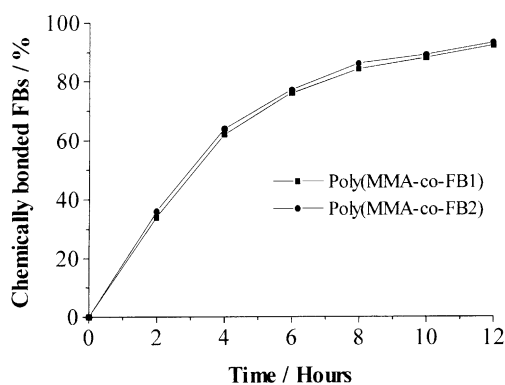


Fig. 1. Dependence of the chemically bonded 1,8-naphthalimide FBs 1 and 2 on the time of polymerization.

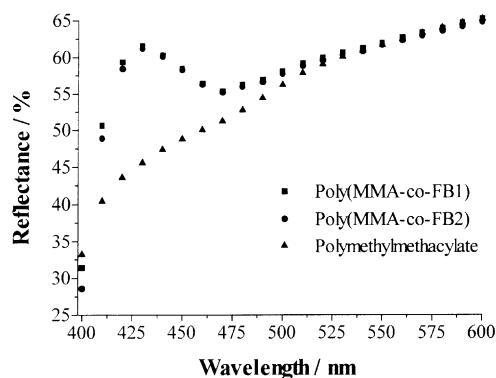


Fig. 2. Reflectance and fluorescence of copolymers and pure polymethylmethacrylate.

Table 2  
Color data of polymethylmethacrylate-based copolymers before and after irradiation

Polymers	Chromaticity		Luminance factor $Y$ (%)	CIELab coordinates		
	$x$	$y$		$L^*$	$a^*$	$b^*$
Before irradiation						
PMMA	0.3385	0.3558	60.98	82.37	0.45	12.14
Poly(MMA-co-FB1)	0.3256	0.3365	61.91	82.87	2.85	3.77
Poly(MMA-co-FB2)	0.3254	0.3365	61.50	82.65	2.78	3.72
After irradiation						
PMMA	0.3344	0.3544	61.01	83.20	-0.72	11.44
Poly(MMA-co-FB1)	0.3307	0.3473	62.25	83.05	0.57	8.17
Poly(MMA-co-FB2)	0.3335	0.3516	61.63	82.72	0.02	10.01

donor–acceptor interaction between the alkoxy substituents at C-4 and the carbonyl groups from the imide structure of the chromophorous system, and may be influenced by the environmental effect of the media upon this interaction.

Basic photophysical characteristics of the monomeric naphthalimide FBs are measured in chloroform solution. In Table 3 the values of the ground state position of the absorption maximum ( $\lambda_A$ ) and the extinction coefficient ( $\varepsilon$ ) of the FBs are presented. The values of fluorescent maxima ( $\lambda_F$ ), Stokes shift  $\nu_A - \nu_F$ , quantum yield of fluorescence ( $\Phi_F$ ) and the energy yield of the FBs are also listed.

In chloroform solution the monomeric FBs display intense blue fluorescence. The absorption maxima  $\lambda_A$  of the monomeric FBs are in the UV region at 366 and 368 nm. Fluorescence emission is observed in the visible region with a well pronounced maxima  $\lambda_F$  at 446 and 449 nm, respectively.

The Stokes shift  $\nu_A - \nu_F$  is an important parameters for the fluorophores. It is a parameter which 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 shift is found by Eq. (4)

$$(\nu_A - \nu_F) = \left( \frac{1}{\lambda_A} - \frac{1}{\lambda_F} \right) \times 10^7 \quad (4)$$

The Stokes shift has values between  $4900 \text{ cm}^{-1}$  as it is common for the 1,8-naphthalimide derivatives [30].

Their oscillator strength,  $f$ , is among the important characteristics of fluorophores. It shows the effective number

of electrons the transition of which from the ground to excited state gives the absorption area in the electronic spectrum. Values of the oscillator strength were calculated using Eq. (5) [31]

$$f = 4.32 \times 10^{-9} \Delta\nu_{1/2} \varepsilon_{\max} \quad (5)$$

where  $\Delta\nu_{1/2}$  is the width of the absorption band (in  $\text{cm}^{-1}$ ) at  $1/2\varepsilon_{\max}$ . The values are 0.342 (FB1) and 0.331 (FB2) in chloroform solution.

The ability of the molecules to emit the absorbed light energy is characterized quantitatively by the quantum fluorescent yield  $\Phi_F$ . From the tabulated data (Table 3), the studied FBs **1** and **2** have quantum fluorescent yield  $\Phi_F = 0.89$  and  $0.82$ , respectively.

Besides  $\Phi_F$  energy yield of fluorescence  $E_F$  can be also used. It is calculated from the Eq. (6) [32]

$$E_F = \Phi_F \frac{\lambda_A}{\lambda_F} \quad (6)$$

The respective results from  $E_F$  is 0.67–0.69.

The study covers the spectral characteristics of structurally modified copolymers as well. The copolymers are soluble in the solvents common for the homopolymers.

Table 4 presents the data obtained from the absorption and fluorescence spectra of the side-group copolymers in chloroform solution and in solid state. An absorption maxima in solution has been observed at 368 and 370 nm for the poly(MMA-co-FB) as well as pronounced fluorescence maxima at 444 and 445 nm, respectively. The absorption and fluorescence maxima of the copolymers in solution are very similar to those of the monomeric FBs in the same solvent indicating further the preservation of the chromophoric system during the copolymerization. The quantum fluorescence yield  $\Phi_F$  of the copolymers with  $\Phi_F = 0.89$ – $0.91$  is higher than that for the monomeric FBs themselves.

This is connected with the decrease of emission less processes and is obviously in relation with the bonding of the fluorophores to the polymer chain.

The absorption maxima  $\lambda_A$  of the copolymers in solid state are at 374 nm for both copolymers (Table 4). The

Table 3  
Photophysical characteristics of the fluorescent brighteners **1** and **2** in chloroform solution

	FB1	FB2
$\lambda_A$ nm	368	366
$\log \varepsilon$	4.41	4.37
$\lambda_F$ nm	449	446
$\nu_A - \nu_F \text{ cm}^{-1}$	4902	4901
$f$	0.342	0.331
$\Phi_F$	0.85	0.82
$E_F$	0.69	0.67

Table 4  
Spectral characteristics of the fluorescent copolymers recorded in solution and on thin films

Polymer	In chloroform solution				In solid film		
	$\lambda_A$ (nm)	$\lambda_F$ (nm)	$\nu_A - \nu_F$ (cm <sup>-1</sup> )	$\Phi_F$	$\lambda_A$ (nm)	$\lambda_F$ (nm)	$\nu_A - \nu_F$ (cm <sup>-1</sup> )
Poly(MMA-co-FB1)	368	445	4944	0.89	374	435	3749
Poly(MMA-co-FB2)	370	444	4736	0.91	374	438	3906

fluorescence maxima of thin solid film are in the region 435–438 nm. However, the fluorescence spectra of the solid polymer films differ significantly from those in chloroform solution being hypsochromically shifted. This effect is obviously connected with rigidity of the structure there.

The blue fluorescence in chloroform solution and in thin solid films which is more intense than that of the monomer FBs. This phenomenon is due to the perfect incorporation of the FB into the polymeric matrixes which hinders the conformational changes in the chromophoric system [33]. Thus, the part of emissionless deactivation during the transition  $S_1 \rightarrow S_0$  is smaller.

#### 3.4. Investigation of the photostability of the monomeric FBs in solution and in thin polymeric film

With regard to the practical usage of the fluorescent brighteners and their copolymers poly(MMA-co-FB) it is worth studying their photodegradation.

Fig. 3 shows the dependence changes of absorption maxima poly(MMA-co-FB1) versus irradiation time and the monomeric FB1 in chloroform solution. As seen the photostability of the FB is more pronounced in the case of polymeric component which might be due to an electron transfer from the FB molecule to the main polymer chain during the transfer from excited state to ground state:  $S_1 \rightarrow S_0$  [34]. Similar spectral dependence are also observed and for poly(MMA-co-FB2). The observations were similar when studying the photodegradation of similar chromophoric systems which exhibited very good photostability [35].

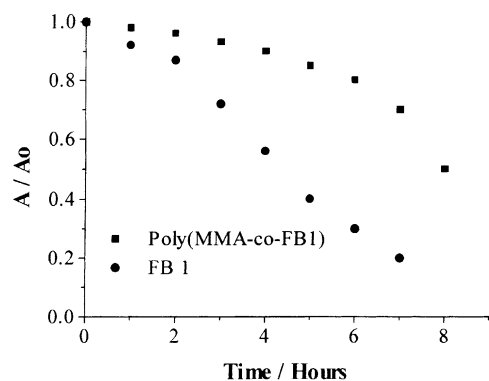


Fig. 3. Photodegradation of FB1 and poly(MMA-co-FB1) in chloroform solution.

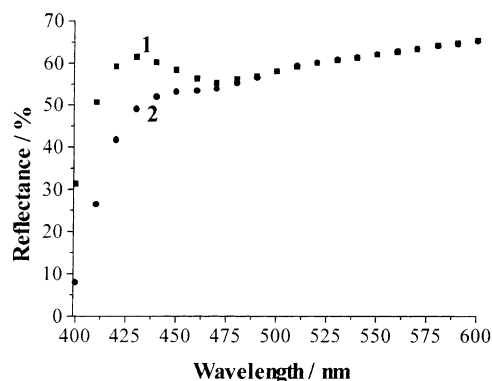


Fig. 4. Reflectance and fluorescence of poly(MMA-co-FB1) before (1) and after (2) irradiation with a light.

Fig. 4 shows the reflectance versus wavelength of solid copolymer films before and after irradiation. The intensity of reflectance is small, due to the destruction of chromophoric FB molecules. The respective color characteristics of PMMA-based copolymers are presented in Table 2.

#### 3.5. Photostability of the polymethylmethacrylates

The effect of monomeric FBs upon the photodestruction of polymethylmethacrylate is worth studying. 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 polymethylmethacrylate.

The number of chain breaks per molecule  $A$  is given by Eq. (6) [36]

$$A = \frac{(M_n)_0}{(M_n)} - 1 \quad (6)$$

where  $(M_n)_0$  and  $(M_n)$  are the number-average molecular weights before and after irradiation, respectively. The results are listed in Table 1. As seen poly(MMA-co-FB) does not change significantly its polydispersity and molecular weight distribution while the values for  $M_w$  and  $M_n$  for PMMA decrease. For the FBs, the results show that the stabilizing effect is greater for FB2. The photostabilization could be explained as a result from the absorbed UV light which is re-emitted as a long wave visible fluorescent emission. Thus, the distraction effect of UV irradiation is choked.

#### 4. Conclusions

Bulk copolymerization of MMA with two polymerizable blue fluorescent 1,8-naphthalimide derivatives has been investigated. It has been found that the fluorescent brighteners take part in the polymerization and are covalently bonded to the polymer chain obtaining blue fluorescent side-group copolymers. The results achieved show that the monomeric 1,8-naphthalimide derivatives investigated are suitable for preparing copolymers of MMA with intensive blue fluorescence emission and good photostability.

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