

Spectrophotometric Investigation of the Copolymerization of Styrene or Methyl Methacrylate with 1,8-Naphthalimide Dyes

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ABSTRACT: The copolymerization of styrene or methyl methacrylate with 1,8-naphthalimide dyes to yield fluorescent side-group copolymers was investigated. During copolymerization, no changes occurred in the chromophoric systems of the dyes. Colorimetrically, it was found that more than 0.90% of the dyes were chemically bonded to the polymer chain. The effect of polymer coloration was proven by appropriate coloristic characterization. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2463–2470, 2001

Key words: 1,8-naphthalimide; polymerizable dyes; fluorescent side-group copolymers; polystyrene; poly(methyl methacrylate)

INTRODUCTION

During the last few years, the copolymerization of monomeric polymerizable dyes with some traditional monomers such as styrene (St) and methyl methacrylate (MMA) have been investigated intensively.^{1–3} The colored copolymers thus obtained are resistant to wet treatment and organic solvents because the monomeric dyes are covalently bonded to the polymer chain. The 1,8-naphthalimide dyes possess many properties that make them applicable as colorants for synthetic polymeric materials. Because of their spectral properties, the 1,8-naphthalimide derivatives are useful as fluorescent dyes for solar-energy collectors,⁴ in laser active media,⁵ in medicine as antiviral compounds⁶ or as analgesics,⁷ and so on.

Some of our previous articles reported fluorescent polymerizable 1,8-naphthalimide dyes that

we synthesized^{8–12} and their ability to be copolymerized with St, MMA, or acrylonitrile to obtain copolymers with an intensive fluorescence.^{13–17} Similar fluorescent copolymers have been recently reported to have a novel use as luminophores in liquid-crystal systems for displays of the guest–host type.^{17–19} The copolymers of 1,8-naphthalimide with vinylcarbazole possess chemiluminescent properties.^{20,21}

In this article, we report the ability of three polymerizable 1,8-naphthalimide dyes to copolymerize with St or MMA in bulk and the color characteristics of the copolymers obtained.

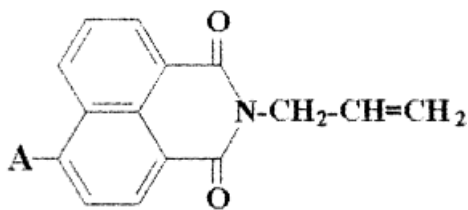
EXPERIMENTAL

Materials

The monomeric fluorescent 1,8-naphthalimide dyes used in the copolymerization process had the following structure:

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where A is $-\text{NHCH}_2\text{CH}_3$ (dye **1**), $-\text{N}(\text{CH}_2\text{CH}_3)_2$ (dye **2**), or $-\text{morpholino}$ (dye **3**).

Their synthesis was previously described.^{8,9} The choice of these 1,8-naphthalimide dyes was made on the basis of their good photophysical and coloristic properties and because of their high photostability.^{8,22}

Commercial St and MMA were used after purification. St was washed with an aqueous NaOH solution, dried over CaH_2 and then distilled under reduced pressure in a pure nitrogen (99.99% N_2) atmosphere. MMA was used after distillation under reduced pressure in a nitrogen atmosphere. Di(benzoyl peroxide) (DBP; Fluka, Steinheim, Germany) recrystallized from chloroform was used as an initiator of the free-radical copolymerization.

Synthesis and Characterization of Fluorescent Copolymers

The radical copolymerization of the 1,8-naphthalimide dyes **1–3** with St or MMA was carried out in ampules, previously purged with pure dry N_2 . The process of copolymerization was conducted under the conditions used with other similar monomers:¹⁷ for St, at 80°C for 8 h, and for MMA, at 70°C for 10 h in the presence of 1.0 wt % dyes and 1.0 wt % DBP under N_2 . The side-chain copolymers thus obtained were several times reprecipitated with ethanol from benzene or chloroform for polystyrene (PS)-based or poly(methyl methacrylate) (PMMA)-based copolymers, respectively. The precipitated copolymers were repeatedly washed with ethanol, recovered by filtration, and dried *in vacuo* to a constant weight. Transparent fluorescent copolymers of intense yellow-green emission were obtained. All spectrophotometric measurements were carried out with precipitated colored polymers.

Determination of Molecular Weight

The molecular weights were determined on a gel permeation chromatography (GPC) Waters 244 (USA) apparatus equipped with a combination of 100-Å and 1000-Å linear Ultrastyrigel columns;

the solvent was tetrahydrofuran at a flow rate of 1.0 mL/min at 45°C . Both differential refractive index and ultraviolet–visible (UV–vis) absorption detectors ($\lambda_A = 420 \text{ nm}$) were used. PS calibration was used for all molecular weight calculations.

Analysis

UV–vis absorption spectra were recorded on a Hewlett–Packard (Palo Alto, CA) 8254A spectrophotometer for the monomeric dyes in organic solvents and for the copolymers of St and MMA in benzene or chloroform, respectively, on their solid films. The polymeric films used in the study were sufficiently thin ($40 \mu\text{m}$) and absorbed in the range of validity of the Lambert–Beer law.

Fluorescence spectra of monomeric naphthalimide dyes and copolymers in benzene and chloroform solutions and in thin polymer films were taken on a PerkinElmer MPF 44.

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

RESULTS AND DISCUSSION

Polymerization Investigations

The free-radical polymerization of St or MMA in the presence of 1 wt % dyes was investigated kinetically. The results obtained are plotted in Figures 1 and 2 and compared with those for the homopolymers. The polymer yield at the initial stage of the copolymerization increased linearly with time without any induction period. As seen, the participation of dyes **1–3** feebly accelerated the process of the polymerization. The yields were 73–80 wt % for poly(St-*co*-dye) and 70 wt % for homopolystyrene and were 80–85 wt % for poly(MMA-*co*-dye) and 75 wt % for homo[poly(methyl methacrylate)] (Table I).

The presence of a covalent bond between the monomeric dye units and the polymer chain was proven by UV–vis spectroscopy methods and GPC techniques. Noteworthy is the effect of the dyes on the molecular weight of the copolymers.

The molecular characteristics of the copolymers obtained by GPC are listed in Table I. The molecular weight and molecular weight distribution confirmed the formation of high-molecular-weight polymers. The molecular weights found

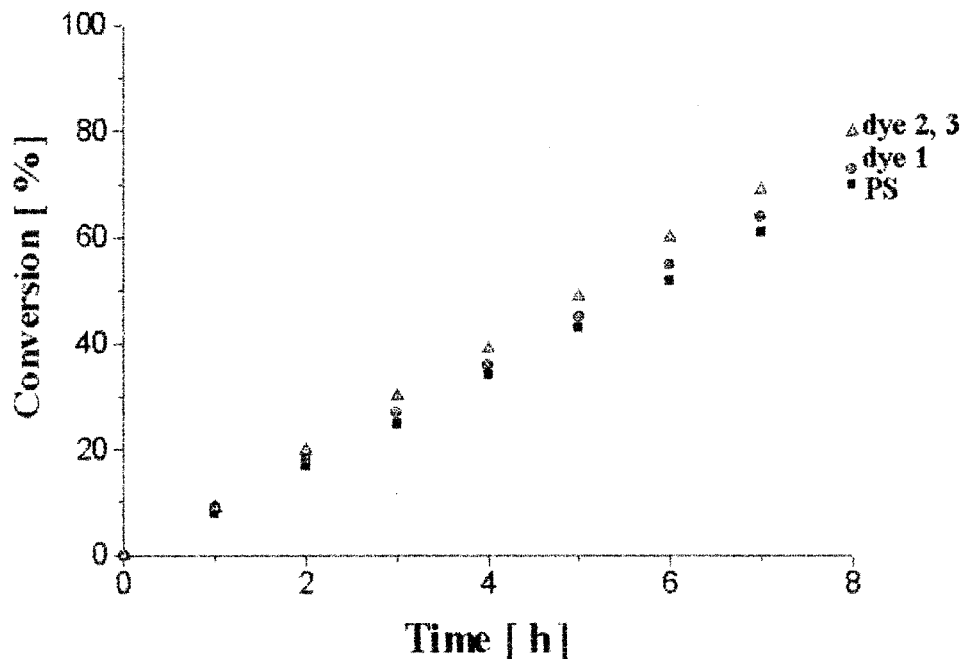


Figure 1 Conversion versus polymerization time dependence for the polymerization of St in the presence of 1,8-naphthalimide dyes.

ranged from 1.91×10^5 to 2.01×10^5 [weight-average molecular weight (\bar{M}_w)] and 1.01×10^5 to 1.10×10^5 [number-average molecular weight (\bar{M}_n)] for PS copolymers and from 1.56×10^5 to

1.82×10^5 (\bar{M}_w) and 0.78×10^5 to 0.83×10^5 (\bar{M}_n) for PMMA copolymers. The double detection showed close values for the elution time in both chromatograms, indicating the presence of copol-

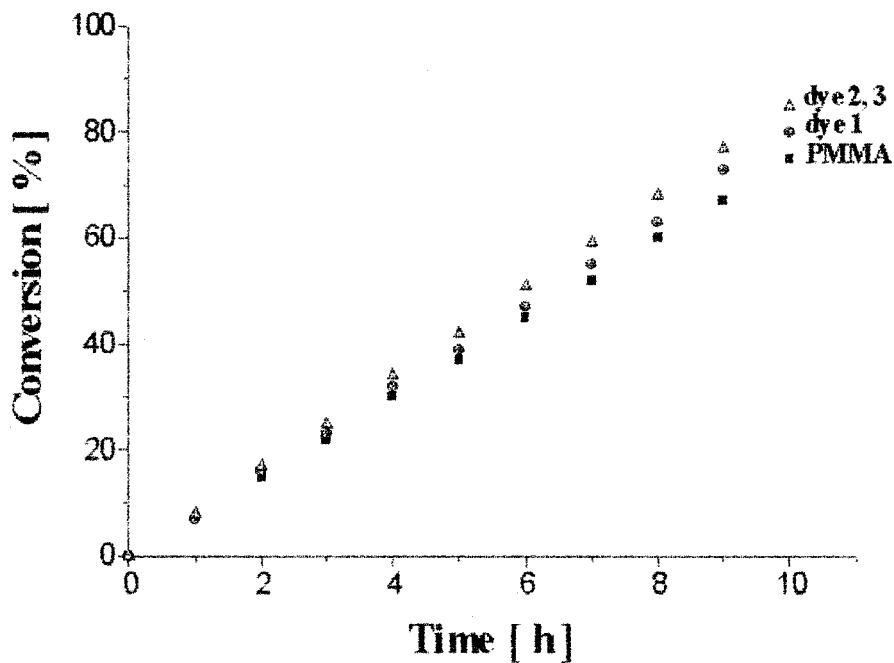


Figure 2 Conversion versus polymerization time dependence for the polymerization of MMA in the presence of 1,8-naphthalimide dyes.

Table I Molecular Characteristics of PS- and PMMA-Based Copolymers

Copolymer	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	\bar{M}_w/\bar{M}_n	Yield (%)	Chemically Bound Dye (%)
Poly(St-co-dye 1)	1.91	1.01	1.9	73	0.90
Poly(St-co-dye 2)	1.98	1.10	1.8	80	0.92
Poly(St-co-dye 3)	2.01	1.06	1.9	80	0.92
Poly(MMA-co-dye 1)	1.56	0.78	2.0	80	0.92
Poly(MMA-co-dye 2)	1.82	0.83	2.2	85	0.92
Poly(MMA-co-dye 3)	1.78	0.81	2.2	85	0.94

ymers that absorb at about 420 nm. The polydispersity (\bar{M}_w/\bar{M}_n) was in the region 1.8–1.9 for PS-based copolymers and 2.0–2.2 for PMMA-based copolymers.

The UV–vis absorption spectra of the precipitated polymers had absorption maxima similar to those of the monomeric dyes, showing that the basic chromophore of the dye did not change either during the polymerization or as a result of its bonding to the polymer chain. This allowed us to use the standard curve method when determining the percentage of the dye chemically bonded to the polymer chain. Over 90–92% for PS and 92–94% for PMMA-based polymers of the initially introduced dyes (1%) were chemically bonded (Table I and Fig. 3). Because the values were obtained for repeatedly precipitated polymers where low molecular fractions were removed during precipitation, the results are rather satisfactory and imply that the dyes are suitable for the production of colored fluorescent copolymers.

Color Measurement

The assessment of the colored PS- and PMMA-based polymers was made in terms of tristimulus

colorimetry. The color range achieved was characterized quantitatively and qualitatively according to the three main CIE Lab parameters (L^* , a^* , and b^*), the chromaticity coordinates (x and y), and Helmholtz coordinates. The color space, defined as CIE Lab space, was determined by planar axes. These are axes a^* and b^* , that is, the axes of undefined length in which the intersection is under the right angle and which can have positive and negative values. CIE Lab values were determined from eqs. (1)–(3):

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

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

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

where X_0 , Y_0 , and Z_0 are the tristimulus values of specified achromatic light used in illumination and X , Y , and Z are the values defined for the colored polymers. The value of Y_0 is normalized in such a way that $Y_0 = 100$.

Table II shows the values of the chromaticity coordinates (x and y), the Helmholtz coordinates

Table II Color Data of PS- and PMMA-Based Copolymers

Polymer	Helmholtz Coordinates							
	Chromaticity		Dominant Wavelength: λ_D (nm)	Luminance Factor: Y (%)	Purity (%)	CIE Lab Coordinates		
	x	y				L^*	a^*	b^*
PS	0.3394	0.3576	571	57.93	14.73	80.70	0.15	12.66
Poly(st-co-dye 1)	0.3698	0.4601	562	65.10	53.43	82.97	-17.74	60.01
Poly(st-co-dye 2)	0.3788	0.4684	562	65.55	56.96	84.77	-22.44	56.96
Poly(st-co-dye 3)	0.3832	0.4741	562	65.56	59.78	84.77	-22.53	60.03
PMMA	0.3367	0.3542	571	64.12	13.03	84.03	0.33	11.55
Poly(MMA-co-dye 1)	0.3593	0.4507	562	70.47	53.42	87.23	-20.21	54.21
Poly(MMA-co-dye 2)	0.3796	0.4594	562	71.35	54.68	87.65	-20.03	55.70
Poly(MMA-co-dye 3)	0.4129	0.4999	562	73.03	75.47	88.45	-20.26	81.55

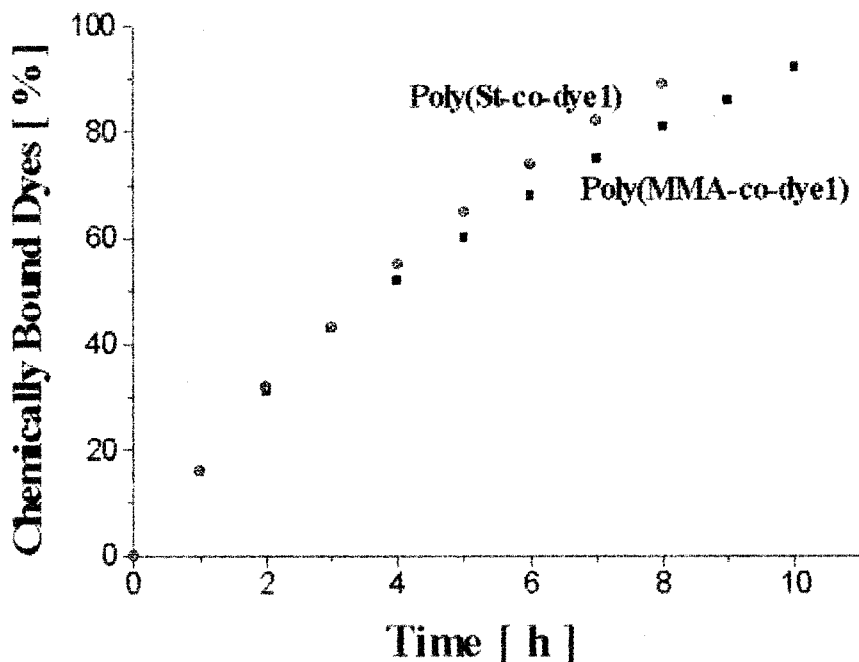


Figure 3 Dependence of the chemically bonded 1,8-naphthalimide dye **1** on the time of polymerization.

(λ_D , Y %, P %), and the position of the color in the CIE Lab color solid (L^* , a^* , b^*). The dominant wavelength, λ_D , showed a bathochromic shift when the dyes were bonded into the polymer chain. The dominant wavelengths were identical for both copolymers based on PS and PMMA. Higher lightness of color was observed for PMMA-based copolymers. The purity of the colors was higher for the copolymers prepared with dye **3** as a comonomer. The data (x , y) and (a^* , b^*) show that the color of the copolymers was in the yellow-green region.

The method for determining the difference in copolymer color as dependent on the polymerization time was used for the first time as a criterion to evaluate the chemical bonding of the dye to the polymer chain. The method is based on the fact that the changes in the percentage of the dye chemically bonded to the polymer chain leads to a change in the color difference, ΔE^* .

The color difference was estimated by eq. (4):

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}, \quad (4)$$

where ΔL^* , Δa^* , and Δb^* are the differences in the coordinates of two points present in the CIE (L^* , a^* , b^*) color scale. For the homopolymers, $\Delta E^* = 0$.

Color difference dependence on the copolymerization time for dye **1** is shown in Figure 3 as an example. ΔE^* increased smoothly, which is evidence that with time the amount of the dye chemically bonded also increased. The plot of ΔE^* follows a pattern similar to the UV-vis recorded one, showing how the amount of the chemically bonded dye increased with time (Fig. 4). This fact reveals that the method of objective colorimetry can be implemented for studying the copolymerization processes of running between colored comonomers and conventional vinyl or methacrylic monomers.

Photophysical Characteristics of Monomeric and Polymeric Dyes

Table III presents the photophysical characteristics of the monomeric naphthalimide dyes measured in toluene and chloroform solutions. In Table III, the values of the ground-state position of the absorption maximum (λ_A) and the extinction coefficient (ϵ) of the dyes are presented. The values of fluorescent maxima (λ_F), Stokes shift ($\nu_A - \nu_F$), and quantum yield of fluorescence (Φ_F) are also presented.

In solution, the monomeric dyes displayed yellow-green color and intense fluorescence. The absorption maxima, λ_A , of the monomeric dyes were

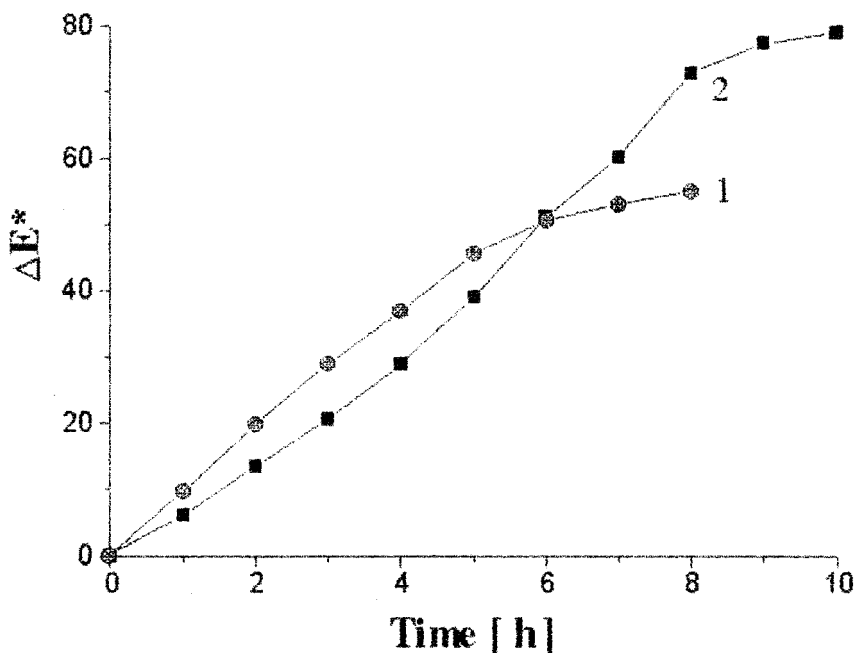


Figure 4 Dependence of the color difference ΔE^* for poly(St-co-dye 1) 1 and poly(MMA-co-dye 1) 2 on the time of polymerization.

in the visible region, at 390–422 nm in toluene and 408–428 nm in a chloroform solution. The hypsochromic shift for dye **3** was probably caused by the rotation of the morpholine group around the single bond between it and the remaining components of the dye molecule.²³ A fluorescence emission was observed in the region of 440–600 nm with a well-pronounced maxima, λ_F , at 488–504 nm.

The Stokes shift ($\nu_A - \nu_F$) is an important parameter for the fluorescent dyes and was found with eq. (5):

$$\nu_A - \nu_F = (1/\lambda_A - 1/\lambda_F) \times 10^7 \quad (5)$$

The Stokes shift was 3205–5232 cm^{-1} in toluene and 3523–4510 cm^{-1} in a chloroform solution (Table II); it became greater in both solvents in the order

$$3 > 2 > 1$$

The significant Stokes shift in dye **3** was caused by the energy losses during the transition into the excited state.

The ability of the molecules to emit absorbed light energy was characterized quantitatively by the quantum fluorescent yield, Φ_F . It was determined on the basis of the absorption and fluores-

Table III Photophysical Characteristics of 1,8-Naphthalimide Dyes in Solution

	Chloroform			Toluene		
	Dye 1	Dye 2	Dye 3	Dye 1	Dye 2	Dye 3
λ_A (nm)	428	419	408	422	408	390
$\log \epsilon$	4.21	4.19	4.30	4.38	4.32	4.41
λ_F (nm)	504	500	500	488	493	490
$(\nu_A - \nu_F)$ (cm^{-1})	3523	3866	4510	3205	4225	5232
Φ_F	0.89	0.32	0.28	0.92	0.38	0.24
E_F	0.75	0.27	0.23	0.79	0.31	0.24

Table IV Absorption and Fluorescence Characteristics of Copolymers

Copolymer	In Solution			In Solid Film		
	λ_A (nm)	λ_F (nm)	$\nu_A - \nu_F$ (cm ⁻¹)	λ_A (nm)	λ_F (nm)	$\nu_A - \nu_F$ (cm ⁻¹)
poly(St-co-dye 1)	420	486	3233	416	484	3377
poly(St-co-dye 2)	405	490	4283	404	488	4260
poly(St-co-dye 3)	388	494	5530	386	490	5498
poly(MMA-co-dye 1)	426	500	3474	422	498	3616
poly(MMA-co-dye 2)	416	500	4038	414	496	3993
poly(MMA-co-dye 3)	408	502	4589	406	496	4469

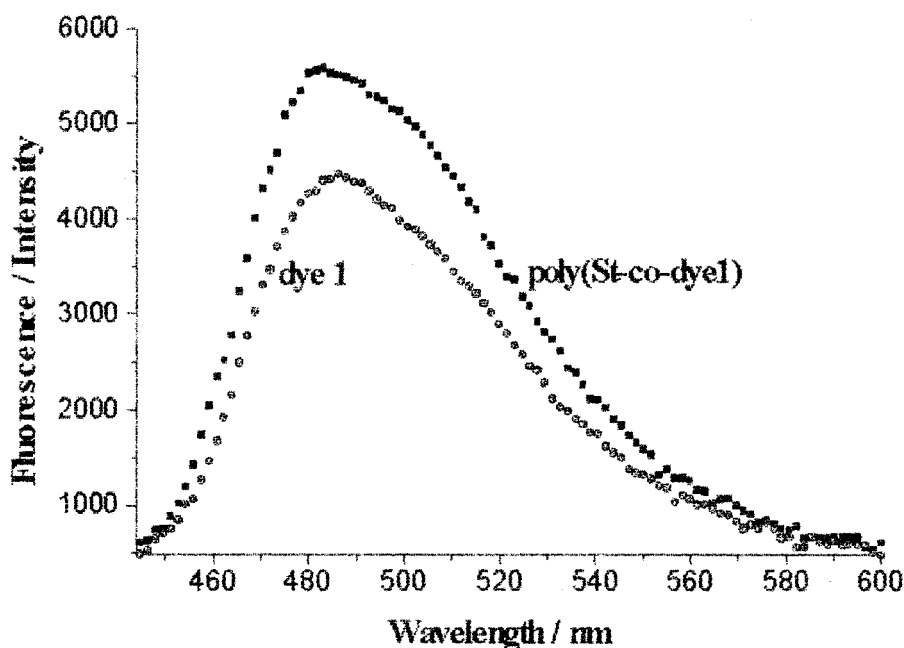
cence spectra of the dyes dissolved in toluene and chloroform at a concentration of 10⁻⁶ mol/L with rodamine 6G ($\Phi_0 = 0.88$) as a standard.²⁴ From the tabulated data (Table III), it can be seen that the studied dyes had a Φ_F value of 0.28–0.89 (in chloroform) and 0.31–0.92 (in toluene). The quantum yield for all dyes increased with the transition from chloroform ($\epsilon = 4.81$) to the less polar toluene ($\epsilon = 2.32$). The Φ_F results were in the region 0.89–0.92 for dye 1, which shows that the fluorescence involved good emission deactivation of the first excited single state S₁. The low values of dyes 2 and 3 were caused by the decrease in the coplanarity of the molecule originating from steric factors. In this case, for dyes 2 and 3, the results show that the fluorescence involved non-emission deactivation of the S₁. Besides Φ_F , the

energy yield of fluorescence, E_F , can also be used:²⁵

$$E_F = \Phi_F \lambda_A / \lambda_F \quad (6)$$

The respective results from E_F were 0.23–0.79.

This study covered the spectral characteristics of structurally modified copolymers as well. The copolymers were soluble in the solvents common for the homopolymers. The copolymers were yellow-green with intensive fluorescence in solution and in solid films that was more intense than that of the monomer dyes. This phenomenon was caused by the perfect incorporation of the dyes into the polymeric matrices, which hindered the conformational changes in the chromophoric sys-


Figure 5 Fluorescence spectra of dye 1 and poly(St-co-dye 1) in a toluene solution.

tem.²⁶ Thus, the part of emissionless deactivation during the transition from S_1 to the ground state S_0 is smaller. Table IV presents the data obtained from the absorption and fluorescence spectra of the side-group copolymers in the isotropic state. An absorption maximum was observed at 386–420 nm for the poly(St-co-dye) and at 406–422 nm for the poly(MMA-co-dye) in addition to pronounced fluorescence maxima at 484–494 nm and 496–500 nm, respectively. The absorption and fluorescence maxima of the copolymers in solution were very similar to those of the monomeric dyes **1–3** in solution. Figure 5 presents, as an example, the fluorescence spectra of dyes **1** and poly(St-co-dye **1**) in a toluene solution. This obviously indicates that during the copolymerization process, there was no change in the chemical structure of the chromophoric system.

CONCLUSIONS

The block copolymerization of St or MMA with three fluorescent 1,8-naphthalimide dyes was investigated kinetically. The kinetics of chemical bonding of the dyes to the polymer was studied for the first time by colorimetric methods. The dyes took part in the polymerization and were covalently bonded to the polymer chain, giving fluorescent side-group copolymers.

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