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Dyes and Pigments 69 (2006) 204–209
DYES and PIGMENTS
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Photobleaching process of xanthene dyes initiated by *N*-phenylglycine in the polyvinylalcohol film

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Received 19 September 2004; received in revised form 12 November 2004; accepted 21 March 2005
Available online 25 May 2005

Abstract

The parameters such as quantum yield and molar absorption coefficients of the photoinitiator that are responsible for holographic sensitivity in photopolymer material are investigated with a single beam exposure experiment. The influence of exposure intensity, the concentrations of *N*-phenylglycine and dye on the photobleaching process of xanthenes dyes are presented. In addition, the effect of diphenyliodonium hexafluorophosphate salt on the quantum yield and molar absorption of xanthene dyes is studied.

Keywords: Photopolymer; Holographic recording; Quantum yield; Molar absorption

1. Introduction

Photopolymers are attractive optical recording materials for holography, holographic interferometry, optical image multiplexing, holographic optical devices etc. [1–3]. The photopolymerization of the photopolymer is the polymerization initiated by the light-induced radicals or ions. In this system, it is important to select a pertinent photoinitiator, which primarily generates initiating species, free radicals or ions, through a photochemical process. Much photoinitiator systems have been developed in order to improve the spectral selectivity and the quantum yield of radicals [4–6]. In this process, the dye's quantum yield, and the molar absorption coefficient are basic parameters that determine the photochemical behavior of the photopolymer materials.

In the presence of appropriate coinitiator partners, xanthene dyes can be used to initiate photopolymerization. Manivannan et al. [7] have studied the photobleaching of xanthene dyes in the presence of triethanolamine (TEA). The poor stability of TEA prompted us to change the TEA for another substance *N*-phenylglycine (NPG) and to design more efficient photoinitiating systems. We study the primary processes involved in the excited states of xanthene dyes that can be used in photoimaging systems for laser-induced polymerization, laser writing, or holographic recording. The influence of exposure intensity, *N*-phenylglycine and dye's concentration on the photobleaching parameters of xanthenes dyes are presented. In addition, the effect of DPI salt on the quantum yield and molar absorption of xanthene dyes are followed.

2. Experiment

2.1. Experimental set-up

In order to obtain the information about the photochemical parameters of the photobleaching, we

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doi:10.1016/j.dyepig.2005.03.011

set up a single beam exposure system, as shown in Fig. 1. An Ar+ laser ($\lambda = 514.5$ nm) is used as the exposure light for photobleaching experiments, because most of xanthene dyes possess the maximum absorption in the range of 400–600 nm. The transmitted light is detected by a photodetector and the time of irradiation is controlled using an electronic shutter. The transmittance is defined as the intensity ratio of the transmittance beam to that of the incident beam.

2.2. Photopolymer film preparations

To prepare the photopolymer films, the gravity settling method is used for its simplicity. The photosensitive solution consists basically of an initiating system – erythrosine B (ErB) as dye and *N*-phenylglycine (NPG) as coinitiator – together with acrylamide (AA) and *N*,*N*′-methylenebisacrylamide (BAA) as monomers, dimethylsulfoxide (DMSO) as plasticizer. These materials are supported by a matrix of polyvinylalcohol (PVA). Then, the solution is deposited on a leveled glass substrate, the liquid being spread uniformly over the whole surface. By changing the quantity of the poured liquid and the concentration of polyvinylalcohol, we can control the final thickness of the film (depending on the relative humidity in the room). Putting the films in a dark room at 60% RH and 25 °C to dry about 24–36 h, we get the dry photopolymer film that would be used in the following experiment.

3. Results and discussion

3.1. Theory

The design of efficient photosensitizer/photoinitiator combination system is partly based on a better understanding of the basic mechanism that is involved.

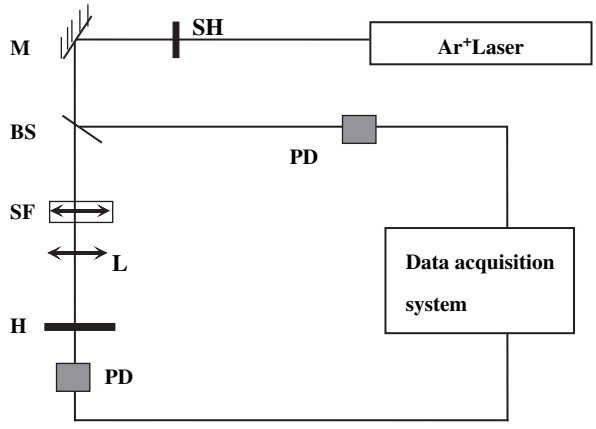

Fig. 1. Experimental set-up for real-time reading of transmittance. SH: Electronic shutter, M: mirror, BS: beam splitter, SF: spatial filter, L: collimating lens, PD: photodetector, H: holographic photopolymer.

The photoinitiating efficiency depends on the efficiency of triplet formation in the polymer matrix. The primary steps of the photoinitiating reaction are mostly explained on the basis of the electron transfer between xanthene and amine.

When a photosensitive dye is exposed to the light of a compatible wavelength, a primary photoprocess ensues. The dye absorbs the light and is promoted to a singlet excited state.

$$\mathrm{Dye} + h\nu \rightarrow {}^{1}\mathrm{Dye}^{*} \quad (1)$$

The singlet excited dye can return to the ground state by fluorescence quenching or fluorescence emission. And the singlet state can also undergo intersystem crossing into the more stable and longer lived triplet excited state.

$${}^{1}\mathrm{Dye}^{*} \rightarrow {}^{3}\mathrm{Dye}^{*} \quad (2)$$

The triplet excited state may revert back to ground state by a radiationless transfer or by delayed fluorescence or phosphorescence emission. At high dye concentrations, it can be deactivated by collision with another dye molecule.

$${}^{3}\mathrm{Dye}^{*} + \mathrm{Dye} \rightarrow 2\mathrm{Dye} \quad (3)$$

Oxygen quenching may also occur which involves an "inhibition period" at the onset of polymerization. This occurs until oxygen contained in the material is used up before polymerization begins.

When triplet state dye reacts with the electron donor by redox processes, the free radicals are generated and the dye is bleached. The electron donor used in this study is *N*-phenylglycine (NPG).

$${}^{3}\mathrm{Dye}^{*} + \mathrm{NPG} \rightarrow \mathrm{LDye} + \mathrm{NPG}^{\bullet} \quad (4)$$

Temporal variations of the transmittance $T(t)$ have been fitted with a photobleaching model developed on the basis of previous researcher's work [8]:

$$T(t) = \frac{T_{\mathrm{sf}}}{1 + (\mathrm{e}^{\varepsilon d[D]_0} - 1)\mathrm{e}^{-\varepsilon \Phi I_0 t}} \quad (5)$$

Where T_{sf} is a parameter related to scattering losses, d the thickness of the film, $[D]_0$ the initial concentration of dye, ε the natural molar absorption coefficient, Φ the quantum yield of generation of radicals and I_0 the exposure intensity. Applying a non-linear procedure based on Levenberg–Marquardt's algorithms, values of the quantum yield and the molar absorption are obtained. In order to study the photochemical processes some parameters like concentration of the dye and coinitiators, intensity have been varied. In addition, the effect of diphenyliodonium hexafluorophosphate (DPI) salt on the quantum yield and molar absorption of xanthene dyes is studied.

3.2. Effect of the concentration of dye

The transmittances obtained in materials with different concentration of erythrosine B are shown in Fig. 2. The threshold exposure time decreases with reducing the concentrations of dye as expected, and the change in transmittance is quite rapid, going from the threshold value to the maximum transmittance value in 20 s, when the erythrosine B concentration is 5×10^{-5} mol L^{-1}. Actually, the color of the film under exposure changes gradually from red to transparent, while the erythrosine B molecules transforming from the fundamental state to the leuco form (colorless). In the very high concentration of erythrosine B, the transmittance cannot be detected, because a great amount of light is absorbed and only a small amount penetrates the recording material.

Normally, the dye molecules convert into leuco form and there is an increase in transmittance until it reaches the saturation value. Before saturation, the evolution of transmittance may be considered to be the rate of bleaching of the dye (unit of s^{-1}). The bleaching kinetics of different concentration of erythrosine B can be compared from Fig. 2 and it increases with the decrease in dye's concentration in the presence of *N*-phenylglycine.

Values of quantum yield and molar absorption are obtained by applying Levenberg–Marquardt non-liner fit based on the transmittance curves as a function of exposure time (Fig. 2). As the concentration of erythrosine B increases, the quantum yield reduces (Fig. 3). At high concentrations of dye the quantum yield of generation of radicals is lesser; this fact can be related with the formation of dimeric species of the dye. Evidence of this fact can be seen from Fig. 4, in which the increase in the concentration of erythrosine B produces the apparition of a band at 527 nm, which is related to the formation of dimeric form [9]. Concentration of dye does not influence the molar absorption obviously, as shown in Fig. 5.

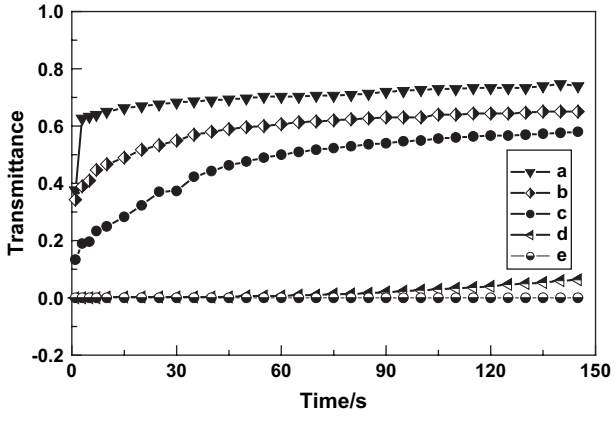

Fig. 2. Transmittance versus exposure time for the different concentration of erythrosine B. The basic composition is: AA: 0.33 mol L^{-1}, PVA: 7%, NPG: 0.88×10^{-2} mol L^{-1} and concentration of ErB: (a) 0.5×10^{-4} mol L^{-1}; (b) 1.0×10^{-4} mol L^{-1}; (c) 2.0×10^{-4} mol L^{-1}; (d) 5.0×10^{-4} mol L^{-1}; (e) 2.0×10^{-3} mol L^{-1}, and the exposure intensity is 34 mW.

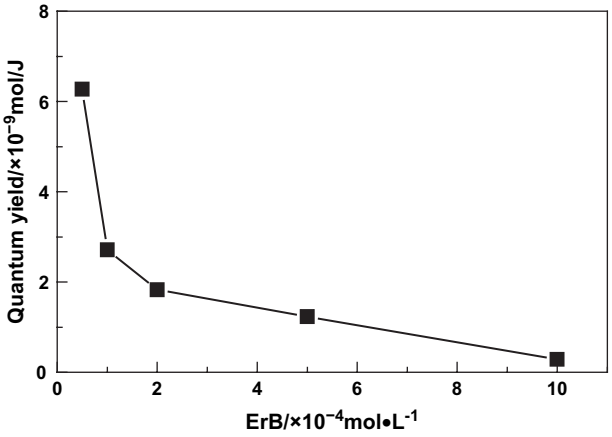

Fig. 3. Quantum yield versus the concentration of erythrosine B. The basic composition is: AA: 0.33 mol L^{-1}, PG: 0.88×10^{-2} mol L^{-1}, PVA: 7%, DMSO: 0.20 mol L^{-1} and the exposure intensity is 34 mW.

3.3. Effect of the concentration of N-phenylglycine

Fig. 6 presents the transmittance variation with the exposure time for different *N*-phenylglycine concentrations. When *N*-phenylglycine concentration is increased, the bleaching time diminishes. The bleaching kinetics of erythrosine B with different *N*-phenylglycine concentrations can be compared from Fig. 6 and it can be deduced that the bleaching rate increases with the increase in the concentration of *N*-phenylglycine. As can be seen from Fig. 7, the quantum yield increased rapidly with the increase in the concentration of *N*-phenylglycine. For the same dye concentration, with same incident intensity, the same number of triplet

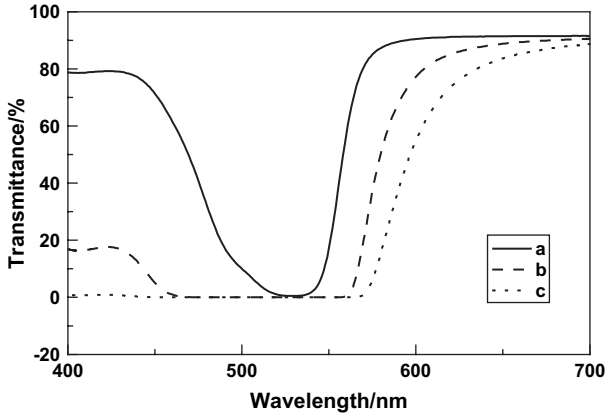

Fig. 4. Transmittance spectra of the material under different concentration of erythrosine B. The basic composition is: AA: 0.33 mol L^{-1}, PVA: 7%, NPG: 0.88×10^{-2} mol L^{-1}, DMSO: 0.20 mol L^{-1} and concentration of ErB: (a) 2.0×10^{-4} mol L^{-1}; (b) 5.0×10^{-4} mol L^{-1}, (c) 2.0×10^{-3} mol L^{-1}.

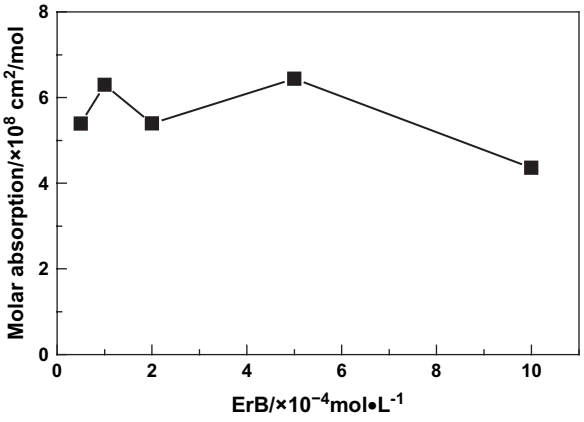

Fig. 5. Molar absorption versus the concentration of dye. The basic composition is: AA: 0.33 mol L^{-1}, PVA: 7%, PG: 0.88×10^{-2} mol L^{-1} and the exposure intensity is 34 mW.

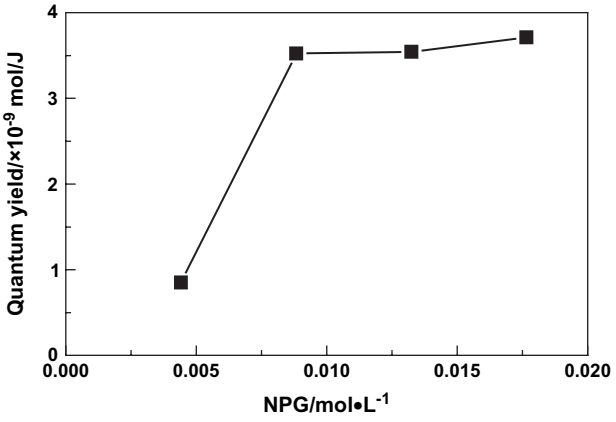

Fig. 7. Quantum yield versus the concentration of *N*-phenylglycine. The basic composition is: AA: 0.33 mol L^{-1}; BAA: 0.030 mol L^{-1}; ErB: 2.0×10^{-4} mol L^{-1}; DMSO: 0.2 mol L^{-1}; PVA: 7%, where the exposure intensity used is 33 mW/cm^2.

excited state dye is produced. When the electron donor (*N*-phenylglycine) is low, there are no enough electron donors to react with the triplet excited state dye, then most of triplet excited state dye revert back to steady state. Thus the quantum yield is not high, and the bleaching reaction is slow, so the time that the dye is bleached completely is long. However, the concentration of *N*-phenylglycine has no obvious effect on the coefficient of molar absorption (Fig. 8).

3.4. Effect of the exposure intensity

Like the concentration of the dye, exposure intensity is also an important parameter because the bleaching of the dye depends on the exposure intensity used. The temporal variations of the transmittance are shown at different intensities (Fig. 9). When incident intensity is lesser than 0.1 mW, the bleaching phenomena cannot be observed. We can see that the transmittance is almost constant for 0.1 mW. When the intensity of the illumination beam is low, the transmittance rises slowly toward saturation, as shown in Fig. 9 on 0.5 mW and 1 mW. As can be appreciated, the transmittance increases until a certain value is reached, after which it remains constant. This behavior can be explained by the so-called saturation effect, which is not specifically induced under laser irradiation, because the same phenomena is observed when laser irradiation is operated at very large and focused high light intensities. The most likely reason for this saturation effect is that once the concentration of the excited photoinitiator reaches a certain high value, it partially recombines to render again the starting dye.

We also notice that quantum yield decreases with the increase in the exposure intensity (Fig. 10). We may understand this behavior in this way: under strong illumination, more triplet excited states are produced

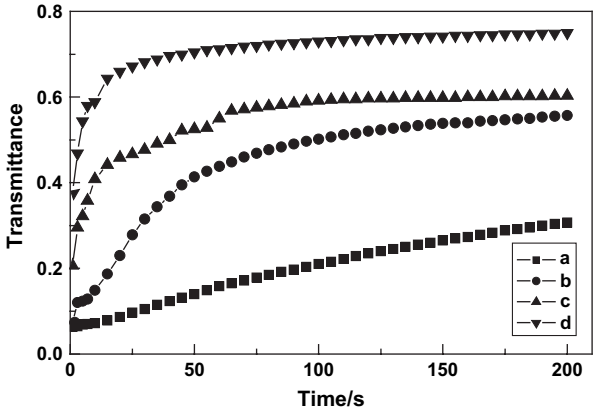

Fig. 6. Transmittance versus exposure time for the different concentration of *N*-phenylglycine. The basic composition is: AA: 0.33 mol L^{-1}; BAA: 0.030 mol L^{-1}; ErB: 2.0×10^{-4} mol L^{-1}; DMSO: 0.2 mol L^{-1}; PVA: 7%, and concentration of NPG: (a) 0.44×10^{-2} mol L^{-1}; (b) 0.88×10^{-2} mol L^{-1}; (c) 1.33×10^{-2} mol L^{-1}; (d) 1.77×10^{-2} mol L^{-1}, where the exposure intensity used is 33 mw/cm^2.

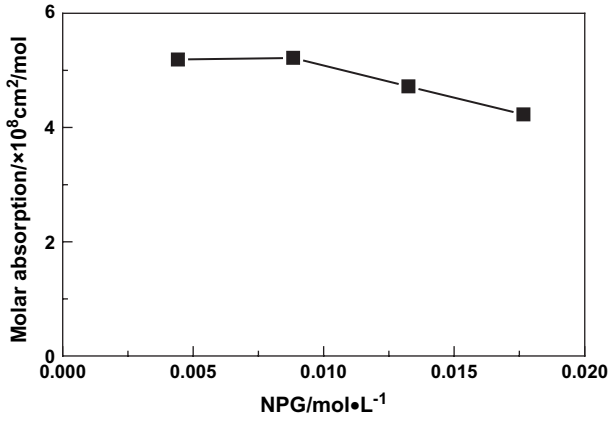

Fig. 8. Molar absorption versus the concentration of *N*-phenylglycine. The basic composition is: AA: 0.33 mol L^{-1}; BAA: 0.030 mol L^{-1}; ErB: 2.0×10^{-4} mol L^{-1}; DMSO: 0.2 mol L^{-1}; PVA: 7%, where the exposure intensity used is 33 mw/cm^2.

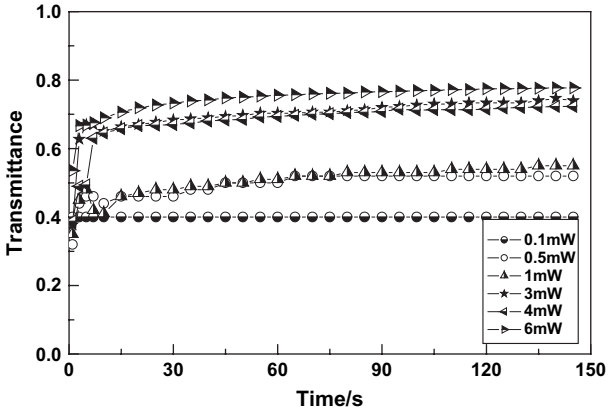

Fig. 9. Transmittance versus exposure time for different incident intensities. The chemical composition is AA: 0.33 mol L^{-1}; BAA: 0.030 mol L^{-1}; ErB: 2.0×10^{-4} mol L^{-1}; NPG: 0.88×10^{-2} mol L^{-1}; DMSO: 0.2 mol L^{-1}; PVA: 7%.

simultaneously; Due to the high viscosity of polyvinylalcohol, the diffusion coefficient of the components of the material will be very low, and the monomer in the dark zone cannot diffuse to the illumination zone quickly, so most excited dyes are deactivated by combining with each other.

However, the coefficient of molar absorption increases with the increase of incident intensity (Fig. 11). The molar extinction coefficient of the sensitizer (dye) at the wavelength of the recording light is necessary to be high so that it can excite the system effectively. However, on the other hand, it makes the light difficult to pass through the system and then decreases the polymerization rate when its concentration is higher.

3.5. Effect of the concentration of diphenyliodonium hexafluorophosphate

In a photoinitiating polymerization, the first step after the excitation of the light-absorbing component is

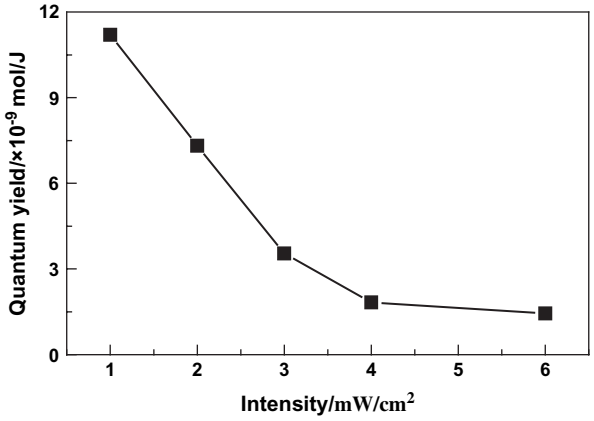

Fig. 10. Quantum yield versus incident intensity. The chemical composition is AA: 0.33 mol L^{-1}; BAA: 0.030 mol L^{-1}; ErB: 2.0×10^{-4} mol L^{-1}; NPG: 0.88×10^{-2} mol L^{-1}; DMSO: 0.2 mol L^{-1}; PVA: 7%.

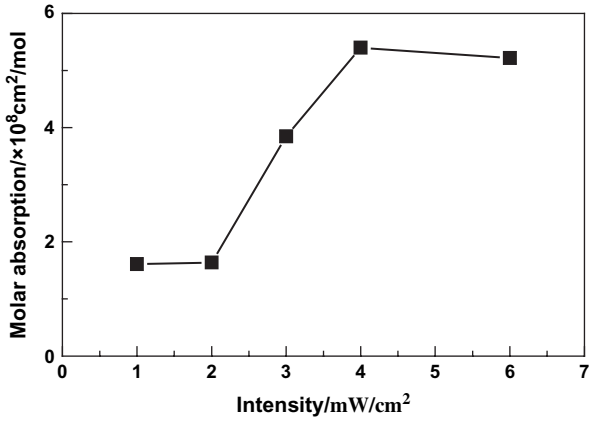

Fig. 11. Molar absorption versus incident intensity. The chemical composition is AA: 0.33 mol L^{-1}; BAA: 0.030 mol L^{-1}; ErB: 2.0×10^{-4} mol L^{-1}; NPG: 0.88×10^{-2} mol L^{-1}; DMSO: 0.2 mol L^{-1}; PVA: 7%.

the generation of active species or radicals, and this step mainly depends on the characteristics of the light source and the specific properties of the dye: sensitivity range, efficiency in the generation of active species, quenching property with other compounds in the medium. Eosin has been recognized as very efficient photoinitiator, especially in the presence of amines and onium salts [10]. The primary steps of the photoinitiation reaction are normally explained on the basis of the electron transfer between the xanthene and amine (*N*-phenylglycine). The onium salt, which acts as a quencher, decreases the rate of termination and generates new initiating radicals. Both the effects lead to an increased rate of polymerization. So Quantum yield increases with the increase of the DPI concentration (Fig. 12). However DPI has no obvious effect on the molar absorption same as the NPG (Figs. 13 and 8).

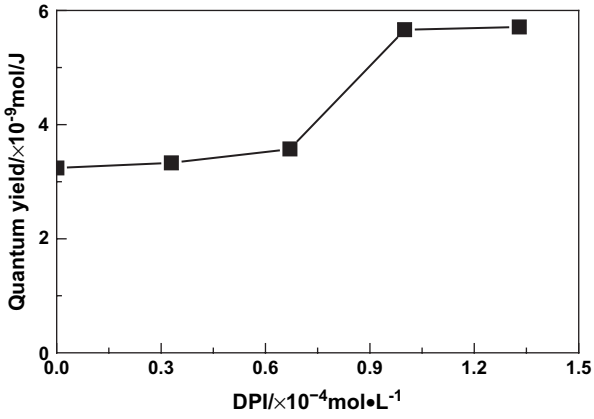

Fig. 12. Quantum yield versus the concentration of diphenyliodonium hexafluorophosphate. The chemical composition is AA: 0.33 mol L^{-1}; BAA: 0.030 mol L^{-1}; ErB: 2.0×10^{-4} mol L^{-1}; NPG: 0.88×10^{-2} mol L^{-1}; DMSO: 0.2 mol L^{-1}; PVA: 7%, where the exposure intensity used is 33 mw/cm^2.

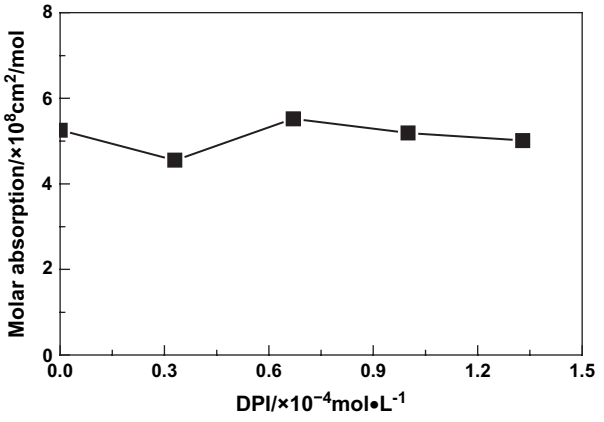

Fig. 13. Molar absorption versus the concentration of diphenyliodonium hexafluorophosphate. The chemical composition is AA:0.33 mol L^{-1}; BAA: 0.030 mol L^{-1}; ErB: 2.0×10^{-4} mol L^{-1}; NPG: 0.88×10^{-2} mol L^{-1}; DMSO: 0.2 mol L^{-1}; PVA: 7%, where the exposure intensity used is 33 mw/cm^2.

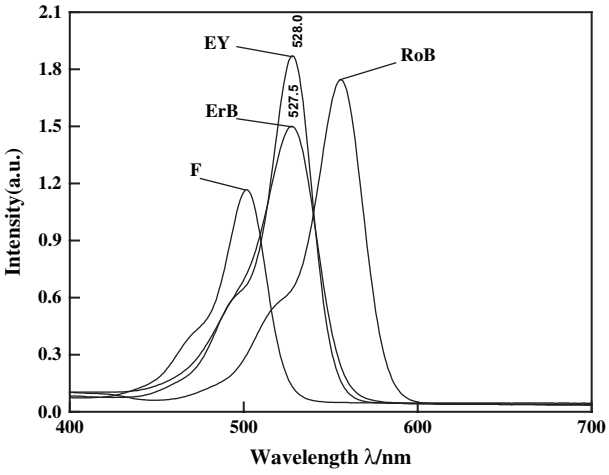

Fig. 14. Absorption spectra for four dyes studied in a PVA film. The chemical composition is AA: 0.33 mol L^{-1}; BAA: 0.030 mol L^{-1}; dye: 2.0×10^{-4} mol L^{-1}; NPG: 0.88×10^{-2} mol L^{-1}; DMSO: 0.2 mol L^{-1}; PVA: 7%.

3.6. Use of different xanthene dyes

As seen from Table 1, erythrosine B shows a higher molar absorption and quantum yield than that of other xanthene dyes. These results agree with the fact that the maximum absorption of ErB is closer to 514 nm than the others shown in Fig. 14. In this table the parameter T_{sf} is represented, it is similar for four dyes.

4. Conclusions

Photobleaching parameters of erythrosine B, eosin Y, Rodamine B and Fluorescein in polyvinylalcohol matrix have been investigated. Among four dyes, erythrosine B shows a higher molar absorption and quantum yield, because the maximum absorption of erythrosine B is closer to laser recording wavelength (514 nm). The bleaching rate of dye increases with the increase in the concentration of *N*-phenylglycine and exposure intensity, but decreases with the increase in the concentration of the dye. As the concentration of dye increases, the quantum yield reduces, because at high concentrations of dye, the dimeric species of the dye is formed. However, the quantum yield increase with the increase in the concentration of PG and DPI, reaching a saturation value when the concentration of photoinitiator is increased. Photoinitiating systems have no obvious effect on the coefficient of molar absorption. With the increase of exposure intensity, the coefficient of molar absorption increases, but quantum yield decreases. These studies will help to explain the mechanism involved and to optimize the experimental conditions such as doping these xanthene dyes in polymer films for various applications such as holographic recording and optical phase conjugation.

Table 1
Quantum yield, molar absorption coefficients and T_{sf} parameters for wavelength 514 nm obtained from non-linear fitting of transmittance curves

	$\varepsilon(\times 10^8$ cm^2/mol)	$\Phi(\times 10^{-9}$ mol/J)	T_{sf}
ErB	5.22	1.44	0.679
EY	4.47	1.39	0.627
RoB	3.13	0.71	0.678
F	2.41	1.12	0.695

The chemical composition is AA: 0.33 mol L^{-1}; BAA: 0.030 mol L^{-1}; dye: 2.0×10^{-4} mol L^{-1}; NPG: 0.88×10^{-2} mol L^{-1}; DMSO: 0.2 mol L^{-1}; PVA: 7%, where the intensity used is 30 mw/cm^2.

Acknowledgements

Authors are indebted to the Science Council of Shanghai (under grant 03JC14073) for the financial support during the tenure of the work.

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