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Dye–polymer interactions controlling the kinetics of fluorescein photobleaching reactions in poly(vinyl alcohol)

M. Talhavini, T.D.Z. Atvars *

Departamento de Físico-Química, Instituto de Química, Unicamp, Caixa Postal 6154, 13083-970, Campinas, SP, Brazil

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Abstract

This work presents results for the temperature dependence of the photobleaching reactions of Fluorescein dissolved in poly(vinyl alcohol) (PVA) irradiated by a continuous 150 W Hg high pressure arc lamp. We observed that the photobleaching process efficiency is dependent on: lamp power, dye concentration and temperature. Although the photobleaching processes can only be described by a single-exponential function for lower concentration samples, a biphasic model must be employed for intermediate concentrations, resulting in one slower and one faster processes, while, for higher concentration samples, even multiple-exponential functions are unable to fit the experimental data. This complex behavior is probably due to the co-existence of many different types of energy transfer and photochemical processes with different rate constants. Therefore, a model based on a sequential distribution of site occupation by the dye molecules in the matrix, controlled by dye–polymer interaction strengths, is proposed to explain the complex-exponential kinetic behavior. Moreover, photobleaching process efficiency is somewhat increased by temperature and, above the PVA glass transition temperature, T_g, (350 K), it follows a first order kinetics, fitted by a mono-exponential function. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Photobleaching; Fluorescein; Poly(vinyl alcohol); Dye–polymer interactions

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1. Introduction

Photobleaching of xanthene dyes (Eosin, Erythrosin, Fluorescein, Rose Bengal, etc.) in several media has been reviewed [1,2]. In general, it has been proposed that a photobleaching process is possible by either reductive or oxidative mechanisms, and the reaction mechanism depends on several factors, including the presence of oxygen, the presence and the concentration of electron-donor groups and the dye concentration. In the presence of amines, two colorless leuco-photoreduction products were reported: the dihydro derivative (DH$_2$) and the cross-coupled product [2].

Transient spectra obtained from flash photolysis studies showed that indoles and oxidable compounds were capable of reacting with the triplet of xanthene dyes by an electron-transform mechanism to form semireductive dye and oxydable radicals, which may either restore the original dye or may undergo disproportionation to form equal amounts of the colorless leuco-base and the original dye [3]. Then, it seems that, whatever is the photobleaching mechanism, it should involve an electron-donor species.

Poly(vinyl alcohol) (PVA) is a commercial polymer usually produced by acidic or basic hydrolysis of poly(vinyl acetate). Its properties depend on its molecular weight and degree of hydrolysis. Among its possible applications, because of the high optical quality of its films, it can be useful as a support in many industrial applications, including non-linear optical devices [4]. In this case, a modified material produced by oxidation with chromate was employed. Moreover, in order to improve spectral sensitivity and holographic efficiency, these films were dyed with electron-donors species and xanthene dyes (Eosin Y, Fluorescein, and Rose Bengal) [4]. Some reports indicate that, under excitation, PVA could itself behave as an electron donor system producing the leuco-form of the dye but others suggested that xanthene-dye-doped PVA without an electron-donor group did not present photobleaching when irradiated with an Ar$^+$ laser, within the time scale of their investigation [5,6].

In earlier works [7,8], we reported that the fluorescence emission of electronically excited Fluorescein dissolved in PVA and some of its blends with poly(vinyl acetate) was dependent on the cooperative motions of the polymer chains, and that, its temperature-dependence was a useful property to follow polymer and polymer blend relaxation processes. We also reported that Fluorescein suffers an irreversible pho-

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* Corresponding author. E-mail: tatvars@iqm.unicamp.br

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tobleaching process which was somewhat increased above the PVA glass transition temperature, T_g. A photobleaching process is occurring even though no extrinsic electron donor additive had been added.

Since the relative importance of the PVA matrix for the photobleaching processes of these dyes is still controversial, the aim of the present work is to describe a kinetic model for the Fluorescein photobleaching process in PVA and to study its dependence on some experimental parameters: lamp power, concentration and temperature. Using samples with three different compositions, we analyzed the role of the dye distribution in different sites of the polymer matrix and how the photobleaching rate constants are affected by those parameters.

2. Experimental

Poly(vinyl alcohol) (PVA) (Aldrich Chemical, average molecular weight $M_w = 124{,}000–186{,}000$, 87–89% hydrolyzed) was used as received. It is composed mainly of an atactic conformation [9,10]. We determined earlier that PVA is a semicrystalline polymer (crystallinity degree ~40%), with a $T_g \cong 350$ K [7,8,11].

Fluorescein (FL) (Aldrich), for microscopy, was purified by crystallization from a ethanolic solution, dried under vacuum and stored in the dark. It was incorporated into the PVA film by casting an aqueous solution containing both the homopolymer and the dye on a glass plate. All the films prepared in this work were dried at 55°C and normal pressure and were then maintained in a desiccator under vacuum and in the dark until the measurements. Their thicknesses were about 58–62 μm. The Fluorescein concentrations were defined as 1, 0.1 and 0.01% in mass, and as reported earlier, they do not perceptively change the PVA crystallinity degree [7,12].

Electronic absorption spectra were recorded at room temperature using a HP8542 A spectrophotometer, with a diode array detector. Samples were supported by a home-made support for polymer films. Fluorescence spectra at several temperatures were performed in a system described elsewhere [13]. The temperature range of the samples was changed from 10 to 400 K by a digital temperature controller (Scientific Instruments Model 9650). The optical holder in the cryo-system was positioned in order to get a 90° angle between the incident light and the emission beams, which was focused by a cylindrical lens on the entrance slit of the spectrometer [13].

Photobleaching process of the dyed films were performed with a xenon lamp selected at 500 ± 10 nm by a combination of cut-off and interference filters (Zeiss Jenalumar). The irradiance of the excitation source was monitored using a radiometer (Applied Physics) with a semiconductor detector. The fluorescence intensity was monitored at 532 nm, using a system described elsewhere [13].

Excitation and prompt fluorescence at room temperature, and delayed fluorescence and phosphorescence spectra at 77 K were performed in a PTI LS100 (Photon Technology) spectrofluorimeter in the steady state mode. Delayed fluorescence and phosphorescence decay curves were recorded after excitation with a pulsed xenon lamp. Prompt fluorescence decay curves were generated using nitrogen pulsed lamps, selecting an appropriate delay channel. A standard software supplied by the manufacturer was used to perform the deconvolution of the lamp pulse and the emission decay signal.

3. Results and discussion

3.1. Photophysical properties of fluorescein in PVA

Normalized absorption, excitation and prompt fluorescence spectra for FL/PVA in three compositions are shown in Fig. 1. The fluorescence spectrum presents a band centered at 530 nm, for samples with the three concentrations, which can be assigned to the isolated molecule. Electronic absorption and fluorescence emission can be compared with a pH 6.4 and pH 8.2 aqueous solutions, respectively, leading to an assignment that Fluorescein in PVA is present in equilibrium involving the quinonoid and monoanionic forms in the electronic ground state and the dianion form in the electronic excited state [14,15].

Excitation spectra of higher concentrated samples are blue shifted due to the excitonic splitting of electronic states in dimers and higher aggregates, suggesting a parallel orientation of the transition dipole moments for both molecules forming the dimer (Fig. 1) [16–18]. The species absorbing in these regions are responsible for the fluorescence emission at higher wavelengths.

Prompt fluorescence (F) (room temperature), delayed fluorescence (F^d) (77 K), phosphorescence (Ph) (77 K) emissions and excitation spectra for the three FL concentrations are shown in Fig. 2. Phosphorescence and delayed fluores-

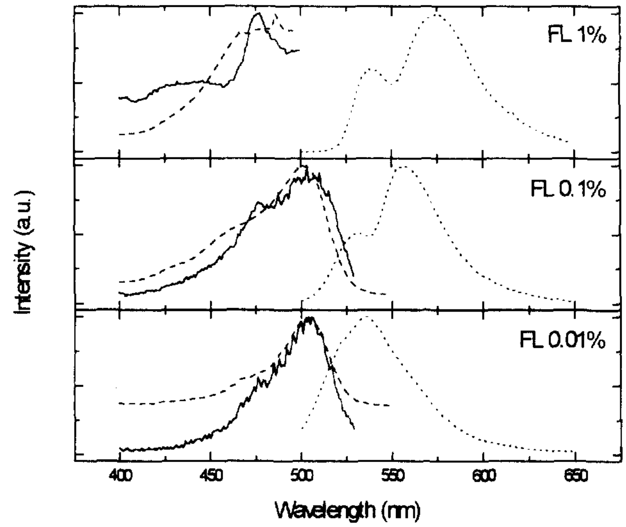

Fig. 1. Normalized absorption (solid line), excitation (dashed line) and prompt fluorescence (dotted line) spectra of FL in PVA (room temperature) in different compositions: 1, 0.1 and 0.01%, by mass.

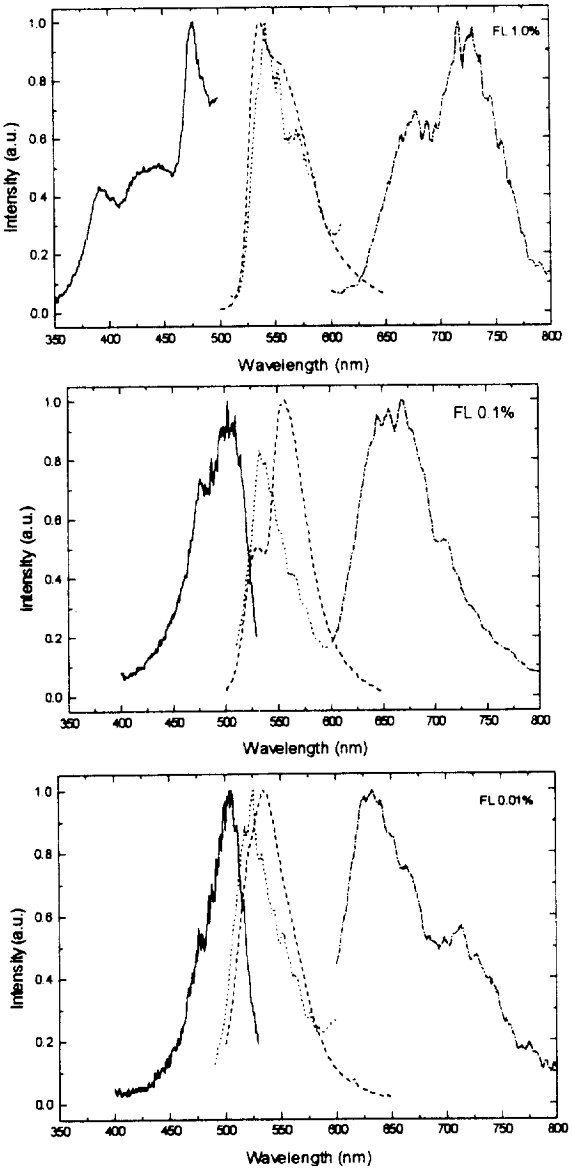

Fig. 2. Excitation (solid line), prompt fluorescence (room temperature, dashed line), delayed fluorescence (77 K, dotted line) and phosphorescence (77 K, dash-dotted line) spectra of FL in PVA in different compositions: 1, 0.1 and 0.01% by mass.

cence spectra were recorded with a 1 ms delay after the lamp pulse, in order to minimize the contribution of the prompt fluorescence. Both fluorescence and phosphorescence spectra are shifted toward higher wavelengths for concentrated samples and, in addition to the two prompt fluorescence signals, two phosphorescence signals were obtained, one at $\lambda_{EM} > 650$ nm for isolated molecules and the other at $\lambda_{EM} > 700$ nm for aggregated molecules.

Decay curves for FL/PVA prompt fluorescence emissions (at room temperature) were deconvoluted from the lamp pulse signal and fluorescence lifetimes were determined. A mono-exponential fluorescence decay curve is obtained for the dilute sample (0.01%) with a fluorescence lifetime value of 6.6 ns, which is higher than that for FL in 0.1 M KOH aqueous solution (Table 1) [19]. A bi-exponential function is necessary to match the decay fluorescence curve for the 0.1% sample, and the two determined lifetime values were: 6.0 ns, similar to the isolate molecule in the matrix and a shorter one, 1.0 ns, probably stemming from an effective self-quenching process [13]. Decay curves for a 1% FL/PVA sample could not be fitted by multiple exponential functions.

Table 1

Emission lifetime data for: τ_{FM} (prompt fluorescence), τ_{FM}^{a} (delayed fluorescence) and τ_{PM} (phosphorescence) for FL in PVA

Dye composition	τ_{FM}^{a} (ns)	τ'_{FM} (ms)[b]	τ_{PM} (ms)[b]
FL 1%	6.0	1.8	1.0
FL 0.1%	1.0	0.2	7.9
FL 0.01%	6.6	2.7	–

[a] Room temperature.

[b] 77 K.

$\tau_{FM} = 4.9$ ns [5]; $\tau_{PM} = 0.09$ ms (0.1 M KOH) [5].

Delayed fluorescence spectra were only significant under low temperature (77 K) conditions. These low temperature, delayed fluorescence decays were not expected for the usual thermally-activated processes reported for xanthene dyes (E-type process), since at this temperature, the thermal activation is not enough to reach the Fluorescein singlet–triplet energy gap.

In order to explain this unusual behavior, we are assuming that this low temperature, delayed fluorescence emission involves a triplet–triplet annihilation process (P-type process) instead of a thermally-activated mechanism (E-type process). Nevertheless, since the PVA matrix is below its T_g in this temperature range, mobility of FL through the matrix must be essentially nil and, then, some type of energy transfer process is required which could be either virtually static or involving $^3M^*$ energy migration process [19]. In addition, delayed fluorescence must be correlated with the micro-heterogeneous distribution of dye molecules in the matrix, since it is observed even at low concentrations, where dimers are absent [12].

It was also reported that the lifetime for P-type delayed fluorescence (τ_{FM}^{a}) of dyes in solutions are, theoretically, correlated with the phosphorescence lifetime (τ_{PM}) by the equation [19]:

$$\tau_{FM}^{a} = (1/2)\tau_{PM}. \qquad (1)$$

However, this theoretical relationship is not followed by the FL/PVA systems, and the reason is probably related to the micro-heterogeneity of the material which introduces several different types of micro-environment for the dye molecules [19].

Böttcher et al. [20,21] reported the existence of E-type delayed fluorescence for some dyes (including Erythrosin and Eosin) dissolved in polymers, at room temperature, and established that the diffusion controlled bimolecular triplet annihilation is improbable due to the restriction of triplet diffusion. However, since in our work, we are obtaining the

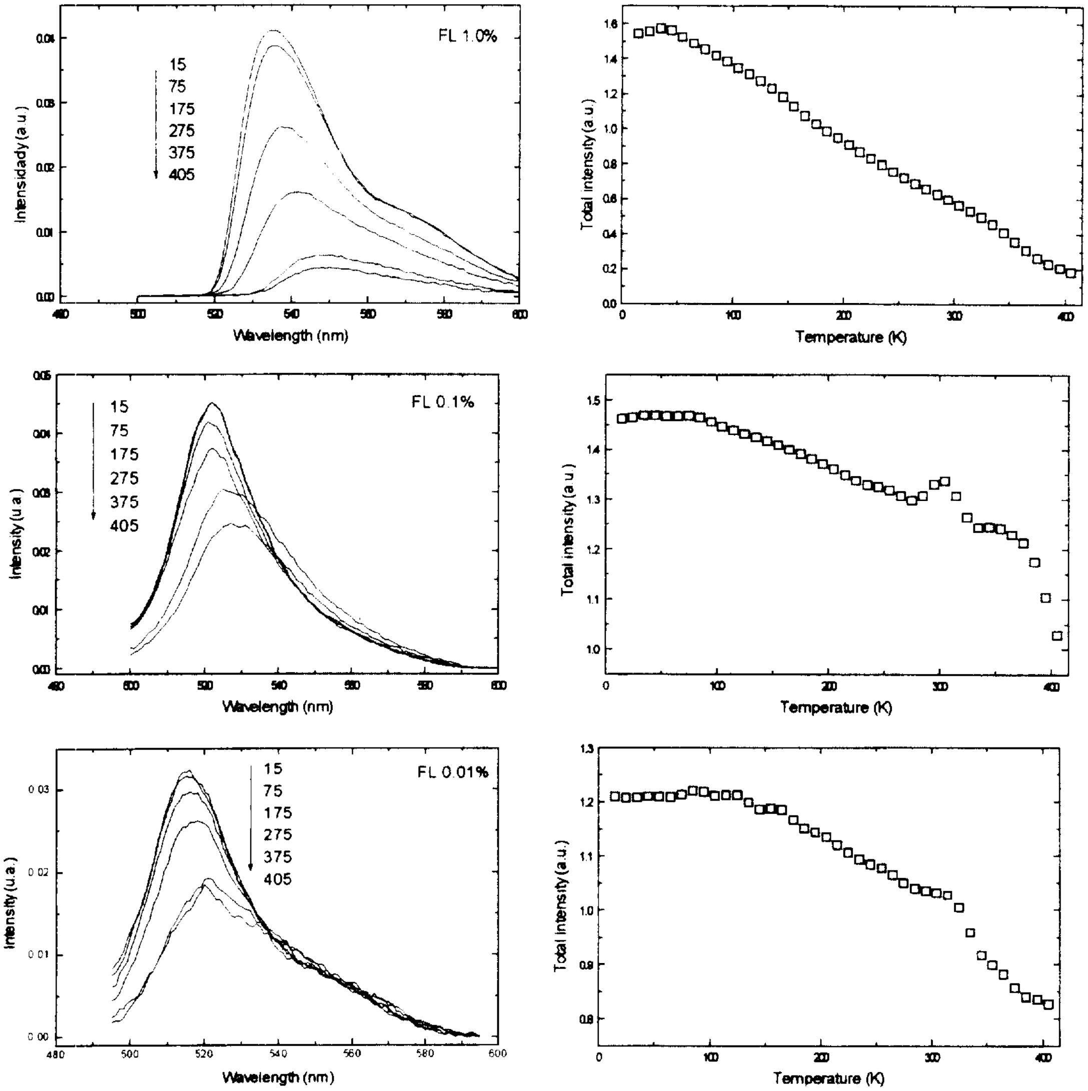

Fig. 3. Left side: total fluorescence intensity of FL in PVA, for compositions: 1, 0.1 and 0.01%. Right side: maximum fluorescence intensity vs. temperature for the same samples.

delayed fluorescence at low temperatures, thermally-activated processes are rather improbable. Therefore, this unexpected emission should involve a heterogeneous dye distribution in the matrix which allows a stochastic probability that some neighboring dye molecules are within an adequate distance to allow the triplet–triplet annihilation without diffusion. Actually, there is some experimental evidence that energy migration and transfer processes in polymer matrix seem to be much more complicated than in isotropic media [12,22].

These spectroscopic results show that a heterogeneous distribution of the dye molecules in different location sites of the matrix is taking place, with some molecules more isolated than others and residing either in the amorphous or at the interface between crystalline and amorphous domains of the semicrystalline PVA matrix. Nevertheless, the micro-heterogeneous distribution of the dye molecules in the semicrystalline polymer media leads to a distribution of photophysical and photochemical rate processes, without similarities with a homogeneous non-viscous medium [7,12].

3.2. Temperature dependence of the fluorescence intensity

Fig. 3 shows the fluorescence spectra of FL/PVA samples at several temperatures. These spectra exhibit a red shift of their maximum on heating that is attributed to the inability of solvent reorientation during the lifetime of the electronic excited state (1–5 ns) [23].

Fig. 3 also shows curves for the fluorescence intensity vs. temperature. These curves are dependent on the dye concentration, and, in a general description, they can be divided into three almost linear segments, changing their slopes at temperatures around 130, 260–270 and 330–350 K (Table 2). It is noteworthy that the slope changes at higher temperatures are more pronounced for the 0.01 and 0.1% samples, exhibiting a maximum fluorescence intensity at 315 K. Finally, at

Table 2
PVA relaxation and glass transition temperatures (K)

Relaxation	Temperature (K)		Description
	This work	Literature [25,26]	
T_γ	125	130–150	Short segments (amorphous and interfaces)
T_β	250–270	250–270	Molecular chains not hydrogen bonded
T_g	350	330–350	Glass transition

$T > 330$–350 K, we observed a pronounced decrease of the fluorescence intensity produced by the PVA glass transition temperature process. Similar to other systems, the temperature dependence of the fluorescence intensity can be discussed in terms of both photophysical and photochemical dye properties and polymer matrix relaxation processes [7,8,12,22,24].

Under steady-state conditions and in the absence of either added quenchers or a photochemical process, the fluorescence quantum yield, q_{FM}, of a molecule in a homogeneous medium, can be described by a general and theoretical equation:

$$q_{FM} = k_{FM}/\{k_{FM} + k_{IM} + k_{ST} + k_{DM}[FL] + k_{MT}[^3FL]^2\}. \tag{2}$$

where the rate constants, k, are defined for: fluorescence emission (k_{FM}); radiationless internal conversion (k_{IM}); intersystem crossing (k_{ST}); quenching by collisional and Förster mechanisms (k_{DM}); and triplet–triplet annihilation (k_{MT}), resulting in delayed fluorescence or fluorescence quenching [12,19,23].

Taking into account the curve for 0.01% FL/PVA sample, the fluorescence intensity is almost constant from 15 to 130 K, suggesting that all the terms of Eq. (2), neglecting the bimolecular processes, are, in this temperature range, almost independent of the temperature. The detectable slope change at 130 K should be related to the onset of some PVA relaxation process involving short segments of the polymer chains. Moreover, considering that this temperature is below T_g, and the matrix is very rigid, molecular diffusion is essentially nil and, then, the most important contribution to the decrease of the fluorescence intensity should be the intramolecular internal conversion processes (k_{IM}).

The other slope change is observed around 260–270 K, suggesting the onset of an additional polymer relaxation process. Since the slope is higher than at lower temperatures, a new competitive photophysical pathway is taking place, which rises the fluorescence intensity signal in spite of the increase of the temperature. The fact that this fluorescence intensity increase is higher for 0.1% than for 0.01% samples leads to the statement that there is a decrease of the efficiency of the bimolecular self-quenching processes.

Following the Garrett and Grubb [25] proposition that PVA is suffering a relaxation process involving segmental motions of the macromolecule which are not hydrogen bonded, and the dependence of the fluorescence intensity on the concentration, we suggest that the PVA relaxation process occurring at 260–270 K involves motions of polymer chain segments with dimensions comparable to the FL molecular diameter. If the molecular diffusion induced by the polymer relaxation process increases the average distance between neighbor dye molecules, the dimer configuration would be destroyed and the self-quenching process would be drastically reduced. In the case of the 1% FL/PVA sample, macromolecular motions are not large enough to separate the molecules forming high order aggregates of FL and, then, the fluorescence intensity is still controlled by the radiationless-temperature dependent process (Fig. 3).

The third slope change is observed between 330–350 K and subsequent heating produces an additional decrease of the fluorescent process. In addition, FL photobleaching efficiency is strongly enhanced at temperatures higher than the PVA glass transition temperature [7,11]. Garrett and Grubb [25] reported that the PVA glass transition is occurring at 358 K for melt-cast films, while for the dried isotropic gel, it is observed at lower temperatures (320 K), in agreement with Nagai and Takayanagi [26]. It is also known that this phenomenon is occurring preferentially at the amorphous region of the polymer matrix and involves mobility of the polymer chains produced by the breakage of the hydrogen bonds [11].

Similar to other systems, the temperature dependence of the fluorescence intensity can be discussed in terms of a synergy effect involving polymer relaxation and either photophysical or photochemical processes of the dye molecules in polymer matrices. The curve profiles for fluorescence intensity vs. temperature should be a result of a convolution among photophysical processes dependent on concentration, bimolecular quenching, unimolecular rate processes and photochemical processes decreasing the dye concentration and mobility of polymer chains. Some of these processes can be minimized at lower concentrations, leading us to expect that unimolecular photophysical and photochemical processes must be predominant for 0.01% FL/PVA than for higher concentrated samples [7,8,12,22,24].

It also seems evident that in anisotropic media, such as a semicrystalline polymer, temperature variations may change the 'local concentration' of guest molecules, leading to aggregation or dispersion in amorphous and interfacial sites, which are induced by the thermal mobility of polymer segments with different sizes. Then, as a consequence of the presence of both a local concentration distribution and a very large difference between the fluorescence quantum yield for both isolated FL molecules and their dimers, we expect a very complex dependence of the fluorescence intensity on the temperature, at least for $T < T_g$ [7,8,12,22,24].

3.3. Effect of irradiation intensity

We performed some experiments in order to study the dependence of the bleaching rate constant on the irradiation energy, using the 0.1% FL/PVA sample. The irradiation intensity was changed from 0.6 to 150 W (Fig. 4). We are considering that, under continuous irradiation, the rate of FL bleaching is proportional to the irradiation intensity:

$$\mathrm{d}[\mathrm{FL}]/\mathrm{d}t=\beta I_0^n, \qquad (3)$$

where β is a constant, and n is a number in the range $0 \leq n \leq 1$.

Making the assumption that the initial FL concentration is low enough that the ability to absorb the excitation light is governed by Beer's law, the fluorescence intensity should be proportional to the number of FL molecules in the electronic ground state, and then Eq. (3) can be rewritten as:

$$\mathrm{d}[I_{\mathrm{FL}}]/\mathrm{d}t=\beta I_0^n. \qquad (4)$$

where: I_{FL} is the fluorescence intensity, and n can be determined by fitting the experimental curve profile.

Experimental curves for the time dependence of fluorescence intensity, assuming that the fluorescence intensity is proportional to the FL concentration in the electronic ground state, for several irradiation intensities, at $T=400$ K, are shown in Fig. 4. The first derivative of the experimental curves can be matched assuming that $n=1$ in Eq. (4). Therefore, for samples in concentration range around 0.1% FL or lower, the light absorption is a linear optical process in agreement with Beer's law.

3.4. Photobleaching process

We have already demonstrated that: (1) FL photobleaching is the most important cause of the drop of the fluorescence intensity at higher temperatures; (2) the absorption process is governed by Beer's law, and, (3) FL fluorescence intensity is considered proportional to the dye concentration in its electronic ground state. Then:

$$\mathrm{d}[I_{\mathrm{FL}}]/\mathrm{d}t=-k_r[\mathrm{FL}], \qquad (5)$$

where I_{FL} is the fluorescence intensity; k_r is the photobleaching rate constant; and [FL] is the concentration of the dye in the electronic ground state.

Experimental plots for the time dependence of the fluorescence intensity, for several temperatures, are shown in Fig. 5 (left side). The photobleaching rate constants can be determined matching a multi-exponential kinetic model to the experimental data:

$$I_{\mathrm{FL}}(t)=C+\sum_i B_i \exp(-k_i t), \qquad (6)$$

where C is an arbitrary constant; B_i is a pre-exponential factor for the ith component; and k_i is the photobleaching rate constant for the ith component.

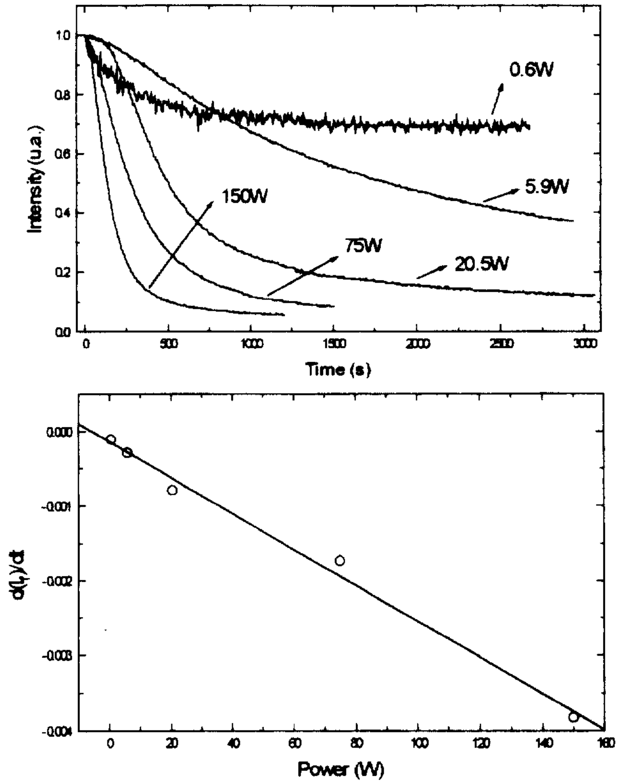

Fig. 4. Top: fluorescence intensity vs. irradiation time, at several lamp powers, for FL/PVA (0.1%), at 400 K. Bottom: first derivative of the decay curves vs. irradiation intensity, and fitting with $n=1$ (Eq. (4)).

The photobleaching curves for the time dependence of the fluorescence intensity for the 0.01% FL/PVA sample is best expressed by a mono-exponential function, in all temperature ranges. On the other hand, a bi-exponential function must be used to match the experimental curve profiles for the 0.1% FL/PVA sample. In this case, two photobleaching rate constants were determined, named k_s (slower process) and k_f (faster process). The associated pre-exponential factors, B_i, in this case, should be considered as weighting factors for both slower and faster rate constants and, interestingly, they present a temperature dependence: while the pre-exponential factor B_f (for the faster process) is predominant at higher temperatures, the opposite is observed at lower temperatures, where the slower process, B_s, becomes more important. As an example, at 260 K: $B_s=0.60$ and $B_f=0.40$.

The photobleaching curves for 1% FL sample exhibit an unusual curve profile which cannot be fitted by any multi-exponential function (Fig. 5). In a general description, there is an initial increase of the fluorescence signal upon irradiation; followed by a subsequent fluorescence decrease. Those curves present an exponential-like behavior after a very long irradiation period. This unusual behavior can be interpreted, taking into account that dye molecules in higher concentration samples are partitioned into isolated, dimeric and higher order aggregates (see the excitation and fluorescence spectra in Figs. 1 and 2), and their total fluorescence intensity are a convolution of the fluorescence quantum yields which are lower for dimers and aggregates than for the isolated molecule. As the photobleaching process develops, the corre-

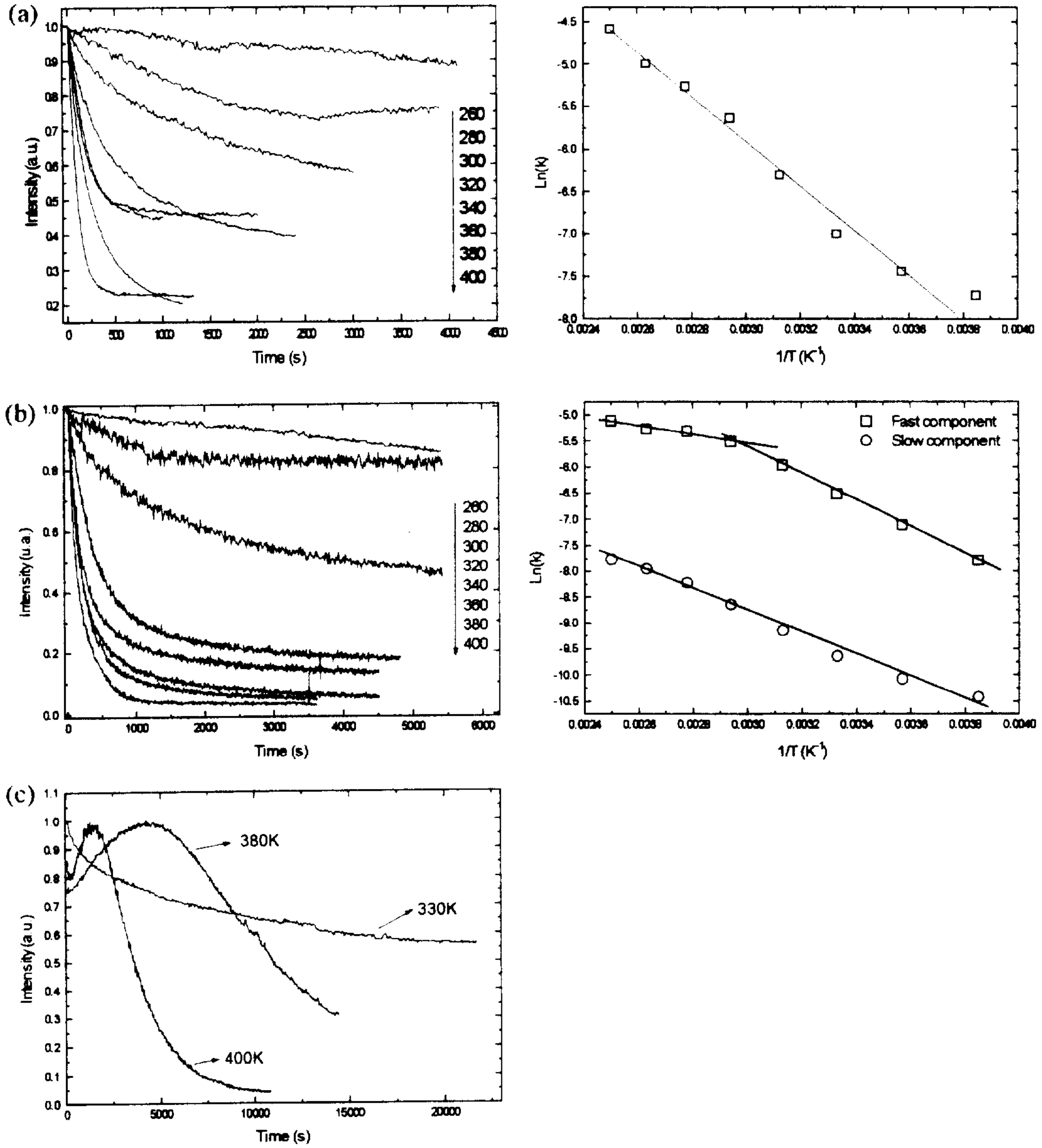

Fig. 5. Left side: fluorescence intensity vs. time, at several temperatures, for FL/PVA: (a) 0.01%, (b) 0.1% and (c) 1%. Right side: Arrhenius plot for rate constants vs. reciprocal temperature: experimental and simulated curves using Eq. (7).

sponding fluorescence intensity increases because the relative amount of dimers and higher order aggregates diminish.

From the above results, we concluded that the faster photobleaching processes are occurring with one molecule belonging to the dimer leading to a decrease in concentration and, in a first instant, to an increase in the net fluorescence intensity. When photobleaching of the isolated molecules takes place, the usual kinetic behavior is dominant, and the experimental curves can be fitted by a bi-exponential function.

In general, the requirement for a bi-exponential function for the kinetic description of any process in a polymer matrix can be interpreted by the presence of at least two different sorption sites for the guest molecules, where the sorbed dye molecules should assume different spectroscopic, photophysical and photochemical properties [27–30].

Using the calculated rate constant values, and, based on the Arrhenius equation for the temperature dependence of the rate constants, the apparent activation energy for the photobleaching process can be determined:

$$\ln k = \ln A - \frac{E_a}{RT}. \qquad (7)$$

where A is a frequency factor, and E_a is an apparent activation energy.

While a single value for the apparent activation energy (20.7 kJ mol^{-1}) is obtained for the 0.01% FL/PVA sample, for the 0.1% sample, two different values were determined. In addition, while the Arrhenius plot (Fig. 5, right side) for the faster rate constant shows two linear segments, with different slopes, with a well-defined break point at 342 K, the slower rate constant follows a single linear dependence on temperature. Calculated values for apparent activation energies for both linear segments were 20.9 kJ mol^{-1} for the lower and 7.0 kJ mol^{-1} for the higher temperature regions, respectively.

It is remarkable that the same value for activation energy for both the lower temperature region of the Arrhenius' plot for 0.1 and 0.01% FL/PVA samples (20.9 kJ mol^{-1}) were obtained. This result suggests that the slower photobleaching process is occurring with isolated FL molecules, all of them interacting with PVA chains in the same way and located in sites submitted to similar restraints produced by the matrix. Since a biphasic kinetic model must be used to fit the photobleaching process for the 0.1% FL/PVA sample, and a faster photobleaching process takes place, an additional type of location site must be available for dye molecules, which is able to accommodate dimer forms of the dye.

According to these results, we must consider two different types of mechanisms: one for the isolated molecules and other allowing dye–dye interactions. It is noteworthy that both of them are occurring in the absence of singlet oxygen, since our experiments were performed under vacuum ($\approx 10^{-4}$ mmHg) and with continuous pumping. Since dye molecules are isolated in lower concentration samples, the most probable photobleaching mechanism would not involve D–D interaction. Following the statement proposed by Leclere et al. [5], we suggest that PVA itself is acting as an electron-donor system and the production of the leuco-form of the dye is a consequence of the electron-transfer process from the own polymer matrix, since no other electron-donor additive was incorporated into the system. Therefore, this should be the most important contribution to the slow rate photobleaching process.

On the other hand, the additional faster photobleaching process for higher concentration samples, 0.1 and 1%, should involve a dye–dye (D–D) interaction and the primary process could be the production of semi-reduced (R) and semi-oxidized (X) radicals [2]. Song et al. [31] provided direct photophysical evidence that, although the quantum yield for the FL triplet state is very small, its long lifetimes provides for a significant accumulation of long-lived triplet excited-state molecules, leading to the formation of the semi-oxidized and of semi-reduced radical forms through triplet–triplet and triplet–ground state reactions. They also showed that the probability of the D–D reaction increases for FL immobilized in a substrate due to the decrease of the intermolecular distance. Moreover, ground state FL molecules can be recovered by different quenching mechanisms, such as triplet–triplet annihilation, triplet quenching by ground state molecules or by semi-oxidized and semi-reduced radicals. They also assumed that the deviation from a single-exponential photobleaching behavior was caused by the proximity-induced triplet–triplet and triplet–ground state dye (D–D mechanism) reactions.

In the present work, we obtained several evidences that the D–D mechanism for the photobleaching processes becomes important for concentrated FL/PVA samples: (1) the presence of a low temperature, delayed fluorescence ascribed to triplet–triplet annihilation; (2) the presence of a phosphorescence emission indicating that there is a significant population of triplet state; (3) a short-lived fluorescence species due to a self-quenching processes; (4) bi-exponential photobleaching processes for higher concentration samples.

As indicated earlier, the photobleaching rate constant for the faster process shows two linear segments with a intersection at 342 K. This temperature corresponds to the PVA glass transition [11,32] indicating that the thermally induced motions of the polymer matrix affect both photophysical and photochemical properties of the guest molecules. Below T_g, the steric constrains inhibited an efficient distribution of the radiant energy that was absorbed by the system and photophysical pathways for deactivation are relatively more important. As a consequence, any excess energy cannot be employed by other molecules. On the other hand, above T_g, the polymeric medium behaves as a thermally viscous bath, redistributing the energy and increasing the average energy values of the FL molecules. Additionally, above the glass transition, there is a dramatic increase in the polymer free-volume, allowing diffusion of FL molecules to distances greater than their own radius. Consequently, after the glass transition, there is a remarkable increase of all non-fluorescent processes, including photobleaching, internal conversion, intersystem crossing and bimolecular diffusional quenching.

Moreover, if the material is above its glass transition, the polymeric matrix sites tend to equalize their properties, and the time dependence of these properties can be described by a single exponential function, as in a viscous homogeneous medium [33,32,34].

4. Conclusions

PVA dyed with Fluorescein shows fluorescence spectra dependent on the concentration and on the temperature. Spectra for low concentration samples are characteristic of isolated molecules, being composed of prompt and delayed fluorescence and phosphorescence components, mainly at low temperatures. These samples also exhibited photobleaching which becomes more important at higher temperatures. It is noteworthy that the photobleaching rate is only significant at temperatures higher than 280 K, in agreement with the depletion of the fluorescence intensities (Fig. 3).

Kinetic description of photophysical or photochemical processes can be performed by a mono-exponential function. Single values for photophysical lifetime processes and a single rate constant for the photobleaching process were determined. Nevertheless, the kinetic description for either fluorescence lifetime or photobleaching processes can only be carried out using bi-exponential functions. In this case, two rate constants were determined: the slower one related to the bleaching of isolated dye molecules and a faster one involving interaction between two neighbor dye molecules.

Therefore, a heterogeneous distribution of dye molecules occurs in this semicrystalline medium, with some dye molecules more isolated by the macromolecules undergoing the slow bleaching process and others being bleached more rapidly due to D–D interactions. For the most isolated molecules, the bleaching mechanism probably involves an electron transfer step from the polymer matrix to the dye molecules, since the system does not contain any extrinsic electron-donor additive.

Temperature dependence of the fluorescence intensity can be described by three linear segments with different slopes and with intersections at temperatures related to the polymer relaxation processes. Finally, we showed that both photophysical and photochemical rate constants are strongly dependent on the cooperative motions of polymer chains and, using these dye properties, we were able to determine temperatures for PVA relaxation processes in agreement with those determined by other techniques.

Acknowledgements

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