



# Double role of squarylium dye: Fluorescence probe for biomolecule determination and photosensitizer in dyeing photoinitiating system



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## ABSTRACT

In the present paper, the double role of one of the squarylium dyes is presented. First it was shown the role of 1,3-bis(*N*-ethyl-2-methylenebenzoxazole)squaraine as a spectroscopic probe for bovine serum albumin determination. Next the photoinitiating ability of squarylium dye incorporated in two- and three-component systems for free radical polymerization of trimethylolpropane triacrylate has been investigated. In such system squarylium dyes act as sensitizer (primary light absorber). The radical photopolymerization of an acrylate was observed upon irradiation with ion-argon laser.

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## 1. Introduction

Squaraine dyes have unique photophysical and photochemical properties and have been found many specialized uses as a kind of important functional dyes [1]. They are commonly used for the light absorbing material for solar cells, optical recording media, nonlinear optical material, bio-labeling, singlet oxygen generation, sensitizer in dyeing photoinitiating systems, etc. [2–7].

Squarylium dyes, which are 1,3-disubstituted compounds are synthesized by condensation of one equivalent of squaric acid with two molar equivalents of electron rich aromatic or heterocyclic methylene bases, or by stepwisely the introduction to squaric acid skeleton of aromatic or heterocyclic compounds via dialkyl squarate or squaryl dichloride [2,8]. The feature of squarylium dyes is that they have a sharp and intense absorption and fluorescence in the red to near-infrared region [2]. Furthermore, the absorption wavelength can be controlled by the functional group connected to each side of the squaric acid [2,9].

These compounds may be used as fluorescence probes for biomolecule determination [10,11], as well as photosensitizers in high-performance photoinitiating systems [7]. There are several kinds of physicochemical mechanism operating in the process of dye adsorption on the serum albumin.

It is well known that the charge on the molecule is of importance, negative ions being adsorbed in preference to positive ions at the sites of adsorption.

It is often supposed that this effect is due to van der Waals forces between the biomolecule and dye molecule (adsorbed molecule). The development of new dyes useful as photoinitiators in dyeing photoinitiating systems of polymerization working under soft visible light irradiation is an ongoing challenge attracting great attention in various fields ranging from radiation curing, imaging, and optic technologies to medicine, material science, or microelectronic areas [7,12,13]. Such families of dyes have been obviously, somewhere mentioned in the patent literature, but only few works have been devoted to their polymerization ability. For example, Wang E. and co-workers used squarylium dye/iodonium salt combination in radical polymerization under a high intensity xenon lamp irradiation. Lalevée and co-workers [7] described squarylium dyes incorporated into high-performance photoinitiating system (containing an iodonium salt and *N*-vinylcarbazole) for cationic polymerization of an epoxide and a vinyl ether under very low intensity light sources. Generally, the dye sensitized photopolymerization is based on the generation of initiating species through either photoreduction or photooxidation reactions of dye with coinitiator [1,14].

In the present paper, we have presented one of squarylium dyes, i.e. 1,3-bis(*N*-ethyl-2-methylenebenzoxazole)squaraine (SQ) which can be used as: (i) fluorescence probe for bovine serum albumin determination and (ii) photosensitizer incorporated in photoinitiating system (containing butyltriphenylborate salt or tetrabutylborate salt and optionally *N*-alkoxyppyridinium salt, diphenyliodonium salt or 1,3,5-

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triazine derivative) for radical polymerization of triacrylate under visible light.

## 2. Experimental

### 2.1. Materials

All substrates used for the synthesis of dye, bovine serum albumin, Tris–HCl, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (trimethylolpropane triacrylate (TMPTA)), 1-methyl-2-pyrrolidinone (MP) and solvents were purchased from Aldrich (Poland) and used without further purification. The purity of all chemical used was as required for spectroscopic studies ( $\geq 99\%$ ).

### 2.2. Spectroscopic measurements

Ultraviolet–Visible (UV–Vis) electronic absorption spectra were obtained using the Agilent Cary 60 UV–Vis Spectrophotometer, steady-state fluorescence was performed using a FLS920 Edinburgh Instruments Spectrophotometer (England) and the fluorescence lifetime measurements were performed on a UV–Vis–NIR Fluorolog 3 Spectrofluorometer (Horiba Jobin Yvon).

### 2.3. Reduction and oxidation potentials

The reduction and oxidation potentials were measured by cyclic voltammetry. An Electroanalytical MTM System model EA9C-4z (Poland), equipped with a small-volume cell, was used for the measurements. A 1 mm platinum disc electrode was applied as the working electrode. A platinum wire constituted the counter electrode, and a silver/silver chloride (Ag/AgCl) electrode served as a reference. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate in dry acetonitrile. The solution was deoxygenated by bubbling argon gas through the solution. The potential was swept from  $-1.8$  to  $1.8$  V at a rate of 500 mV/s to record the current–voltage curve.

### 2.4. Polymerization

Photoinitiated polymerization rate ( $R_p$ ) profiles were determined by differential scanning calorimetry (DSC) under isothermal conditions at room temperature using a photo-DSC apparatus constructed on the basis of a TA Instruments DSC 2010 Differential Scanning Calorimeter (USA). The sample ( $0.035 \pm 0.002$  g) was polymerized in open aluminum pans with a diameter of 6.6 mm. Irradiation of the polymerization mixture was carried out using emission of the air-cooled Ion Laser Systems model 177-G01 (Spectra-Physics, USA). The average power of irradiation was 15 mW/0.196 cm<sup>2</sup>. The light intensity was measured by a Coherent Model Fieldmaster power meter (Germany).

The polymerization solution was composed of 1 mL of MP and 9 mL of TMPTA. The photoinitiator concentrations used in the experiments were  $7.5 \times 10^{-3}$  M. As a reference sample, a polymerizing mixture containing alone dye was used. The polymerizing mixture was not deaerated. In order to reduce the effect of diffusion-controlled termination, the effect of a network formation, the Norrish–Trommsdorff effect and the radical trapping effect, the initial rates of polymerization were taken into account for further consideration.

The degree of conversion of the monomer (C%) into polymer determined after a specific irradiation time was also presented here. The conversion percentages were obtained integrating the area under the exothermic peak (Eq. (1)).

$$C\% = \frac{\Delta H_t}{\Delta H_0} \times 100 \quad (1)$$

where  $\Delta H_t$  is the reaction heat evolved at time  $t$  and  $\Delta H_0$  is the heat evolved assuming total conversion. Polymerization rates were calculated using Eq. (2).

$$R_p = \frac{dH/dt}{\Delta H_0} \quad (2)$$

### 2.5. Computational details

Gaussian 09 [15] software package was used for all calculations.

The B3LYP [16] functional with 6-31 + G(d,p) basis set were used for the geometry optimization of the ground and first excited state of the SQ dye molecule. Frequency analysis was performed at the same level. Excitation and emission energies were calculated using time-dependent density functional theory (TD-DFT). The hybrid (B3LYP, PBE0 [17]) and long-range corrected (CAM-B3LYP [18], LC-BLYP [19], LC- $\omega$ PBE [20–22]) functionals with 6-311 + +G(d,p) basis set were used for this calculations. All calculations were performed in the gas phase and in acetonitrile solutions (PCM model of solvation [23] was used). For visualization of the surfaces of molecular orbitals Gabedit software [24] was used.

## 3. Results and discussion

1,3-Bis(*N*-ethyl-2-methylenebenzoxazole)squaraine (SQ) was used as: (i) fluorescence probe for bovine serum albumin determination and (ii) photosensitizer incorporated in photoinitiating system (containing butyltriphenylborate salt or tetrabutylborate salt and optionally *N*-alkoxyppyridinium salt, diphenyliodonium salt or 1,3,5-triazine derivative) for the radical polymerization of triacrylate under visible light source (Scheme 1).

It is well known, that the squaraine dyes both in the ground state and excited state exhibit intramolecular donor–acceptor–donor (D–A–D) charge transfer form with partially negative charge located at the oxygen atom on central four-member ring [1,25,26].

The absorption and fluorescence spectra of investigated dye in acetonitrile are shown in Fig. 1.

From Fig. 1, it can be seen that there are two absorption bands in ultraviolet region. The absorption of squarylium dye (maximum located at 280 and 320 nm with a molar absorption coefficient for second band,  $\epsilon = 19\,400$  M<sup>-1</sup> cm<sup>-1</sup>) exhibits very poor overlapping with the emission spectra of the argon ion laser at 488 nm. TDDFT calculations show that the  $S_0 \rightarrow S_1$  transition in the studied squarylium dye corresponds to the HOMO  $\rightarrow$  LUMO transition and involves a charge transfer from the oxygen atoms at both sides of the squaric ring to the nitrogen atoms (Fig. 2). Values of excitation energies of SQ calculated using different methods ( $\lambda_{ab}$  in Table 1) are 510–533 nm in the gas phase and 520–539 nm in acetonitrile solution. On the other hand, calculated emission wavelengths ( $\lambda_{em}$  in Table 1) corresponds very well to the experimental values ( $\lambda_{em(expt)} = 547$  nm in acetonitrile solution).

A very poor signal from the HOMO  $\rightarrow$  LUMO transition may be the result of intramolecular interactions in solution of the studied dye (for example, formation of aggregates).

As was mentioned above the squarylium dye studied may be used as fluorescence probe for bovine serum albumin determination. The complexation between dye and macromolecule leads to the changes in absorption and fluorescence spectra of dye. The fluorescence of 1,3-bis(*N*-ethyl-2-methylenebenzoxazole)squaraine (SQ) is increased when dye is adsorbed on the bovine serum albumin without a change in color. The fluorescence intensity increases about thirty times. The slightly red shift of the fluorescence spectrum is also observed (Fig. 3).

In addition, characteristic shift in the absorption spectrum towards the red occurred. In Fig. 4, the sharp absorption band of the free and of the adsorbed dyes, which are clearly separated at the maximum is observed.

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