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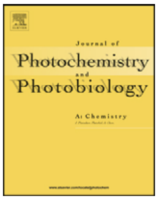

Fluoflavin dyes as electron transfer photosensitizers for onium salt induced cationic photopolymerization

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ABSTRACT

Photoredox pairs consisting of fluoflavin dyes and commercially available diphenyliodonium salts and triarylsulfonium salts are effective visible wavelength initiators of the cationic polymerization of cyclohexene oxide. The efficiency of these initiator systems is discussed on the basis of the free energy change for electron transfer from fluoflavin dyes to onium compounds. Photosensitization occurs through electron transfer, which is confirmed by the observation of a radical cation of the fluoflavin dyes. The singlet state of the dyes is involved in the photosensitization of triarylsulfonium salts, whereas both the singlet and triplet states of the dyes are involved in the photosensitization of iodonium compounds. The experimental results show that the photoinitiating ability of the tested photoredox pairs strongly depends upon the rate of electron transfer, which is reflected in the rate of radical cation formation. This determines the subsequent release of protic acid, a crucial component for the application of these systems as cationic initiators.

1. Introduction

Light-induced photopolymerization has several advantages over other comparable methods. For instance, the process occurs at a low temperature and can be controlled by manipulating the intensity and wavelength of the radiation source. In contrast to commonly used free radical polymerization, the cationic photopolymerization is not inhibited by oxygen. This method may be used to polymerize important classes of monomers, e.g., epoxides and vinyl ethers [1]. Moreover, the cationic photocuring of epoxides is becoming increasingly popular in the coating industry and the graphic arts industry. This method has low shrinkage, high mechanical performance and good adhesion [2]. Over the past decade, the most commonly used photoinitiators for cationic polymerization have been diaryliodonium and triarylsulfonium salts. These salts undergo an irreversible photofragmentation in response to UV excitation to produce radical, cationic and radical cation fragments, as shown in Scheme 1 for diphenyliodonium compounds. The aryl cations and aryliodine radical cations generated from UV photolysis further react with solvent molecules or monomers to generate a strong protic acid (H^+X^-). This acid then initiates the polymerization of monomers [3].

The most significant photoinitiators of the past decade have been compounds with more efficient long-wavelength absorbance. This is significant for two reasons: first, the development of efficient, long-wavelength UV and visible emitting light sources, such as lasers and LEDs for imaging, printing and medical applications, has created an increasing demand for an initiator system that is effective in the 400–500-nm spectral region; second, in exterior, durable photopolymers, the key has been the development of photoinitiators that absorb outside of the UV absorption curve of traditional UV absorbers used to protect organic coatings from the harmful rays of the sun.

Our study aimed to extend the absorption of onium salt initiator systems and subsequently to improve the curing rate and monomer conversion. To accomplish this, several photosensitizers, including carbazole [4], thioxanthone [5], anthracene [6], phenothiazine [7], dithienothiophene [8] and benzodioxinone [9], have been used. The most efficient and generally applicable mechanism of the photosensitization of diaryliodonium [10] and triarylsulfonium [7,11] salts is the photo-induced intermolecular electron transfer process. In such a sensitization process, the photo-excited sensitizer (Dye^*) is oxidized by the onium salt ($X–Ph^+$) to form the corresponding radical cation ($Dye^{\bullet +}$) and onium salt radical ($X–Ph^\bullet$). This radical then undergoes cleavage as depicted in Scheme 2. The radical cation, $Dye^{\bullet +}$, may itself initiate cationic polymerization. Alternatively, it may interact with solvents or monomers, resulting in the release of a strong protic acid. This acid may then initiate cationic polymerization.

There are very few visible wavelength initiator systems available for cationic polymerization. Photopolymerization can be initiated by perylene [11], coumarin [12], curcumin [13], 5,12-dihydroquinoxalino[2,3-b]pyridopyrazine [14] or 12H-quinoxalino[2,3-b][1,4]benzothiazine [15] dyes as sensitizers and

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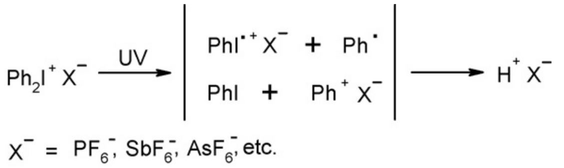


Scheme 1.

onium salts as initiators. Therefore, the main goal of this study was the application of fluoflavin dyes **1–5** as visible photosensitizers. These dyes were combined with the commercially available onium salts Irgacure 250 (**On1**) and triarylsulfonium salt (**On2**) to create visible photoinitiation systems for the cationic polymerization of cyclohexene oxide (CHO). Both onium salts are available as a solution in propylene carbonate at 75% solids and 50% solids, respectively. CHO was chosen as the epoxide because it cannot be polymerized by a radical mechanism. The structure of the studied dyes, initiators and monomer are presented in Scheme 3.

2. Experimental

2.1. General

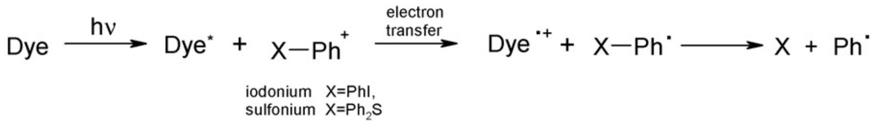
The synthesis of each dye was performed as previously described [16]. The **On1** (Irgacure 250) salt was obtained from CIBA (Lodz, Poland). **On2** (mixed salts of triarylsulfonium hexafluorophosphate), cyclohexene oxide (CHO), 1-methyl-2-pyrrolidone and methanol were purchased from Sigma–Aldrich (Poznan, Poland). All solvents were refluxed over CaH_2 and freshly distilled before use.

The absorption and steady state fluorescence spectra were recorded using a Jasco V-670 spectrophotometer and Jasco FP 6300 spectrofluorimeter (Jasco, Japan), respectively. All photochemical experiments were carried out in a Rayonet Reactor RPR 200 (The Southern New England Ultraviolet Co., USA) equipped with lamps emitting light at 419 nm. A specific spectral band was isolated by the use of band-pass filters at 419 ± 10 nm. Illumination intensity was measured using uranyl oxalate actinometry [17].

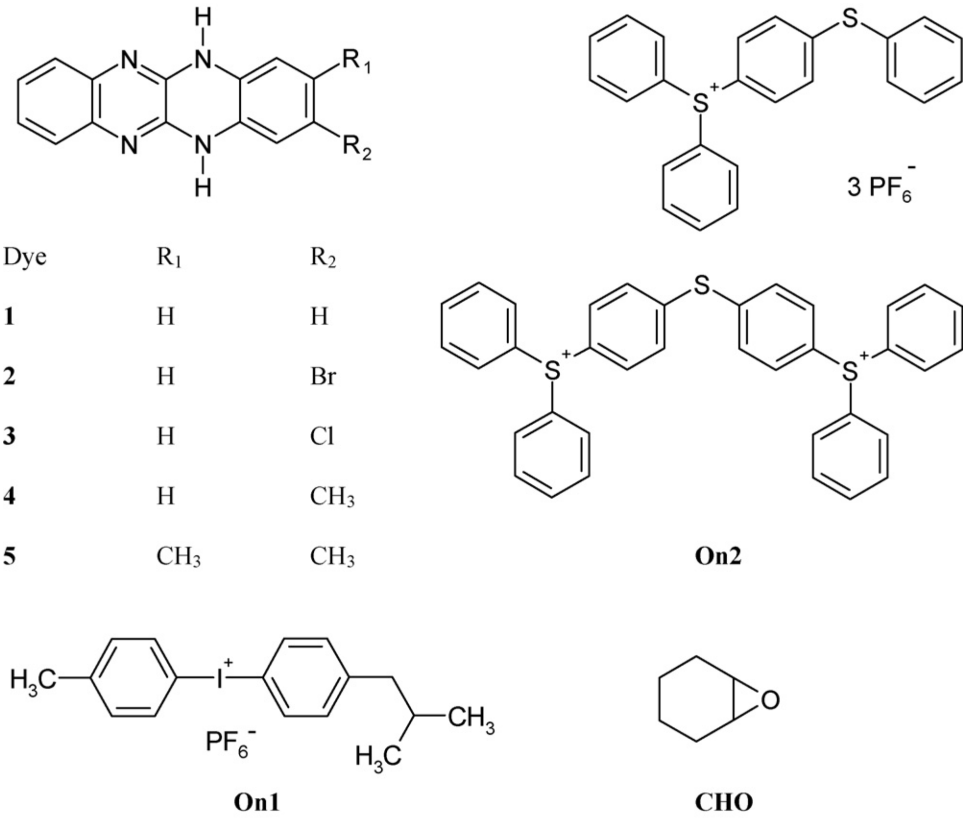
The singlet quenching constants were obtained from fluorescence quenching experiments. The fluorescence spectra of solutions of dye (5–10 μM) in CHO containing various amounts of quenchers were measured at room temperature in air by excitation at λ_{max}. Relative fluorescence intensities (I_0/I) were determined by measuring the heights of the peak at λ_{em}.

2.2. Electrochemical experiments

The electrochemical experiments were carried out in dimethylformamide (DMF) solutions containing 0.1 M tetra-n-butylammonium perchlorate as the supporting electrolyte. All experiments were carried out at room temperature, and solutions



Scheme 2.



Dye	R_1	R_2
1	H	H
2	H	Br
3	H	Cl
4	H	CH_3
5	CH_3	CH_3

Scheme 3.

Table 1
Spectroscopic and electrochemical properties of the onium salts.

	λ_{max}[a] (nm)	E_{red}[b] (V)
On1	250	−0.64
On2	234	−1.00

[a] CH_2Cl_2.
[b] DMF vs. ferrocene.

Table 2
Spectroscopic and electrochemical properties of dyes **1–5**.

Dye	λ_{max}[a] (nm)	E^{00}[a] (kJ mol^{-1})	E_{ox}[b] (V)	Φ ($^1O_2$)[c]
1	413	267	0.21	0.08
2	416	264	0.24	0.65
3	416	266	0.25	0.25
4	415	264	0.17	0.06
5	417	264	0.16	0.05

[a] CHO.
[b] DMF from Ref. [16].
[c] 1-Methyl-2-pyrrolidone from Ref. [16].

were degassed prior to experiments by bubbling with argon. During each experiment, a blanket of argon was maintained over the solution. The concentration of the onium salt was 1 mM. Cyclic voltammograms were recorded on an AUTOLAB potentiostat (Ecochemie, Holland). Platinum was used as both the working and auxiliary electrodes, and ferrocene was used as the reference electrode.

2.3. Photochemical experiments

The photosensitized cationic polymerization of CHO was monitored using Fourier transform real-time infrared spectroscopy (FT-RTIR). Photocured samples were analyzed with a Bio-Rad 175C spectrophotometer with a resolution of 8 cm^{-1} as the absorbance mode. An attenuated total reflection (ATR) accessory with a germanium crystal was used to determine the FTIR spectra. All photopolymerizations were conducted under ambient air conditions using a light of wavelength of 419 nm. The concentrations of dye and onium salt were 0.5 and 50.0 mM, respectively. The kinetic parameter Rp/M_0 was determined from the initial slopes of the irradiation time–conversion curves according to Eq. (1) [6]:

$$\frac{\mathrm{Rp}}{M_0} = \frac{[\mathrm{conversion}]_{t_2} - [\mathrm{conversion}]_{t_1}}{t_2 - t_1} \qquad (1)$$

Here, Rp is the rate of polymerization, and M_0 is the initial monomer concentration. Conversion is determined from the curves at the irradiation times t_1 and t_2.

CHO (5 mL) was also polymerized by exposure to radiation for a specific time. The resulting solution was poured into 50 mL of methanol containing roughly 1 mL of NH_3 (30%). The precipitated polymers were isolated by filtration, washed with cold methanol and dried overnight in a vacuum oven at 45 °C. The conversion of the monomer into polymer was then determined gravimetrically.

Photochemical reactions of dyes in composition with onium salt in CHO were carried out in a glass tube. The rate of each dye's radical cation formation (k_{fr}) was determined according to the increase in the absorption at λ_{475}. The quantum yield of sensitized proton formation ($\Phi(H^+)$) was measured as described in Ref. [14]. The kinetic parameters Rp/M_0, k_{fr}, $\Phi(H^+)$ and the CHO conversion were calculated from at least three determinations.

3. Results and discussion

3.1. Spectroscopic and thermodynamic properties of fluoflavin dye/onium salt systems

Onium salts are among the main class of photoinitiators for cationic polymerization. Unfortunately, these compounds have their absorption band in the UV region (Table 1), and they are efficient photoinitiators of cationic polymerization when irradiation is carried out using light in the short- to mid-wavelength UV regions (230–300 nm). In order to extend the spectral sensitivity to visible light, fluoflavin dyes **1–5** were used as oxidizable sensitizers. The spectroscopic and electrochemical properties of these dyes are presented in Table 2. The fluoflavin dyes have an absorption band at about 415 nm and could be applied as visible sensitizers for the collection of light >400 nm. The well-known mechanism of the dye-sensitized photodecomposition of onium salts [7,10,11] is presented in Scheme 2. Irradiation of these photoredox pairs leads to electron transfer from the excited sensitizer (Dye*) to the onium salt (X–Ph$^+$). The resulting onium salt radical (X–Ph$^\bullet$) is then cleaved to yield a phenyl radical (Ph$^\bullet$), neutral molecule X (iodobenzene or diphenyl sulfide) and a sensitizer radical cation (Dye$^{\bullet+}$). The rapid decomposition of the onium salt radical retards any reverse electron transfer and renders the overall process irreversible.

To facilitate the intermolecular photo-induced electron transfer from the excited dyes **1–5** to the onium salt, the corresponding Gibbs free energy change (ΔG_{et}) must be negative. In our study, values for ΔG_{et} were calculated from the Rehm–Weller equation (Eq. (2)) [18]:

$$\Delta G_{et}(\mathrm{kJ\,mol^{-1}}) = 97[E_{ox}(S/S^{\bullet+}) - E_{red}(A^{\bullet-}/A)] - E^{00}(S) - Z_1Z_2/\varepsilon r_{12} \qquad (2)$$

Here, $E_{ox}(S/S^{\bullet+})$ and $E^{00}(S)$ are the oxidation potential of the dye and the singlet excited state energy of the dye, respectively. Both parameters are given in Table 2. The last term represents the Coulombic energy necessary to form an ion pair with charge Z_1 and Z_2 in a medium of dielectric constant ε over a distance r_{12}. Since the neutral radical of the onium compound is formed ($Z = 0$) in the electron transfer process, this term is negligible. $E_{red}(A^{\bullet-}/A)$ is the reduction potential of the onium salt. It was measured using staircase voltammetry. The cyclic voltammograms of studied onium salts are presented in Fig. 1, and the measured reduction potentials (E_{red}) are listed in Table 1. Our results agree well with the previously reported electrochemical data for diaryliodonium and triarylsulfonium salts [19]. In both cases, the electrochemical reduction of the onium salt is irreversible and results in carbon–iodine or carbon–sulfur bond cleavage. Moreover, the iodonium salt is

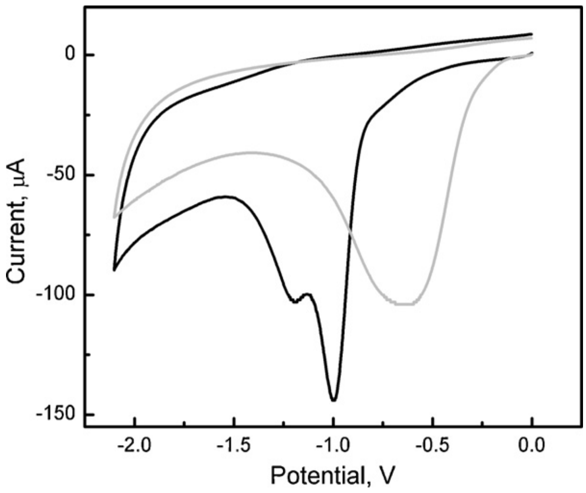


Fig. 1. Cyclic voltammograms of **On1** (gray) and **On2** (black) in DMF. Scan rate: 0.1 V s^{-1}.

Table 3
Thermodynamic parameters of the studied photoredox pairs.

Dye	On1		On2	
	ΔG_{el}	$k_q \times 10^9$	ΔG_{el}	$k_q \times 10^9$
1	−184.5	2.9	−149.6	3.88
2	−178.6	3.6	−143.7	2.51
3	−179.7	3.0	−144.7	3.18
4	−185.4	3.5	−150.5	4.16
5	−186.4	14.2	−151.5	5.04

reduced at the lowest potential ($E_{red} = -0.64$ V) in comparison with triarylsulfonium salts ($E_{red} = -1.0$ V).

Once the reduction potentials of the onium salts had been measured, the values of ΔG_{et} could be calculated using Eq. (2). The calculated thermodynamic parameters listed in Table 3 indicate that all combinations of the dye/onium salt systems posses a high driving force ($-\Delta G_{et} > 140\,\text{kJ mol}^{-1}$) upon exposure to light. This means that their photoelectron transfer process easily occurs through the excited state. It can be assumed based on this calculation that the photodecomposition of the onium salt caused by the studied dyes is initiated by photo-induced intermolecular electron transfer from the dyes to the onium compound.

The quenching experiment in CHO also shows that fluorescence of fluoflavin dyes was effectively quenched by **On1** and **On2** (Fig. 2). The absence of any new peak in the emission spectra excludes any exciplex formation. The bimolecular quenching constant k_q was calculated from Eq. (3) using the fluorescence lifetime of the dye (τ_0) without any quencher [16].

$$\frac{I_0}{I} = 1 + k_q \tau_0 [\textbf{On}] \tag{3}$$

The calculated singlet quenching constants (k_q) are summarized in Table 3. These values are close to the diffusion-controlled limit ($k_q \sim 1 \times 10^9$ to $1 \times 10^{10}\,\text{M}^{-1}\,\text{s}^{-1}$). Dye 5 has the highest value of k_q as well as the lowest oxidation potential. This suggests that fluorescent quenching proceeds via electron transfer.

3.2. Sensitized cationic photopolymerization

The dye/onium salt photoredox pairs were examined for their usefulness as photoinitiators in the cationic polymerization of CHO. CHO was deliberately chosen as a monomer since it polymerizes only by cationic mechanisms and does not react with radicals to form oxidizable radicals. Moreover, the commercially important epoxides, such as 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexanecarboxylate undergo ultimately gelation. Therefore it was not possible to study the exact role of the photosensitizer in these cycloaliphatic diepoxides. Preliminary experiments show that CHO does not polymerize at 419 nm if any of the components of the photoinitiator system are missing.

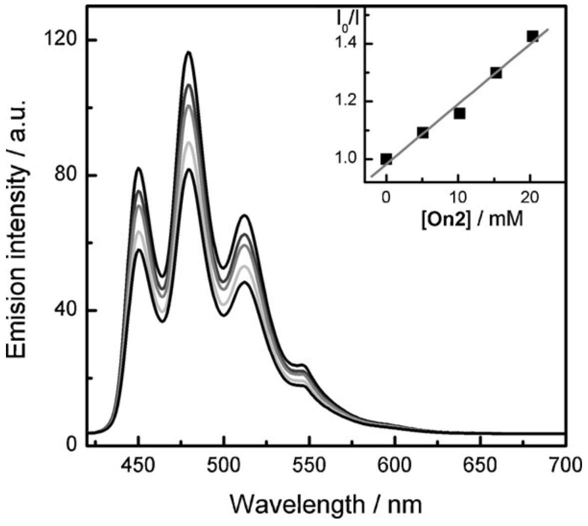


Fig. 2. Fluorescence quenching of dye **5** by **On2**. Inset: Stern–Volmer plot of fluorescence quenching of dye **5** (10 μM) by **On2** in CHO.

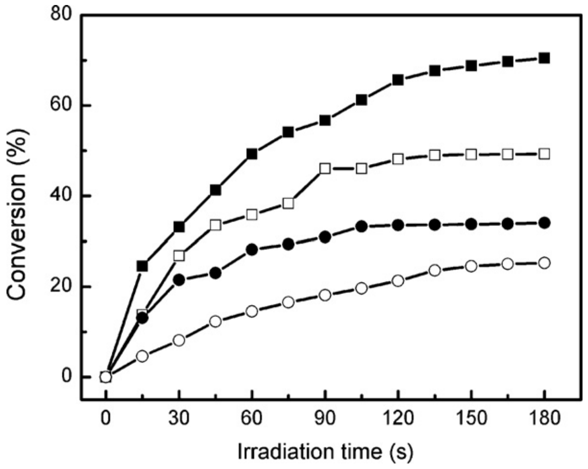


Fig. 3. Photopolymerization of CHO initiated by **3**/**On1** (■), **3**/**On2** (□) and **4**/**On1** (●), **4**/**On2** (○) systems. [Dye] = 0.5 mM, [**On**] = 50 mM, light intensity = 1.6×10^{17} quant s^{-1}.

Cationic polymerization of CHO was studied in a thick layer (130 μm). Fourier transform infrared spectroscopy was employed to monitor the kinetics of functional group disappearance in CHO (781 cm^{-1}) undergoing photoinitiated cationic polymerization. Fig. 3 shows an example of a FT-RTIR study in which the photopolymerization of CHO was carried out. In this study, dyes **1–5** were used as photosensitizers and onium salts were used as the photoinitiator. The kinetic parameter Rp/M_0 was determined from the slope of the initial portion of the conversion versus time curve (Table 4). Additionally, the polymerization of CHO into polymers was determined after a specific irradiation time (Table 4). The Rp/M_0 value and the conversion of the monomer indicate that the efficiency of CHO polymerization depends on both the dye and onium salt used. The highest efficiency for CHO cationic polymerization was obtained for **On1**. The lowest efficiency was obtained for triarylsulfonium salt **On2**. These results can be related to differences in the reduction potentials of these onium salts (see Table 1). **On1** is more readily reduced than **On2** due to its lower reduction potential. Therefore, the photoredox systems containing **On1** have higher values of ΔG_{et} (Table 3). When fluoflavin dyes **1–5** were used in combination with the iodonium salt, dyes **2** and **3** significantly accelerated CHO polymerization in comparison with the other dyes. These two dyes in particular also have the two highest quantum

Table 4
Conversion (%) of CHO and FT-RTIR kinetic data (s^{-1}) for photosensitizers **1–5**.

	On1		On2	
	Rp/M_0 [a]	Conv [b]	Rp/M_0 [a]	Conv [b]
1	0.65	8	0.58	7
2	1.49	43	0.69	5
3	1.10	37	0.76	5
4	0.72	17	0.27	7
5	0.29	7	0.22	4

[a] 180 s of irradiation; [Dye] = 0.5 mM, [**On**] = 10 mM, light intensity 1.6×10^{17} quant s^{-1}.

[b] Determined gravimetrically after 5 min of irradiation; [Dye] = 0.15 mM, [**On**] = 10 mM, light intensity 1.6×10^{17} quant s^{-1}.

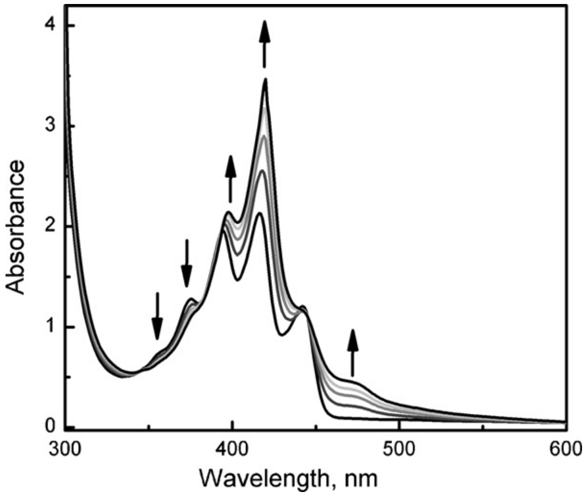


Fig. 4. Electronic absorption spectra obtained upon photolysis of the dye **3** (0.15 mM)/**On1** (10 mM) system in CHO under air atmosphere (time interval 30 s).

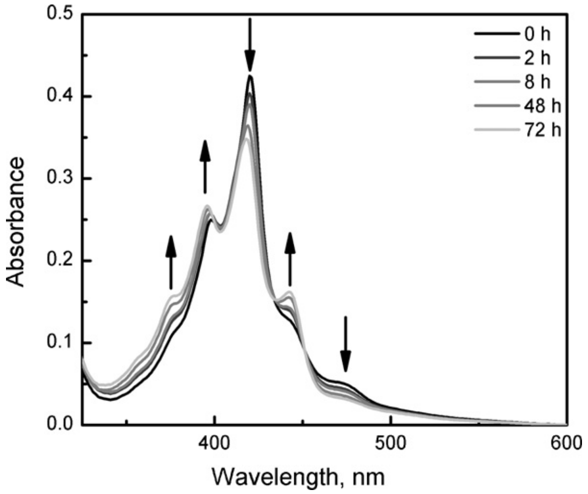


Fig. 5. Electronic absorption spectra obtained upon the addition of 2.8 mL of CHO to 0.2 mL of photochemical generated $3^{\bullet +}$ (0.15 mM)/**On1** (10 mM) system in CHO under air atmosphere.

yields of singlet oxygen generation (Table 2). This may suggest that in the case of dyes **2** and **3**, electron transfer may also occur via the triplet state. When dyes **1–5** were used as sensitizers in photoredox pairs with the triarylsulfonium salt, the highest conversion of CHO was obtained for dyes **1** and **4**. In all cases, however, the conversion of CHO was comparable (6 ± 1%) for all dyes with the exception of dye **5**. The photoreaction of that dye and the initiation mechanism were studied to explain this effect.

3.3. *Dye photoreaction and initiation mechanism*

In our study, the photochemical reactions of dyes **1–5** in combination with **On1** or **On2** were measured in CHO solution under an air atmosphere. An example of the absorption spectra of the combination of fluoflavin dye **3** and onium salt **On1** before and during irradiation are shown in Fig. 4. Decay of the dye absorption bands (377 and 396 nm) is accompanied by the growth of a band at 420 nm and small bands at 470 nm. The same effect was observed during photolysis of the others studied photoredox pairs. The isosbestic points at 445 nm (Fig. 4) indicate direct conversion of the dye into the stable product. We concluded that the product formed after photolysis is a radical cation of the fluoflavin dye ($\mathbf{3}^{\bullet +}$). The rates of radical cation formation (k_{fr}) for all of the dyes are presented in Table 5. These data clearly indicate that the rate of radical cation formation depends on the electron acceptor that is present in the photoredox pairs. When **On1** was used as an electron acceptor, the highest rate of radical cation formation was observed for dyes **2** and **3**. As previously mentioned, these two dyes also have the higher values for the quantum yield of singlet oxygen generation, and electron transfer may occur via the triplet state. Surprisingly, when the triarylsulfonium salt was used as an electron acceptor, the higher rates of radical cation formation were observed for dyes without any halogens in their structure (dyes **5**, **4**, **1**). The highest value of k_{fr} was observed for dye **5**. This dye also has the highest value of k_{q} (see Table 3). The relationship between k_{fr} and k_{q} may suggest that in the fluoflavin/**On2** photoredox pair electron transfer occurs via the singlet state.

Table 5
Rate of radical cation formation ($\times 10^3\ \mathrm{s}^{-1}$) for each dye and quantum yield of acid release (Φ_{acid}) (mmol quant^{-1}).

	On1		**On2**	
	k_{fr}[a]	$\Phi(\mathrm{H}^+)$[b]	k_{fr}[a]	$\Phi(\mathrm{H}^+)$[b]
1	1.67	10.8	1.58	5.8
2	7.20	62.0	0.45	2.3
3	5.99	45.8	0.48	3.6
4	3.41	22.4	1.39	4.9
5	1.94	12.5	2.36	4.4

[a] [**On**] = 10 mM; [Dye] = 0.15 mM; light intensity = 6×10^{16} quant s^{-1}.
[b] Calculated for 9 ± 2%.

Additionally, in all the dye/onium salt combinations studied, the solution acidity increased, whereas photolysis of the dyes alone did not change the solution pH. The calculated quantum yields of acid release $\Phi(\mathrm{H}^+)$ are presented in Table 5. With the exception of the dye **5**/**On2** system, there is relationship between k_{fr} and $\Phi(\mathrm{H}^+)$. This suggests that the radical cation of the dye is responsible for proton formation. This hypothesis was confirmed by the fact that the addition of CHO to the photochemically generated $\mathbf{3}^{\bullet +}$ (Fig. 5) caused the decay of the dye's radical cation absorption bands (419 and 475 nm) and the regeneration of the dye's original absorption bands (377, 396, 418 and 442 nm). The same effect was observed for the other dyes. Moreover, a relationship was observed between the conversion of CHO and the rate of radical cation formation in each dye (Fig. 6).

Based on the results presented above, a mechanism for proton formation during photolysis was proposed (Scheme 4). Fluoflavin

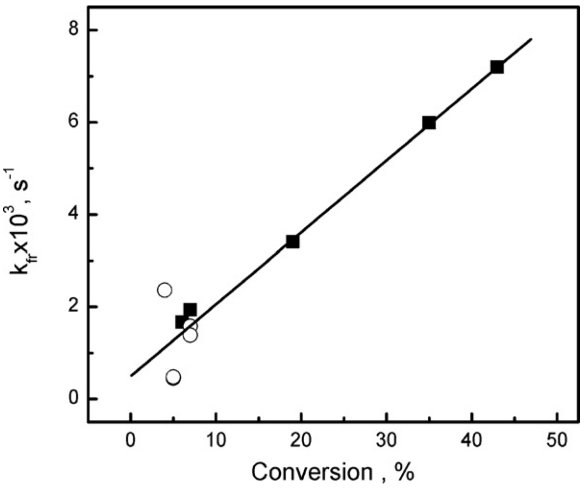
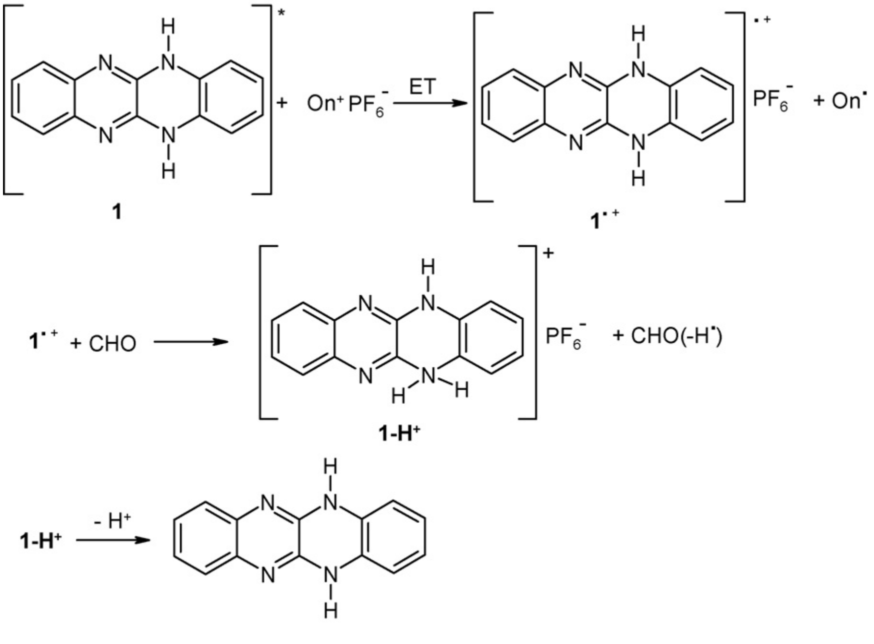
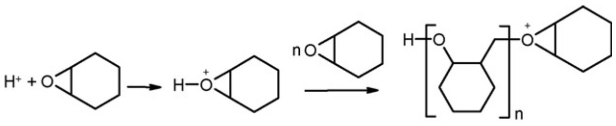


Fig. 6. Relationship between the rate of dye radical cation formation and the conversion of CHO initiated by the dye/**On1** (■) and the dye/**On2** (○) systems (R = 0.96).



Scheme 4.



Scheme 5.

dyes are efficient sensitizers for the decomposition of iodonium and sulfonium salts. In the first case, electron transfer occurs from both the triplet and singlet states of the dye, whereas electron transfer in sulfonium salts occurs only from singlet state of dyes. The same effect was observed when acridinedione dyes were used as sensitizers for the decomposition of iodonium and sulfonium salts [10]. Radical cation $\mathbf{1}^{\bullet+}$ reacts with CHO via hydrogen abstraction followed by proton formation and sensitizer regeneration. The proton formation then initiates the cationic polymerization of the epoxide monomer (Scheme 5). However, in the case of dye **5**, the presence of the two methyl groups may further stabilize the radical cation $\mathbf{5}^{\bullet+}$ and cation **5-H**$^{+}$. This effect may be responsible for the low conversion of CHO.

One should to mentioned, that the conversion of CHO depends on the concentration of the studied dye. The data obtained from the gravimetric analysis (Table 6) clearly indicate that the conversion to poly(cyclohexene oxide) increased as the concentration of sensitizers increased. The highest conversion of the monomer was obtained for 0.45 mM of sensitizers. Increasing the concentration of the dyes to 0.75 mM decreased the monomer conversion. The presence of nitrogen atoms in studied dyes may be responsible for this retardation. Nevertheless, from practical point of view the photoredox systems which are composed with iodonium salts and dyes **2** and **3** are the most promising photoinitiators for visible cationic polymerization of cycloaliphatic diepoxides.

Table 6
Photoinitiated polymerization of CHO using various concentration of dyes **1–5**.

	Conversion %[a]					
	On1			**On2**		
	0.15 mM	0.45 mM	0.75 mM	0.15 mM	0.45 mM	0.75 mM
1	11	54	44	10	18	15
2	71	90	79	12	23	21
3	42	81	60	10	26	25
4	24	48	35	13	20	17
5	17	45	28	9	17	12

[a] Determined gravimetrically after 15 min of irradiation; [**On**] = 10 mM, light intensity 1.6×10^{17} quant s^{-1}.

4. Conclusions

Fluoflavin dyes, when combined with commercially available onium salts such as Irgacure 250 (**On1**), may have practical applications as visible light photoinitiators of cationic polymerization. The ability of a photoredox pair to act as a photoinitiator strongly depended upon the rate of radical cation formation. The heavy atoms present in dyes **2** and **3** could promote the formation of the each dye's excited triplet state and thereby facilitate electron transfer from these triplet states in the dye/**On1** systems. In the dye/**On2** systems, electron transfer occurs via only the singlet state of the dye. The initiating species of both systems are formed as a result of hydrogen abstraction by the radical cation of the dye followed by proton formation and sensitizer regeneration.

Acknowledgements

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