



12H-Quinoxalino[2,3-b][1,4]benzothiazine derivatives as novel visible photosensitizers in cationic photopolymerization

Radosław Podsiadły*

Institute of Polymer and Dye Technology, Technical University of Lodz, Stefanowskiego 12/16, 90-924 Lodz, Poland

ARTICLE INFO

Article history:

Received 11 May 2009

Received in revised form 23 July 2009

Accepted 8 September 2009

Available online 16 September 2009

Keywords:

Dyeing photoinitiator

Cationic photopolymerization

Photoinduced electron transfer

Cation radical

ABSTRACT

Photoredox pairs consisting of dyes based on a 12H-quinoxalino[2,3-b][1,4]benzothiazine skeleton and iodonium salt are found to be effective initiation systems for cationic polymerization of epoxide monomers and tetrahydrofuran using VIS light. The efficiency of these initiator systems is discussed on the basis of the free energy change for electron transfer from benzothiazine dyes to the iodonium compounds. Three products, phenyl derivatives of dye **1** were isolated after photolysis of **1**/onium salt system. These compounds were characterising by chemical ionization mass spectra. The reactions created the phenylated analogues of dye **1** and protons were proposed.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Light-induced photopolymerization has several advantages over other comparable methods. For instance, the process occurs at 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, such as epoxides and vinyl ethers [1]. Moreover, the cationic photocuring of epoxide 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 salts. These salts undergo irreversible photofragmentation in response to UV excitation to produce free radical, cationic, and radical cation fragments (Scheme 1). The aryl cations and aryl iodine radical cations generated from photolysis further react with solvent molecules or monomers to generate a strong protic acid, H^+X^- . This acid initiates the polymerization of monomers [3].

Our study aimed to extend the absorption of this initiator system and subsequently improve the curing rate and monomer conversion. To accomplish this, several photosensitizers have been used, including carbazole [4], thioxanthone [5], anthracene [6], and phenothiazine [7]. The most efficient and generally applica-

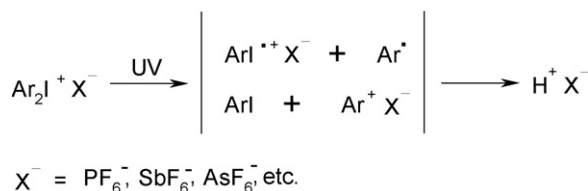
ble mechanism of photosensitization of diaryliodonium [8] salts is photoinduced intermolecular electron transfer processes. In such sensitization process, the photo-excited sensitizer (Dye^*) is oxidized by the iodonium salt (Ph_2I^+) to form the corresponding radical cation ($Dye^{\bullet+}$) and onium salt radical (Ph_2I^\bullet). This radical then undergoes cleavage as depicted in Scheme 2. The radical cation, $Dye^{\bullet+}$, may initiate the 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.

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 which is effective in the 400–500 nm spectral region. Cation-induced initiator systems operating upon visible radiation have been obtained using perylene [9], coumarin [10], or curcumin [11] dyes as sensitizers and onium salts as an initiator. Recent studies have revealed that photoredox pairs consisting of dyes based on a 5,12-dihydroquinoxalino[2,3-b]pyridopyrazine skeleton [12] and diphenyliodonium salts efficiently initiate the polymerization of cyclohexene oxide. More recently, Crivello investigated photosensitized vinyl and ring opening polymerization using 12H-benzo[b]phenothiazine (**BPT**)/triarylsulfonium systems [13].

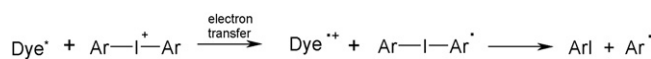
The main goal of this study was the application of dyes based on a 12H-quinoxalino[2,3-b][1,4]benzothiazine skeleton (**1–3**) as photosensitizer. These dyes were combined with diphenyliodonium salts (**Io1**) to create visible photoinitiation systems for cationic polymerization of epoxide monomers and tetrahydrofuran. This paper also proposes the mechanism of proton formation

* Tel.: +48 42 631 32 37; fax: +48 42 636 25 96.

E-mail address: radekpod@p.lodz.pl.

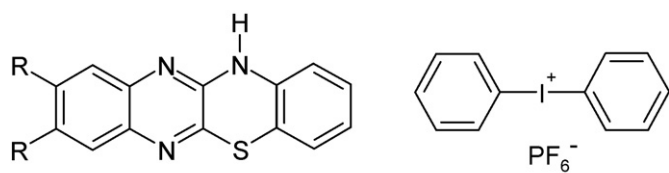


Scheme 1.



Scheme 2.

and the mechanism of dye fading during photolysis of iodonium (**1o1**)/benzothiazine dye systems. The mechanism proposed here is supported by spectroscopic characterization of products formed during the photolysis of the dye/onium salt system.

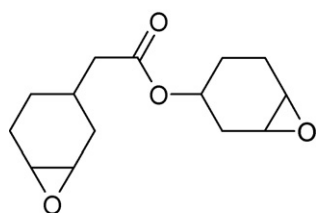
**1o1**

	R
1	H
2	CH ₃
3	Cl

2. Experimental

2.1. General

The procedure of dye preparation has been described elsewhere [14]. Diphenyliodonium hexafluorophosphate (**1o1**), cyclohexene oxide (CHO), 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate (CADE) and 1-methyl-2-pyrrolidone (MP) were purchased from Sigma–Aldrich (Poznan, Poland). Tetrahydrofuran (THF), acetonitrile (MeCN) and ethanol (EtOH) were from POCh (Gliwice, Poland). All solvents were refluxed over CaH₂ and freshly distilled before use.



CADE

The absorption and steady-state fluorescence spectra were recorded using a JASCO V-670 spectrophotometer (Jasco, Japan) and a FluoroLog 3 spectrofluorimeter (Horiba Jobin Yvon, USA), respectively. All photochemical experiments were carried out in a Rayonet

Reactor RPR 200 (The Southern New England Ultraviolet Co., USA) equipped with eight lamps emitting light at 419 nm. Illumination intensity was measured using uranyl oxalate actinometry [15].

The Stern–Volmer constants were obtained from fluorescence quenching experiments. The fluorescence spectra of dye solutions (15–20 μM) in EtOH containing various amounts of quenchers were measured at room temperature in an air atmosphere using excitation at λ_{max}. Relative fluorescence intensities (*I*₀/*I*) were determined by measuring the heights of the peak at λ_{em}.

2.2. Photochemical experiments

The photosensitized cationic polymerization of the cyclohexene oxide (CHO) and 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate (CADE) were monitored using Fourier transform real-time infrared spectroscopy (FT-RTIR). Photocured samples were analyzed with a Bio-RAD FTS 175C spectrophotometer with a resolution 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 light of 419 nm. The concentrations of dye and diphenyliodonium salt were 0.5 and 50.0 mM, respectively. The kinetic parameter, *R*_p/*M*₀, was determined from the initial slopes of the irradiation time–conversion curves according to Eq. (1) [6]:

$$\frac{R_p}{M_0} = \frac{([\text{conversion}]_{t_2} - [\text{conversion}]_{t_1})}{(t_2 - t_1)} \quad (1)$$

*R*_p and *M*₀ are the rate of polymerization and the initial monomer concentration, respectively. The conversions are determined from the curves at the irradiation times *t*₁ and *t*₂.

CHO (5 ml) and THF (3 ml) were polymerized using a specific time exposure to radiation. The resulting solution was poured into 50 ml of methanol containing roughly 1 ml of NH₃ (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 monomers into polymers was then determined gravimetrically.

Photobleaching of dyes in composition with **1o1** in THF was carried out in a glass tube. The extent of the dye fading or the dye's cation radical formation was determined according to the decrease or increase in the absorption at λ_{max}. The quantum yield of sensitized proton formation (Φ(H⁺)) was measured as described in Ref. [12].

The quantum yield of dye bleaching (Φ_{bl}), the quantum yield of sensitized proton formation (Φ(H⁺)) and the rate of dye fading (or the dye's cation radical formation) were calculated from at least three determinations.

The products formed after photolysis (90 min, THF) were separated by preparative layer chromatography [Uniplat Silica Gel 60 GF (Analtech, USA), thickness 2000 μm; eluent: toluene–ethyl acetate (4:1, v/v)]. The chemical ionization mass spectra were recorded on a Finnigan MAT 94 spectrometer with isobutane application.

3. Results and discussion

3.1. Spectroscopic and electrochemical properties

Phenothiazine and benzo[b]phenothiazine are among the main class of photosensitizers. When combined with onium salts, they effectively initiate cationic polymerization [13]. Unfortunately, phenothiazine compounds have their absorption band in the UV region. In order to extend the spectral sensitivity to visible-light, dyes based on the 12H-quinoxalino[2,3-b][1,4]benzothiazine skeleton (**1–3**) were used as sensitizers. The spectroscopic proper-

Table 1
Spectroscopic and photophysical parameters of benzothiazine dyes **1–3** [10] and **BPT** [16].

Dye	λ_{\max}^a (ϵ) nm ($M^{-1} \text{ cm}^{-1}$)	λ_{em}^a (nm)	Φ_{em}^a	τ^a (ns)	E^{00} (kJ/mol)	$\Phi(^1\text{O}_2)^b$	E_{ox}^c (V)
1	421(6600)	530	0.22	4.6	253.5	0.78	0.97
2	424(6500)	532	0.20	4.3	252.9	0.79	0.79
3	442(5000)	544	0.23	4.1	246.7	0.79	0.90
BPT	365 ^c						0.79 ^d

^a In EtOH.^b In MP.^c In CH_3CN vs. ferrocene.^d vs. Ag/AgCl.

ties (absorption and fluorescence) and electrochemical properties of the studied dyes are presented in Table 1. The dyes derived from 12H-quinoxalino[2,3-b][1,4]benzothiazine had an absorption band at about 420 nm. Compared to benzo[b]phenothiazine (**BPT**) [16], the presence of two additional nitrogens in **1** caused a red shift of the band into the visible range. These dyes show a high molar absorption coefficient. This coefficient allowed us to decrease their concentration in the polymer composition. Phenothiazine derivatives showed comparatively weak values of quantum yields of fluorescence (0.20–0.25). However, their quantum yields of singlet oxygen generation were ~ 0.8 . Compared to **BPT**, the studied dyes were oxidized at higher potentials.

3.2. Sensitized cationic photopolymerization

The spectroscopic studies revealed that dyes **1–3** could be applied as visible sensitizers for the collection of light >400 nm. The well-known mechanism of the dye-sensitized photodecomposition of iodonium salts [8] is presented in Scheme 2. Irradiation of these photoredox pairs leads to electron transfer from the excited sensitizer (Dye^*) to the iodonium salt (Ph_2I^+). The resulting iodine radical

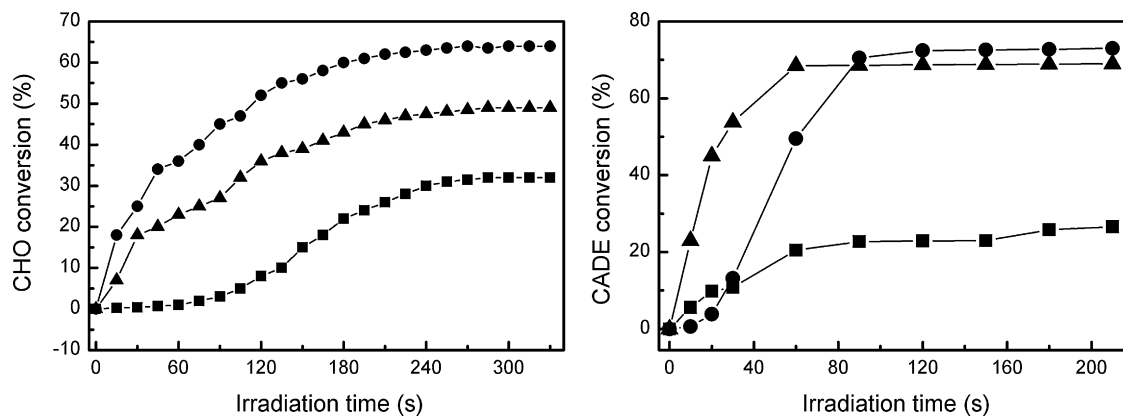
Table 2
Thermodynamic data (kJ mol^{-1}), Stern–Volmer (M^{-1}) and singlet quenching ($M^{-1} \text{ s}^{-1}$) constants for the **1–3/IO** photoredox pair.

	IO 1 ($E_{\text{red}} = -0.725 \text{ V}$)		
	ΔG_{el}	K_{SV}	$k_{\text{q}} (\times 10^{-10})$
1	–96.9	175.1	3.8
2	–113.7	154.6	3.5
3	–97.8	73.7	1.8

(Ph_2I^*) is then cleaved to yield a phenyl radical ($\cdot\text{Ph}$), iodobenzene and a sensitizer radical cation ($\text{Dye}^{\bullet+}$) [8]. The rapid decomposition of the iodine radical retards the reverse electron transfer and renders the overall process irreversible.

The free energy change of the photoinduced electron transfer from the excited dyes **1–3** to the onium salt were calculated from the Rehm–Weller equation as follows (Eq. (2)) [17]:

$$\Delta G_{\text{el}} (\text{kJ mol}^{-1}) = 97 \left[E_{\text{ox}} \left(\frac{S}{S^{\bullet+}} \right) - E_{\text{red}} \left(\frac{A^{\bullet-}}{A} \right) \right] - \frac{Z e^2}{\epsilon a} - E^{00}(S) \quad (2)$$

**Fig. 1.** Photopolymerization of CHO and CADE initiated by photosensitizers **1** (■), **2** (●), **3** (▲) and **IO1**.**Table 3**
Conversion (%) of monomers and FT-RTIR kinetic data and the quantum yield of acid release (mmol quant^{-1}) for photosensitizers **1, 2** and **3**.

	IO1									
	CHO			CADE			THF			MP ^f
	Rp/M ₀ ^a (s ⁻¹)	Conv ^b (%)	Φ_{pl}^b	Rp/M ₀ ^c (s ⁻¹)	Conv ^c (%)	Conv ^d (%)	Φ_{pl}^d	Conv ^e (%)	$\Phi(\text{H}^+)$	
1	0.19	64	24.8	0.13	70	11	4.8	10	25.5	
2	0.73	75	35.9	1.51	95	15	6.5	14	32.8	
3	0.39	65	23.4	0.25	73	12	4.9	11	27.2	

^a [dye] = 0.2 mM, [IO] = 10 mM, 135 s of irradiation.^b [dye] = 0.1 mM, [IO] = 5 mM, 30 min of irradiation.^c [dye] = 0.5 mM, [IO] = 50 mM, 240 s of irradiation.^d [dye] = 1 mM, [IO] = 5 mM, 60 min of irradiation under air atmosphere.^e [dye] = 1 mM, [IO] = 5 mM, 30 min of irradiation under N₂ atmosphere.^f [dye] = 1 mM, [IO] = 10 mM, [BPhBI] = 20 μM .

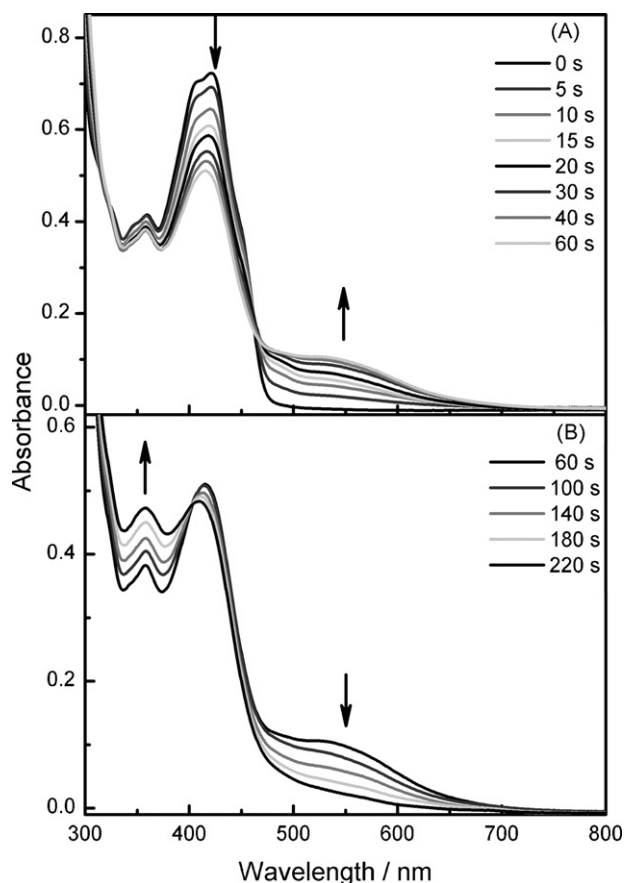
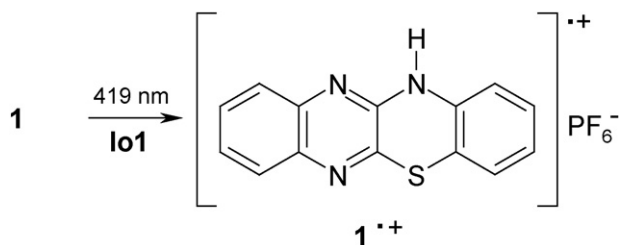


Fig. 2. Electronic absorption spectra obtained upon photolysis of the dye **1** (0.1 mM)/**Io1** (5 mM) system in THF under air atmosphere.

In this equation, $E_{ox}(S/S^{*+})$ and $E_{red}(A^{\bullet-}/A)$ are the oxidation potential of the dye and the reduction potential of the onium salt, respectively. $E^{00}(S)$ is the singlet excited state energy of the dye, which is given in Table 2. In this calculation, the Coulombic energy ($Ze^2/\epsilon a$) was omitted because the dye **1–3**/onium salt system that was employed had photoredox pairs without electrostatic interactions in the ground state and after electron transfer.

The calculated thermodynamic parameters listed in Table 2 indicate that all combinations of the dye/iodonium systems possess a high driving force ($-\Delta G_{et} > 96 \text{ kJ mol}^{-1}$) upon exposure to light. This means that their photoelectron transfer process easily occurs through the excited state. On the basis of this calculation, it can be assumed that the **Io1** photodecomposition caused by the studied dyes is initiated by the photoinduced intermolecular electron transfer from the dyes to the iodonium compound. Moreover, the fluorescence of benzothiazine dyes was effectively quenched by iodonium salt. The absence of any new peak in the emission spectra excludes the exciplex formation. The obtained Stern–Volmer constants (K_{SV}) and calculated singlet quenching constants k_q are



Scheme 3.

summarized in Table 2. The k_q values are close to the diffusion controlled limit ($k_q \sim 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).

The dye **1–3**/iodonium photoredox pairs were examined for their usefulness as photoinitiators for the cationic polymerization of CHO, CADE, and THF. Preliminary experiments show that THF and epoxide monomers do not polymerize at 419 nm if any of the components of the photoinitiator system are missing.

Cationic polymerization of epoxide monomers was studied in a thick layer. Fourier transform infrared spectroscopy was employed to monitor the kinetics of the disappearance of the functional groups of CHO (781 cm^{-1}) and CADE (748 cm^{-1}) undergoing photoinitiated cationic polymerization. Fig. 1 shows the results of a FT-RTIR study in which the photopolymerization of epoxide monomers was carried out. In this study, benzothiazine dyes **1–3** were used as photosensitizers and iodonium salts were used as the photoinitiator. The kinetic parameter R_p/M_0 was determined from the slope of the initial portion of the conversion versus time curve (Table 3). The R_p/M_0 value and the conversion of the monomer indicate that the photoredox pairs consisting of benzothiazine dyes **1–3** act as sensitizers and the **Io1** acts as an initiator. This system is promising for the initiation of cationic photopolymerization of epoxide monomers.

The polymerization quantum yields (Φ_{pl}) were determined from the slopes of converted monomers versus the absorbed energy (Table 3). The results presented in Table 3 indicate that among the studied dyes, the most efficient sensitizer is dye **2**. This dye was oxidized at the lowest potential. Therefore, the **2/Io1** systems possess the highest $-\Delta G_{et}$.

3.3. Dye photobleaching and initiation mechanism

The photopolymerization of the monomers is initiated by the dye photoredox pairs. The most important properties are the high

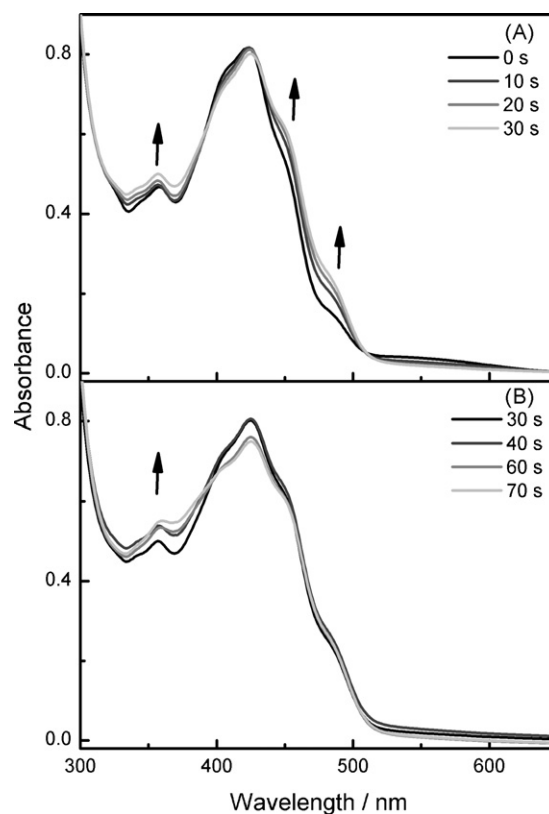


Fig. 3. Electronic absorption spectra obtained upon photolysis of the dye **1** (0.1 mM)/**Io1** (5 mM) system in THF under an N_2 atmosphere.

Table 4

The quantum yield of dye photobleaching (mmol quant^{-1}) and the rates (10^3 s^{-1}) of dye bleaching (k_{bl}) and cation radical formation (k_{cr}) in THF.

Concentration of 1								
0.05 mM			0.1 mM			0.2 mM		
k_{bl}	k_{cr}	Φ_{bl}	k_{bl}	k_{cr}	Φ_{bl}	k_{bl}	k_{cr}	Φ_{bl}
4.4	4.1	6.0	6.3	5.0	9.8	9.8	7.6	13.4

initiation reactivity and the photobleaching of the dye. The detailed mechanisms for the photoinitiated cationic polymerization and the photobleaching were studied for dye **1** and **Io1**. The absorption spectra of the combination of benzothiazine dye **1** and iodonium salt **Io1** before and during irradiation for 20–60 s are presented in Fig. 2A. Decay of the dye absorption at 421 nm is accompanied by the growth of the broad band at 550 nm. The isosbestic point at 466 nm (Fig. 2A) indicates direct conversion of the dye into stable product. It is well known that phenothiazine derivatives are easily oxidized to yield stable radical cations [18]. A low nucleophilic anion, such as BF_4^- or PF_6^- , stabilized the phenothiazine radical cation. One can conclude that the stable product formed after the photolysis is a radical cation of the benzothiazine dye (Scheme 3). A similar absorption spectrum was observed for radical cation of **BPT** (Table 5).

The calculated quantum yield of dye photobleaching (Φ_{bl}), the rate of dye disappearance (k_{bl}) and the rate of cation radical formation are presented in Table 4. From this table, it is clear that $k_{\text{bl}} > k_{\text{cr}}$. One can conclude that radical cation $\mathbf{1}^{\bullet+}$ undergoes subsequent reactions.

Extending the irradiation time to 220 s causes a delay in the absorption of radical cation $\mathbf{1}^{\bullet+}$. This change is accompanied by the growth of a band around 358 nm (Fig. 2B). The isosbestic point at 401 nm (Fig. 2B) indicates that there is direct conversion of the radical cation $\mathbf{1}^{\bullet+}$ into the new product. The same effect was observed during irradiation under an N_2 atmosphere (Fig. 3B). One can assume that the radical cation $\mathbf{1}^{\bullet+}$ undergoes one electron oxidation by the iodonium compound to form the dication $\mathbf{1}^{2+}$ (Scheme 4). A similar absorption spectrum was observed for the dication of **BPT** (Table 5).

Photolysis was completed in an N_2 saturated solution using benzothiazine dye **1** (0.2 mM) and iodonium salt **Io1** (5 mM). In this system, the absorption band of $\mathbf{1}^{\bullet+}$ was not observed (Fig. 3A). Moreover, new bands at 455 and 485 nm were observed. The forma-

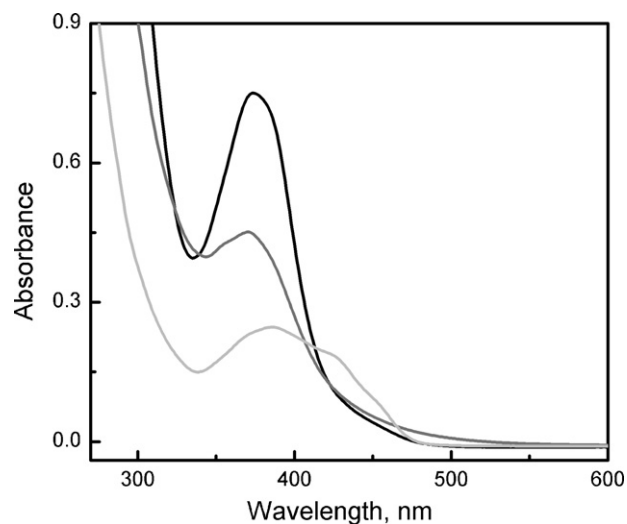
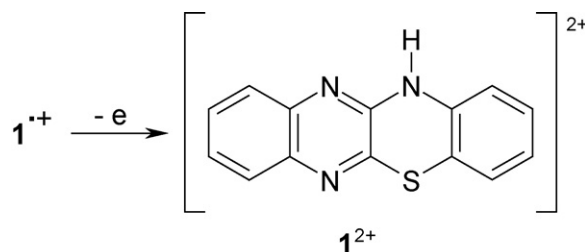


Fig. 4. Electronic absorption spectra of three products isolated after photolysis of the dye **1** (2 mM)/**Io1** (50 mM) system in THF under an N_2 atmosphere.

Table 5

Observed absorption maxima of radical cation, dication of dye **1** and **BPT**.

Compound	Absorption maxima (nm)	Compound	Absorption maxima (nm)
$\mathbf{1}^{\bullet+}$	550 ^a	$\mathbf{1}^{2+}$	358 ^a
$\mathbf{1}^{\bullet+}$	454, 486, 582 ^b	$\mathbf{1}^{2+}$	377 ^b
BPT $^{\bullet+}$	305, 425, 540 ^c	BPT $^{2+}$	261, 300, 331, 526 ^d

^a In THF.

^b In CH_3CN .

^c In CH_3CN from Ref. [16].

^d In $\text{H}_2\text{SO}_4/\text{EtOH}$ from Ref. [16].

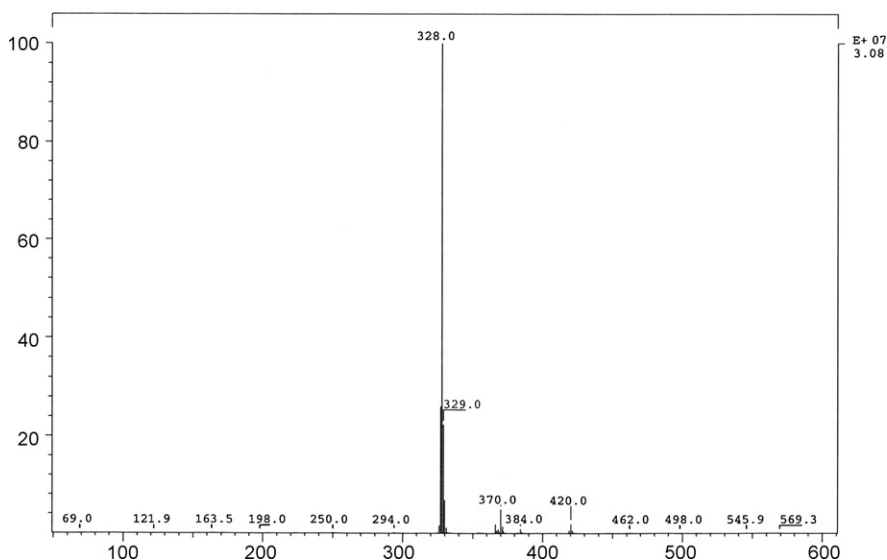
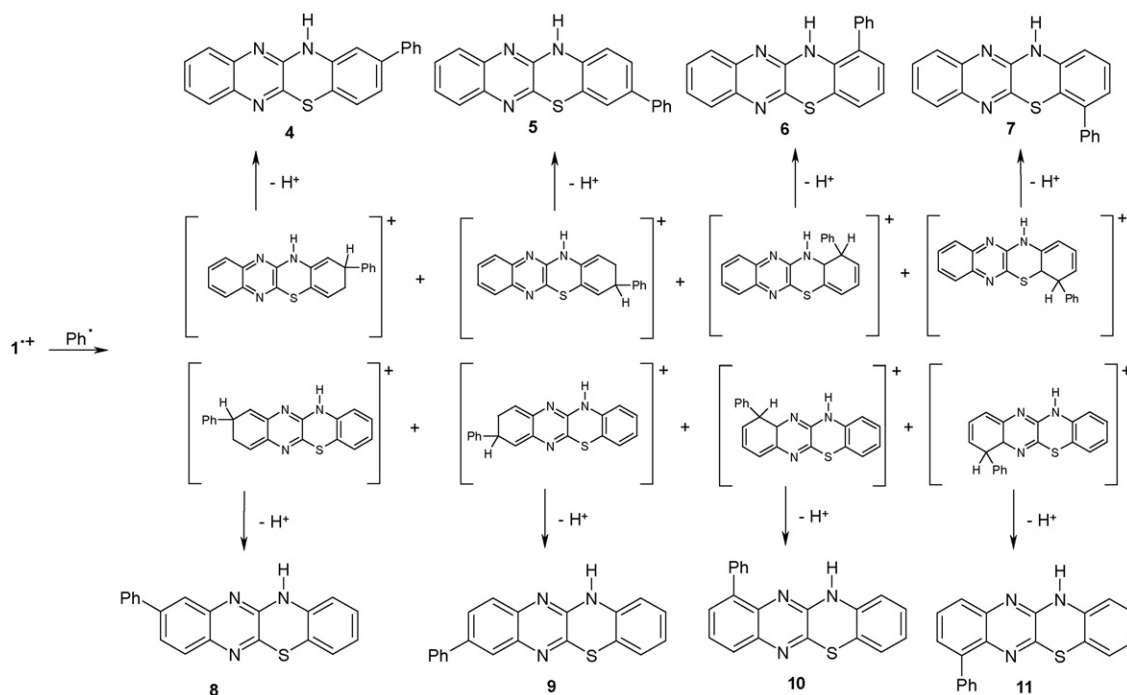
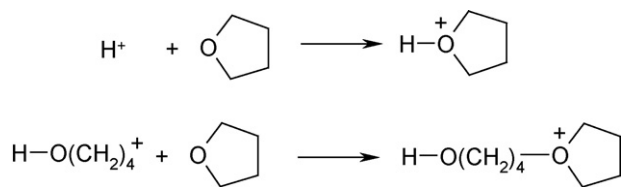


Fig. 5. CI mass spectrum of the product isolated after photolysis of the dye **1** (2 mM)/**Io1** (50 mM) system in THF under an N_2 atmosphere.



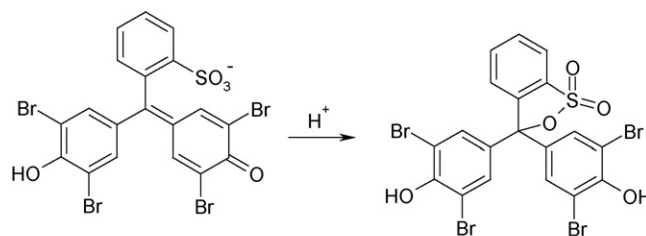
Scheme 5.



Scheme 6.

tion of a new product with an absorption peak red-shifted relative to that of the sensitizer was observed during photodecomposition of anthracene-sensitized Ph_2IPF_6 [19]. Mechanisms were proposed for these systems involving a reaction between the anthracene cation radical and the phenyl radical. In our studies, the products formed after photolysis were separated by preparative layer chromatography. The chemical ionization mass spectra of these compounds were recorded. The absorption UV–vis spectra of these substances are presented in Fig. 4. As can be seen, these compounds have an absorption band in UV region (370, 374 or 386 nm) with a shoulder at shorter wavelengths (~ 450 , ~ 480 nm). Moreover, all the CI mass spectra show an ion at m/z 328 $[\text{M}+\text{H}]$ (Fig. 5). This ion is consistent with an addition of a phenyl ring to dye **1**. On the basis of this information, one can conclude that the cation radical $1^{\bullet+}$ reacts with the phenyl radical to form fluorescent dyes. These structures of the possible products are presented in Scheme 5. These reactions created protons which initiated the cationic polymerization of THF (Scheme 6).

In order to confirm the above mechanism, the quantum yield of acid release [$\Phi(\text{H}^+)$] in the solution upon photolysis was measured using sodium bromophenol blue (BPhBI, Scheme 7). Its absorption at the peak wavelength of 606 nm decreased during irradiation. The amount of acid released was estimated from the calibration curve of BPhBI. In all the dye/**101** combinations, the solution acidity increased. However, the photolysis of the dyes alone did not change the solution pH. The calculated quantum yields of acid release are presented in Table 3. Dye **2** demonstrated the highest quantum yield of acid release.



BPhBI

Scheme 7.

On the basis of the results presented above, the mechanism of proton formation during photolysis was proposed. Electron transfer occurs from the excited dye to the iodonium salt (**101**). The transfer is followed by cleavage of the iodine radical (**101** $^{\bullet}$) to give a phenyl radical ($^{\bullet}\text{Ph}$), neutral iodobenzene, and a dye radical cation ($1^{\bullet+}$). The cation radical may react with the phenyl radical ($^{\bullet}\text{Ph}$) to yield cation species. Next, there is proton release and formation of a phenyl derivative of benzothiazine dye (**4–11**). Under an air atmosphere, the phenyl radical reacts with the oxygen first. This reaction causes the conversion of THF to be lower than with the deoxygenated monomer (Table 3).

4. Conclusions

Novel dyes based on the 12H-quinoxalino[2,3-b][1,4]benzothiazine skeleton (**1–3**) were combined with onium salts (diphenyliodonium hexafluorophosphate (**101**)). These systems may have practical applications as visible-light photoinitiators of cationic polymerization. The photolysis in air atmosphere of the dye/iodonium system yields radical cations of the dyes. These cations undergo a one-electron oxidation reaction to form dication dyes. The initiating species of the benzothiazine dye/iodonium systems are the protons. The protons are formed in the reaction of the dye's cation radical with the phenyl radical, which is formed from rapid decomposition of the iodine radical.

Acknowledgement

This work was supported by the Polish Ministry of Science and Higher Education (Project no. N N205 1454 33).

References

- [1] J.P. Fouassier, J. Rabek, *Radiation Curing in Polymer Science and Technology*, vol. 1, Elsevier, London, 1993, pp. 49–113.
- [2] C. Decker, T.V.T. Nguyen, P.T. Hon, Photoinitiated cationic polymerization of epoxides, *Polym. Int.* 50 (2001) 986–997.
- [3] J.V. Crivello, The discovery and development of onium salt cationic photoinitiators, *J. Polym. Sci. A: Polym. Chem.* 37 (1999) 4241–4254.
- [4] M. Sangermano, G. Malucelli, A. Priola, S. Lengvinaite, J. Simokaitiene, J.V. Grazulevicius, Carbazole derivatives as photosensitizers in cationic photopolymerization of clear and pigmented coatings, *Eur. Polym. J.* 41 (2005) 475–480.
- [5] J.-D. Cho, J.-W. Hong, Photo-curing kinetics for the UV-initiated cationic polymerization of a cycloaliphatic diepoxide system photosensitized by thioxanthone, *Eur. Polym. J.* 41 (2005) 367–374.
- [6] J.V. Crivello, M. Jang, Anthracene electron-transfer photosensitizers for onium salt induced cationic photopolymerizations, *J. Photochem. Photobiol. A: Chem.* 159 (2003) 173–188.
- [7] M.R. Rodrigues, M.G. Neumann, Cationic photopolymerization of tetrahydrofuran: a mechanistic study on the use of sulfonium salt–phenothiazine initiation system, *J. Polym. Sci. A: Polym. Chem.* 39 (2001) 46–55.
- [8] C. Selvaraju, A. Sivakumar, P. Ramamurthy, Excited state reactions of acridine-dione dyes with onium salts: mechanistic details, *J. Photochem. Photobiol. A: Chem.* 138 (2001) 213–226.
- [9] M.G. Neumann, M.R. Rodrigues, A study of the elemental reactions involved in the initiation of the polymerization of tetrahydrofuran induced by the photo-sensitization of a triphenylsulfonium salt by perylene, *J. Braz. Chem. Soc.* 14 (2003) 76–82.
- [10] Q.Q. Zhu, W. Schnabel, Cationic photopolymerization under visible laser light: polymerization of oxiranes with coumarin/onium salt initiator systems, *Polymer* 37 (1996) 4129–4133.
- [11] J.V. Crivello, U. Bulut, Curcumin: a naturally occurring long-wavelength photosensitizer for diaryliodonium salts, *J. Polym. Sci. A: Polym. Chem.* 43 (2005) 5217–5231.
- [12] R. Podsiadły, The synthesis of novel, visible-wavelength oxidizable polymerization sensitizers based on the 5,12-dihydroquinoxalino[2,3-b]pyridopyrazine skeleton, *Dyes Pigments* 80 (2009) 86–92.
- [13] J.V. Crivello, Benzophenothiazine and benzophenoxazine photosensitizers for triarylsulfonium salt cationic photoinitiators, *J. Polym. Sci. A: Polym. Chem.* 46 (2008) 3820–3829.
- [14] R. Podsiadły, Synthesis and photochemical reaction of novel, visible-wavelength oxidizable polymerization sensitizer based on the 12H-quinoxalino[2,3-b][1,4]benzothiazine skeleton, *J. Photochem. Photobiol. A: Chem.* 202 (2009) 115–121.
- [15] W.B. Leighton, G.S. Forbes, Precision actinometry with uranyl oxalate, *J. Am. Chem. Soc.* 52 (1930) 3139–3152.
- [16] N. Urasaki, S. Yoshida, T. Ogawa, K. Kozawa, T. Uchida, Oxidation potential and absorption spectra of phenothiazine derivatives. I. Benzophenothiazine and triphenodithiazine, *Bull. Chem. Soc. Jpn.* 67 (1994) 2024–2030.
- [17] D. Rehm, A. Weller, Kinetics of fluorescence quenching by electron and H-atom transfer, *Isr. J. Chem.* 8 (1970) 259–271.
- [18] I.I. Abu-Abdoun, A. Ledwith, Cationic polymerization photochemically and thermally induced by phenothiazine cation radical salts, *Eur. Polym. J.* 33 (1997) 1671–1679.
- [19] H. Kura, K. Fujihara, A. Kimura, T. Ohno, M. Matsumura, Y. Hirata, T. Okada, Initial step of anthracene-sensitized photoacid generation from diphenyliodonium hexafluorophosphate in an epoxy matrix studied by steady-state and laser-flash photolyses, *J. Polym. Sci. B: Polym. Phys.* 39 (2001) 2937–2946.