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N-substituted quinoxalinobenzothiazine/iodonium salt systems as visible photoinitiators for hybrid polymerization

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ABSTRACT

Sensitizers based on the 12-substituted 12*H*-quinoxalino-[2,3-*b*][1,4]-benzothiazine skeleton were synthesized and characterized using ¹H NMR spectroscopy, mass spectrometry and elemental analysis. Their electrochemical and spectral properties, including absorption and emission spectra, fluorescence quantum yield and singlet lifetime were also measured. These benzothiazines combine with commercially available diphenyliodonium hexafluorophosphate to create novel visible initiator systems of free radical/cationic hybrid polymerization of glycidyl methacrylate. The efficiency of these initiator systems is discussed on the basis of the free energy change for electron transfer from the benzothiazines to the iodonium compound. During the photopolymerization photobleaching of the benzothiazines was observed; a mechanism to account for this bleaching is proposed.

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1. Introduction

Photopolymerization is of great practical interest due to its applicability for curing coatings and printing inks and for resist technology [1,2]. Initially, photoinitiating systems that were sensitive to ultraviolet light were used. However, at present, systems in which polymerization is sensitive to visible light are used in conjunction with visible emitting light sources, such as lasers and LEDs. These systems are of particular interest because of their use in many special applications, such as dental filing materials, photoresists, printing plates, highly pigmented coatings, holographic recording and nanoscale micromechanics [3]. One way to create a system in which polymerization can be photoinduced by visible light is to use a dye. In such dye based photoinitiator systems, the initiating species are typically generated by a photoinduced electron transfer. These systems involve a second component, an appropriate co-initiator that participates in the electron transfer process. Many attempts have been made to develop such two

component systems [3–12]. Depending on the nature of the dye involved, two distinct sensitizations need to be considered: the electron transfer from the co-initiator to the excited, photoreducible dye [4-7] and the electron transfer from the excited, photo-oxidizable dye to the co-initiator (Scheme 1) [8-12]. Then the initiating radicals are formed from cleavage of the oxidized or reduced form of the co-initiator. In photo-reducible sensitization, the commonly used co-initiators are *N*-phenylglycine [4,5], phenylthioacetic acid [5–7], amine [8,10] and alkyltriphenylborate [11,12], whereas in photo-oxidizable sensitization, the commonly used co-initiators are N-alkoxypyridinium salts [13,14] and the derivatives of 2,4,6-tris(trichloromethyl)-1,3,5-triazine [15-17]. For example, in photo-reducible sensitization the sulfur centered radical zwitterions from phenylthioacetic acid decayed rapidly into •CH₂-S-C₆H₅ and CO₂. In photo-oxidizable sensitization singleelectron transfer to an N-alkoxypyridinium results in N–O bond cleavage and the formation of an alkoxy radical. These dye based photoinitiator systems have been mainly applied to initiate free radical polymerization.

The second important application of oxidizable sensitization is the cationic photopolymerization of epoxide monomers [18-21]. In this case the dyes have been combined with diphenyliodonium salts and photoinduced electron transfer forms several cationic





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Scheme 1. (a) Photo-reducible and (b) photo-oxidizable sensitization.

species (Scheme 2), which can also initiate the cationic polymerization: the radical cation (Dye^{Φ +}), formed after electron transfer to an onium salt, the strong protic acid formed from the reaction between the Dye^{Φ +} and solvent or monomer; and the carbocation of the monomer (M⁺), which is formed during the oxidation of the monomer radical (M^{Φ}) by the iodonium salt [22].

In recent years, cationic and free radical polymerizations have been combined to form hybrid polymerization systems. The combination of these polymerization methods has led to the preparation of unusual hybrid polymer structures such as multi-block [23], graft [24] and random [25] copolymers and interpenetrating polymer networks [26,27]. Nearly all of the reports of hybrid photopolymerization have used separate radical and cationic photoinitiators with one or two UV light sources. There are only two published reports that describe the application of two component visible initiator systems which were applied to initiate a dual curing. In these report, dye derivatives of quinoxaline [28] and 3,3'-carbonylbis(7-diethylaminocoumarin) [29] were combined with either triarylsulfonium [28] or diphenyliodonium [29] salts, respectively. The photoinduced electron transfer between dyes and onium salt gives an unstable onium radical, which rapidly decomposes to generate an aryl radical to induce radical polymerization. The dye radical cation, or the proton generated from it, induces cationic polymerization. The main goal of the current study is the synthesis of N-substituted benzothiazines (2–4), the evaluation of their spectroscopic, photophysical, electrochemical properties and their application in a hybrid polymerization as visible photoinitiators of glycidyl methacrylate (GMA) in the presence of diphenyliodonium hexafluorophosphate (Ph₂IPF₆). The structures of the studied quinoxalinobenzothiazines, iodonium salt and monomer are presented in Scheme 3.

2. Experimental

2.1. General

The hybrid monomer glycidyl methacrylate (GMA), diphenyliodonium hexafluorophosphate, and the necessary synthesis reagents were purchased from Sigma–Aldrich (Poznan, Poland). The starting compound 12H-quinoxalino-[2,3-b][1,4]-benzothiazine (1) was synthesized according to the procedure described in Ref. [30]. The dyes 2–4 were identified and characterized via ¹H NMR



Scheme 2. Formation of cationic species during photo-oxidizable sensitization.



2, X = Ph; 3, X = COPh, 4, X = Ac



spectroscopy [Bruker Avance DPX 250, CDCl₃, TMS standard, δ (ppm)]. Their purity was confirmed using TLC. The chemical ionization mass spectra were recorded on a Finnigan MAT 95 spectrometer with isobutane application. Electrochemical experiments were measured as described in Ref. [30]. The absorption and steady-state fluorescence spectra were recorded using a JASCO V-670 spectrophotometer (Jasco, Japan) and a Lumina fluorescence spectrometer (Thermo Scientific, USA), 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 using band-pass filters at 419 ± 10 nm, and illumination intensities were measured using uranyl oxalate actinometry [31].

2.2. Synthesis

2.2.1. Synthesis of 12-phenyl-12H-quinoxalino-[2,3-b][1,4]-benzothiazine (**2**)

12*H*-Quinoxalino-[2,3-*b*][1,4]-benzothiazine **1** (10 g, 0.04 mol), Na₂CO₃ (4.22 g, 0.04 mol) and some copper shavings were heated under reflux in iodobenzene (50 mL) until disappearance of **1**. The progress of the reaction was monitored by TLC [Merck Silica gel 60, solvent: 4:1 (v/v) toluene/ethyl acetate]. After 10 h unreacted iodobenzene was distilled off under reduced pressure. Absolute alcohol was then added, the mixture heated and filtered after dissolution of the product. The filtrate was cooled giving yellowish crystals of the product **2** (12.3 g, 94%), m.p. 202 °C, ¹H NMR (350 MHz, CDCl₃) δ = 6.10–6.14 (m, 1H), 6.84–6.89 (m, 2H), 7.02– 7.07 (m, 1H), 7.29–7.40 (m, 5H), 7.50–7.54 (m, 1H), 7.58–7.61 (m, 3H); MS (Cl): *m/z* 327.0 (M⁺), 328.0 (M + H⁺), 329.0 (M + 2H⁺); Elemental analysis: found C 73.5; H 3.8, N 12.9; S 9.7% C₂₀H₁₃N₃S required C 73.37; H 4.00; N 12.83; S 9.79%.

2.2.2. Synthesis of 12-benzoyl-12H-quinoxalino-[2,3-b][1,4]-benzothiazine (3) [32]

Benzoyl chloride (1.65 mL, 0.0096 mol) was added dropwise during 30 min to a stirred suspension of 12*H*-quinoxalino-[2,3-*b*] [1,4]-benzothiazine **1** (1 g, 0.004 mol) in dry pyridine (8 mL) at 35 °C. The mixture was further heated at 90 °C for 3 h. After cooling, the mixture was poured into 10% aqueous HCl (40 mL). The precipitate was filtered, washed with NaHCO₃ (10% aq., 25 mL) of, dried and recrystallized from ethanol. The product **3** (1.19 g) was obtained with an 84% yield. M.p. 200 °C (194 °C [32]); ¹H NMR (350 MHz, CDCl₃) δ = 7.06–7.26 (m, 4H), 7.31–7.39 (m, 3H), 7.44–7.61 (m, 4H), 7.85–7.89 (m, 1H), 8.10–8.14 (dd, *J* = 1.36, 1H); MS (Cl): *m*/*z* 356.1 (M + H⁺); Elemental analysis: found C 71.1; H 3.6, N 11.7; O 4.6; S 9.0% C₂₁H₁₃N₃OS required C 70.97; H 3.69; N 11.82; O 4.50; S 9.02%.

2.2.3. Synthesis of 12-acethyl-12H-quinoxalino-[2,3-b][1,4]-benzothiazine (**4**)

The synthesis was conducted using the modified procedure [32]. 12*H*-Quinoxalino-[2,3-*b*][1,4]-benzothiazine **1** (1 g, 0.004 mol) and sodium acetate (5.5 g, 0.067 mol) were heated under reflux in acetic anhydride (100 mL). The reaction was monitored by TLC [Merck



Scheme 4. i) lodobenzene, Cu, reflux; ii) benzoyl chloride, pyridine; iii) acetic anhydride, reflux.

Silica gel 60, solvent: 7:3 (v/v) benzene/acetone]. After disappearance of **1** the precipitate was filtered and dissolved in hot acetone. The sodium acetate was filtered and the acetone was evaporated in vacuum. The product **4** (0.80 g) was obtained with a 68% yield. M.p. 195–196 °C (196 [32]); ¹H NMR (350 MHz, CDCl₃) $\delta = 2.43$ (s, 3H), 7.29–7.37 (m, 1H), 7.41–7.54 (m, 2H), 7.74–7.90 (m, 3H), 8.02–8.13 (m, 2H); MS (CI): *m*/z 294.0 (M + H⁺); Elemental analysis: found C 65.7; H 3.7, N 14.2; O 5.5; S 10.8% C₁₆H₁₁N₃OS C, 65.51; H, 3.78; N, 14.32; O, 5.45; S, 10.93%.

2.3. Photochemical experiments

The fluorescence quantum yield of the dye (Φ_{DYE}) was calculated from the following equation:

$$\Phi_{\rm DYE} = \Phi_{\rm ST} \frac{G_{\rm DYE} \cdot \eta_{\rm DYE}^2}{G_{\rm ST} \cdot \eta_{\rm ST}^2} \tag{1}$$

where the subscripts ST and DYE denote standard and test respectively, Φ is the fluorescence quantum yield, *G* is the gradient from the plot of integrated fluorescence intensity versus absorbance, and η is the refractive index of the solvent. Rhodamine 101 in ethanol was used as the standard ($\Phi_{\text{ST}} = 1.0$ [33]).

Time-resolved fluorescence was measured using a timecorrelated single photon counting system, Edinburgh Analytical Instruments FL 900CDT. Fluorescence lifetimes were calculated from intensity decay analysis with goodness of fit judged in terms of residual distributions using software supplied by Edinburgh Instruments.

Singlet quenching constants were obtained from fluorescence quenching experiments, and the fluorescence spectra of the solutions of the dyes (6–10 μ M) in ethanol, which contained various amounts of Ph₂IPF₆, were measured at room temperature in the air by excitation at λ_{max} . The relative fluorescence intensities (*I*₀/*I*) were determined by measuring the heights of the peaks at λ_{em} .

In photopolymerization studies the concentrations of the benzothiazine and iodonium salt were 1 mM and 85 mM, respectively. The mixture for photopolymerization was deposited onto transparent polypropylene film at a thickness of 30 μ m using polypropylene film as a spacer. Another 30 μ m thick polypropylene film was laminated onto top of the sample. The photosensitized hybrid polymerization of the GMA was monitored using Fourier transform real-time infrared spectroscopy (FT-RTIR). Photocured samples were analyzed with an IR Nicolet (Thermo Scientific, USA) spectrophotometer with a resolution of 4 cm⁻¹ in the absorbance mode. All photopolymerizations were conducted using 419 nm light (2 \times 10¹⁵ quant s⁻¹). Epoxide group and methacrylic bond conversions were determined by monitoring the peak area at 909 cm⁻¹ and 1637 cm⁻¹, respectively. From the FTIR spectra, the conversion of each functional group was calculated using the following equation:

$$Conversion = 1 - \frac{A_{X,t}}{A_{X,0}} \cdot \frac{A_{ST,0}}{A_{ST,t}}$$
(2)

where A_0 and A_t are the initial peak area of functional group and at a given irradiation time. The subscripts ST and X denote the internal reference ester carbonyl peak area at 1730 cm⁻¹ and functional group, respectively. The kinetic parameter, R_p/M_0 , was determined from the initial slopes of the irradiation time—conversion curves according to Eq. (3):

$$R_p/M_0 = \left([\text{conversion}]_{t_2} - [\text{conversion}]_{t_1} \right) / (t_2 - t_1)$$
(3)

where R_p and M_0 are the rate of polymerization and the initial monomer concentration, respectively. The conversions are determined from the curves at irradiation time t_1 and t_2 .

2.4. Coating formulation, curing procedure and film property test

The GMA were poured onto a glass plate to form a layer ca. 3 mm thick, and then the samples were exposed to visible radiation for a given time. The concentration of dye and Ph_2IPF_6 was 0.33 mM and 28 mM, respectively. The photopolymerizations were conducted in air using 419 nm light with an intensity of 3.2×10^{17} quant s⁻¹. Pencil hardness was conducted to evaluate the surface and curing properties of the cured films according to the standard ASTM methods D3363-74. The gel content was determined on the cured films by measuring the weight loss after 24 h extraction in 2-butanone at room temperature according to the standard test method ASTM D2765-84. Shore durometer HPE II (Bareiss Prüfgerätebau GmbH) was employed to measure the hardness of GMA cured film. Five measurements were made in each sample, and the results presented are an average of these measurements.

The DSC experiments were carried out using a Mettler Toledo Stare TGA/DSC1 (Leicester, UK) unit, under nitrogen. Samples (ca. 5 mg) were placed in aluminum pans and were cooled down to -150 °C and then heated to 250 °C at constant heating rate of 10 °C min⁻¹.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization of benzothiazines

The basis of the design of these novel oxidizable initiator systems were literature reports that concerned the oxidation of N-substituted phenothiazines to the stable radical cations [34-36] and the ability of these radical cations to initiate the cationic polymerization [37]. Due to continuing interest in the applications of oxidizable sensitizers in photopolymerization, the compounds based on the N-substituted 12*H*-quinoxalino-[2,3-b][1,4]-benzo-thiazine (2-4) were synthesized according to stage shown in



Fig. 1. Normalized absorption (black) and emission (gray) spectra of dye 2 (12 μ M, A) and dye 4 (10 μ M, B) in MeCN.

Scheme 4. Our route to dyes **2** starts with **1**, which react with iodobenzene to give the corresponding derivatives of 12-phenyl-12*H*-quinoxalino-[2,3-*b*][1,4]-benzothiazine (**2**) in 94% yield. Compounds **3** and **4** are obtained by reaction of appropriate benzothiazine (**1**) with benzoyl chloride or acetic anhydride, respectively.

The crude dyes were purified by recrystallization from ethanol or acetone until a constant molar extinction coefficient and TLC purity were obtained. Dyes **2–4** were synthesized in excellent yield (68–94%), and their chemical structures were verified by ¹H NMR spectroscopy, mass spectrometry and elemental analysis.

The electronic absorption (UV–VIS) and emission spectra of benzothiazines **2** and **4** are presented in Fig. 1. For all studied compounds, the absorption and the fluorescence spectra were nearly mirror images of each other with overlapping bands corresponding to the $0 \rightarrow 0$ transition.

The spectroscopic properties (absorption and fluorescence) of compounds **2**–**4** are presented in Table 1. It is evident that the position of the absorption band depended on the character of a compound's X group. In comparison with 12*H*-quinoxalino-[2,3-*b*][1,4]-benzothiazine (**1**) [30], the presence of phenyl in **2** caused a small blue shift of the longest wavelengths absorption band.

Table 2

Oxidation potential (V) of benzothiazines, thermodynamic data (kJ mol⁻¹), Stern–Volmer (M^{-1}) and singlet quenching ($M^{-1} s^{-1}$) constants for benzothiazines/Ph₂IPF₆ photoredox pair.

Dye	$E_{\rm ox}^{a}$	$\Delta G_{\rm et}$	K _{sv}	$k_{ m q} imes 10^{10}$
2	1.44	-103.3	132.9	2.91
3	1.62	-108.4	-	-
4	1.71	-99.6	20.4	0.79

^a In DMF versus SCE.

A larger hypsochromic effect was observed for **3** and **4**. In these compounds, the absorption bands were located at approximately 370 nm.

The fluorescence quantum yields ($\Phi_{\rm fl}$) of benzothiazines are presented in Table 1. As can be seen from these data, the $\Phi_{\rm fl}$ of these compounds range from 0.02 to 1.0 with dyes **2** having the highest values of $\Phi_{\rm fl}$.

3.2. Sensitized hybrid photopolymerization

The studied benzothiazines **2-4** were synthesized in order to obtain the sensitizers which are able to work via an electron transfer process. To predict the potential applicability of these compounds as electron sensitizers, the free energy change of the electron transfer (ΔG_{et}) between the oxidizing agent (Ph₂IPF₆) and benzothiazines must be known. The electron transfer from these excited benzothiazines to the iodonium salt is thermodynamically favorable if the free energy (ΔG_{et}), calculated from the Rehm–Weller equation (Eq. (4)) [38] is negative.

$$\Delta G_{\text{et}}\left(\text{kJ mol}^{-1}\right) = 97\left[E_{\text{ox}}\left(D/D^{\bullet+}\right) - E_{\text{red}}\left(A^{\bullet-}/A\right)\right] - E^{00}(D)$$
$$-Z_1Z_2/\varepsilon r_{12}(4)$$

In this equation, $E_{\text{ox}} (D/D^{\bullet+})$ and $E^{00}(D)$ are the oxidation potential of the electron donor (benzothiazines) and the singlet excited state energy of the electron donor, respectively. $E_{\text{red}} (A^{\bullet-}/A)$ is the reduction potential of Ph₂IPF₆. The last term represents the Coulombic energy necessary to form an ion pair with charges Z_1 and Z_2 in a medium of dielectric constant ε for a distance r_{12} . The Coulombic energy coefficient $(Z_1Z_2/\varepsilon r_{12})$ was omitted in these calculations because a neutral radical of the onium compound was formed (Z = 0) in the electron transfer process.

In order to be able to calculate ΔG_{et} , the oxidation potentials of the benzothiazines **2–4** were measured in separate experiments. The obtained results (Table 2) indicate that the location of the oxidation peak depends on the structure of the benzothiazines. *N*-phenyl substituted benzothiazines **2** are more readily oxidized in comparison with the *N*-benzoylated **3** and *N*-acetylated analog **4**.

Once the E_{ox} of benzothiazines had been measured, the ΔG_{et} could be calculated using equation (4). The calculated thermodynamic parameters listed in Table 3 indicated that all the tested benzothiazines/Ph₂IPF₆ systems posses a favorable thermodynamic driving

Table 1Spectroscopic and photophysical parameters of the compounds 1–4.

Dye	λ_{max}^{a}	ε^{a}	λ_{max}^{b}	$\varepsilon^{\rm b}$	λ_{fl}^{b}	$\Phi_{\mathrm{fl}}{}^{\mathrm{b}}$	SS	$\tau^{\mathbf{b}}$	E ^{OOb}
	[nm]	$[dm^3 mol^{-1} cm^{-1}]$	[nm]	$[dm^3 mol^{-1} cm^{-1}]$	[nm]		[nm]	[ns]	$[kJ mol^{-1}]$
1	425	7400	416		530 ^c	0.22	109	4.6 ^c	253.5°
2	416	9400	413	8200	500	1.0	87	4.57	262.4
3	373	9200	370	9800	499	0.02	129	4.33	284.9
4	371	9800	367	9750	497	0.45	130	2.56	284.9

^a In 1-methyl-2-pyrrolidone.

^b In CH₃CN.

^c In EtOH from Ref. [30].

force upon exposure to light ($-\Delta G_{et} > 99 \text{ kJ mol}^{-1}$). Moreover, the fluorescence of benzothiazines **2** and **4** were effectively quenched by diphenyliodonium salt. The example of the fluorescence spectra of dye **2** recorded in EtOH containing various amounts of Ph₂IPF₆ are presented in 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. (5) using the fluorescence lifetime of the benzothiazines (τ_0) without any quencher (Table 1).

$$I_0/I = 1 + k_q \tau_0[\text{On}]$$
 (5)

The calculated singlet quenching constants (k_q) are summarized in Table 2. These values are close to the diffusion-controlled limit $(k_q \sim 1 \times 10^9 - 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1})$. Dye **2** has the highest value of k_q , which also has the lowest oxidation potential. This suggests that fluorescent quenching proceeds via electron transfer.

Finally, the benzothiazine/Ph₂IPF₆ two component systems were examined for their usefulness as photoinitiators in the free radical/cationic hybrid photopolymerization of GMA, which contains a methacrylate double bond and an epoxide ring. From a practical point of view, the most important property of the initiator system is the ability to initiate the photopolymerization of monomers in the presence of air. Therefore, in our investigation, the efficiency of the polymerization initiated by the studied photoredox systems was measured in an air equilibrium composition. FTIR spectroscopy was used to measure the conversion of methacrylate double bonds and epoxide groups as a function of irradiation time. Conversions were determined by monitoring the peak area at characteristic wavenumber (909 cm^{-1} for the epoxide group [39] and 1637 cm⁻¹ for methacrylate bonds [39]) and calculating the ratio of this area relative to that of the ester carbonyl peak at 1720 cm⁻¹. Fig. 3 shows an example of an FTIR spectra recorded before and after irradiation of the GMA initiated by a $2/Ph_2IPF_6$ photoredox pair. The reduction in the absorption of the characteristic peak on visible irradiation shows that both epoxy groups as well as the double bonds underwent polymerization. Moreover, the increase of the absorption at 3450–3550 cm⁻¹ attributable to OH stretching also confirms that the epoxy rings of GMA underwent ring-opening polymerization. The kinetic parameters R_p/M_0 were determined from the slopes of the initial portion of the conversion of the epoxide ring and methacrylate double bonds versus time curves (Fig. 4) and are presented in Table 3.



Fig. 2. Fluorescence quenching of dye 2 by Ph_2IPF_6 in EtOH. Inset: Stern–Volmer plot of fluorescence quenching of dye 2 (10 μ M) by Ph_2IPF_6 in EtOH.



Fig. 3. IR absorption spectra of GMA recorded before (black) and after (red) 6000 s of the irradiation in the presence of $2/Ph_2IPF_6$. Characteristic peaks in IR spectrum of GMA: internal reference band at 1720 cm⁻¹, epoxide ring at 909 cm⁻¹ and C=C double bond at 1637 cm⁻¹. Inset: IR absorption region of OH stretching. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

From the foregoing data, it is evident that systems composed with benzothiazines 2-4 and diphenyliodonium hexafluorophosphate are able to simultaneously initiate cationic and radical polymerization. In all of the photosystems studied here, a higher conversion of methacrylate double bond compared to conversion of the epoxide ring was observed. Similar effect was observed in hybrid photopolymerization of 3,4-epoxycyclohexylmethyl methacrylate initiated by 2,2-dimethoxy-2-phenylacetophenone (radical initiator) and diaryliodonium hexafluoroantimonate (cationic initiators) [40]. These low conversions of epoxide can be explained by difference in reactivity of double bond and epoxide ring. The epoxide group react more slowly than double bonds. Moreover, the mobility of the cationic reactive centers was restricted due to vitrification resulting from the conversion of C=C double bonds [40].

The effectiveness of the studied two component systems depends on the applied benzothiazines. The compounds **2** significantly accelerated the polymerization of GMA compared to dyes **3** and **4**. However, it is evident that the hybrid polymerization initiated by the **3**/Ph₂IPF₆ photoredox pairs showed a significant inhibition time (Fig. 4 and Table 3). Among the studied benzothiazines, the 12-benzoyl analog has the lowest quantum yield of fluorescence (see Table 1). It is possible that the electron transfer between this compound and the iodonium salt occurs via the triplet state. Therefore, the molecular oxygen dissolved in the composition quenched the triplet state of the benzothiazine **3**. After consumption of the oxygen, the initiating species are formed via electron transfer.

In the photopolymerization initiated by a dye photoredox pair, the most important properties are high initiation reactivity and photobleaching of the dye. The photobleaching of benzothiazines **2**–**4** was measured in GMA in the presence of air. An example of the absorption spectra of the combination of dye **2** and Ph₂IPF₆ before and during irradiation in GMA are shown in Fig. 5. The same photochemical behaviour was observed for benzothiazines **3** and **4**. Decay of the dye absorption at 415 nm is accompanied by the growth of the band at 370 nm. It is well known that phenothiazine derivatives are easily oxidized to yield stable radical cations [37]. A low nucleophilic anion, such as BF₄ or PF₆, stabilized the phenothiazine radical cation. It is also known, that the phenothiazine radical cation undergoes one electron oxidation by the iodonium compound to form the phenothiazine dication, which absorbs in the UV region



Fig. 4. Conversion of acrylate (B) and epoxy (A) groups during photopolymerization of GMA initiated by Ph_2IPF_6 and **2** (\bullet), **3** (\Box) or **4** (\blacksquare).

[41,42]. Therefore, it is possible that during photolysis in GMA, the studied N-substituted benzothiazines may work as two electron transfer sensitizers. First, they are oxidized by Ph₂IPF₆ to radical cations, which are then oxidized to a dication (Scheme 5). A similar mechanism of oxidation was proposed for photobleaching of benzothiazine 1 [41].

The calculated photobleaching quantum yields are presented in Table 4. These data clearly indicate that in these oxidizable sensitization systems the oxidation potential of benzothiazines determine the photoreactivity of these compounds. Among the studied benzothiazines, dye 2 shows the highest photobleaching quantum yield and this compound is the most promising photosensitizer for VIS dual curing.

In industry, both the physical properties of coatings and stability of the formulation must be tailored to the ultimate application. Therefore, the polymerizations of GMA were carried out for freshly prepared formulation and after 7 days of storage. The comparison of epoxy group and double bond conversion these two formulation are presented in Table 4. It is evident from these data that the initiator systems composed with 12-substituted 12H-quinoxalino-[2,3-b][1,4]-benzothiazine dye and Ph₂IPF₆ leads to a slow degradation and should be prepared just before application.

Table 3

Conversion (%) of epoxy group and methacrylate bond of GMA, and photobleaching quantum yield (mmol quant⁻¹) of compounds **2**–**4**.

	Ероху			Methaci		$\Phi_{\rm bl}$	
	t _{inh}	Conv	R_p/M_0	t _{inh}	Conv	R_p/M_0	
2	0	39	1.37	0	50	1.82	9.3
3	1200	19	0.30	1800	25	0.47	4.5
4	0	34	1.94	0	39	1.94	2.8

Table 4

Conversion (%) of epoxy group and methacrylate bond of GMA obtained for photopolymerization of freshly prepared or stored formulation and properties of the VIS-cured films obtained in the presence of the presented photoredox pairs.^b

Dye	Ероху		Methacrylate		Gel	T_g , ^c DSC	Hardness	Pencil
	Conv ^a	Conv ^b	Conv ^a	Conv ^b	content ^c (%)	(°C)	shore D ^c	hardness
2	45	28	80	70	96.0	61	86	5H
3	30	20	60	53	94.6	56	82	8B
4	20	15	76	69	95.4	58	84	Н

Freshly prepared formulation; light intensity 1.6×10^{17} quant s⁻¹. b

Formulation stored by seven days; light intensity 1.6×10^{17} quant s⁻¹. Irradiated for 15 min with light intensity 3.2×10^{17} quant s⁻¹; properties were measured after 72 h.

To analyze the properties of the photocured film, the GMA were photopolymerized in a photochemical reactor with a higher radiation intensity $(3.2 \times 10^{17} \text{ quant s}^{-1})$ for 15 min. All coatings were stored in the dark for 72 h to ensure that no additional photochemical reactions occur in formulation. The resulting film was $300 \,\mu\text{m}$ thick with a gel content above 94% (Table 4) indicating the formation of a highly crosslinked network.

The thermal characterization of the films obtained upon the photopolymerization of GMA using dye/iodonium photoredox pair is reported in Table 4. The thermogram of this film shows one glass transition temperature around 58 °C. All coatings were tested by both pencil hardness and Shore hardness. Pencil hardness is a generally accepted method to measure the resistance of a coating (also known as its pencil hardness). It is determined as the hardest pencil grade that does not mark the coating when pressed firmly against it at a 45° angle.

The results of these tests are presented in Table 4. The mechanical properties of the cured GMA were found to depend on the dye that was employed as the sensitizer. The coating with the best properties was obtained with aid of sensitizers 2. This dye demonstrates a highest $\Phi_{\rm fl}$. Therefore one can conclude and at a depth of 1 μ m, where O₂ can quench the radical and sensitizers' triplet state, electron transfer reaction between iodonium salt and dye 2 may occur via a singlet state. This is particularly apparent on the top layer of the coatings. The lowest pencil hardness has coating obtained with aid of dyes **3** which have the lowest $\Phi_{\rm fl}$. While the top layer of the film was polymerized via cationic mechanism the diffusion of molecular oxygen was inhibited. Therefore, at deeper layers, the radicals initiate the polymerization of GMA. The overall



Fig. 5. Electronic absorption spectra obtained upon photolysis of the dye 2 (66.7 μ M)/ Ph₂IPF₆ (5.67 mM) system in GMA under air atmosphere. Arrows indicate changes in the spectra during irradiation.



Scheme 5. Photobleaching of studied benzothiazines.

hardness of the coatings, measured as Shore hardness, is a result of these two polymerizations.

4. Conclusions

12-substituted 12*H*-quinoxalino-[2,3-*b*][1,4]-benzothiazines were successfully synthesized and characterized using ¹H NMR spectroscopy, CI mass spectrometry and elemental analysis. These compounds, when combined with diphenyliodonium hexa-fluorophosphate, may be applied as electron transfer photosensitizers. These two component systems were employed as initiators for visible-light initiated free radical and cationic photo-polymerization of an acrylate/epoxide hybrid system. The FT-IR data revealed that these photoredox pairs are able to simulta-neously initiate both cationic and radical polymerization in the presence of air. The kinetic data and photobleaching quantum yield indicated, that when combined with iodonium salts, benzothiazine **2** may have practical applications as a visible-light hybrid initiator.

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