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Novel visible photoinitiators systems for free-radical/cationic hybrid photopolymerization

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Free radical/cationic hybrid photopolymerization of acrylates and epoxides was induced using an initiator system comprised of the dye derivative 5,12-dihydroquinoxalino[2,3-b]quinoxaline or 5,12-dihydroquinoxalino[2,3-b]pyridopyrazine as the sensitizers and hexafluoroantimonate triarylsulfonium salt as the initiators. The curing experiments were carried out in the presence of air and the consumption of each monomer upon VIS-radiation was monitored in situ by real-time infrared spectroscopy. Hardness (*H*), elastic modulus (*E*) and the *H*/*E* ratio of the coatings obtained by visible-initiated acrylate/epoxide hybrid photopolymerization were determined using nanoindentation. DSC measurements show that the initiator system presented here may produce an interpenetrating polymer network. The pencil hardness of the obtained coatings indicates that the dye/hexafluoroantimonate triarylsulfonium salts systems studied here may have practical applications as visible-light hybrid initiators.

1. Introduction

Hybrid polymers, which are formed from a combination of co-monomers with different reactive groups and curing mechanisms, can be considered as special class of polymer blends. The properties of the two constituent homopolymers often combine synergistically in the hybrid polymer. For example, the combination of free radical and cationic polymerization methods has led to the preparation of unusual hybrid polymer structures such as multi-block [1,2], graft [3,4] and random [5,6] copolymers and interpenetrating polymer networks (IPNs) [7,8].

Nearly all of the reports of hybrid photopolymerization have used separate radical and cationic photoinitiators with one or two UV light sources. A variety of radical initiators have been used including 2,2-dimethoxy-2-phenylacetophenone [2,9,14,16], 1,2-diphenylethanedione [9], hydroxyphenyl-ketone [7,10,11], bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide [12], and benzoin [2], whereas sulfonium [2,9,16], iodonium [2,7,10,11,12,16] and pyridinium [2] salts have been employed as cationic initiators. UV curing was then performed on these hybrid initiator systems that contained bifunctional crosslinkable monomers glycidyl meth/acrylate [9], methacrylate–silicone–epoxycyclohexanepoxide [13], 3,4-epoxycyclohexylmethyl methacrylate [14], 3-(1-propenyl-oxypropyl) acrylate [17] or mixtures of certain acrylates and either epoxides [2,7,10], vinyl ethers [1,6,12], or oxetanes [2,16].

The most significant photoinitiators of the past decade have been compounds with more efficient absorbance at long wavelengths. Absorbance at lower energies 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. Secondly, 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.

There are only two published reports describing the application of visible light to initiate a hybrid photopolymerization. In the first one, Oxman reported a tri-component initiator system containing camphorquinone as a photosensitizer, with electron donors (typically an amine) and iodonium or sulfonium salts [15]. These systems generate two initiating free radicals and one initiating cation by a series of electron–proton transfer reactions (Scheme 1). The crucial species in these system are the amines, which have a low oxidation potential (<1.34 V vs. SCE) and a pK_b above 8. Highly basic amines are proton scavengers, which may cause the inhibition effect during cationic polymerization of epoxide monomers.

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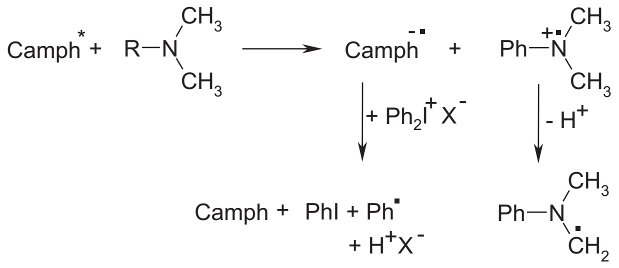


Scheme 1. Tri-component initiator system – camphorquinone, amine, onium salt.

In the second report [18], the photoinduced electron transfer between 3,3′-carbonylbis(7-diethylaminocoumarin) and diphenyliodonium hexafluorophosphate gives an unstable diaryliodine radical, which rapidly decomposes to generate an aryl radical to induce radical polymerization. The coumarin cation radical, or the proton generated from it, induces cationic polymerization (Scheme 2).

Therefore, the main goal of this study was the application of a novel two component initiator system for dual curing under visible irradiation. These systems contain the dye derivatives 5,12-dihydroquinoxalino[2,3-b]quinoxaline (**1a**–**1c**) or 5,12-dihydroquinoxalino[2,3-b]pyridopyrazine (**2a**–**2c**) as sensitizers and the commercially available triarylsulfonium salt **3** as the initiator. The structure of the dyes and sulfonium salts are presented in Scheme 3 and 4, respectively. These photoredox pairs were applied to initiate hybrid polymerization of a mixture of trimethylolpropane triacrylate (TMPTA) and 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexanecarboxylate (CADE). Fourier transform real-time infrared spectroscopy (FT-RTIR) was used to obtain kinetic data of the conversion of acrylates and epoxides. Moreover, in this report the influence of the sensitizers on the surface properties of the coatings obtained via hybrid photopolymerization of the film TMPTA/CADE were measured.

2. Experimental

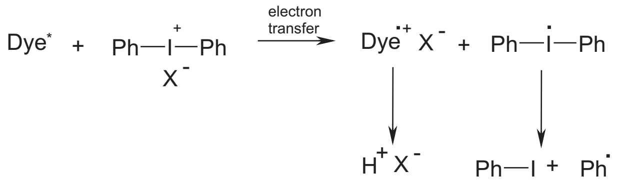
2.1. Materials

The procedure for preparing the dyes has been described elsewhere [19,20]. Mixed salts of triarylsulfonium hexafluoroantimonate (**3**), trimethylolpropane triacrylate (TMPTA), 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexanecarboxylate (CADE) and chloroform were purchased from Aldrich (Poznan, Poland).

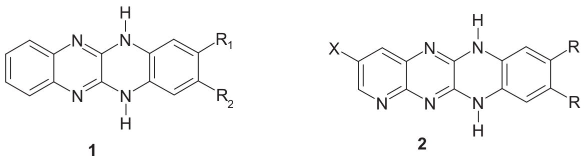
2.2. Photochemical experiments

All photochemical experiments were carried out in a Rayonet Reactor RPR 200 (The Southern New England Ultraviolet Co) 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 [21].

The photosensitized hybrid polymerization of the mixture of CADE and TMPTA (3:2 v/v) was monitored using Fourier transform real-time infrared spectroscopy (FT-RTIR). Photocured samples were analyzed with a Bio-RAD FTS 175C spectrophotometer with a resolution of 4 cm^{-1} in the absorbance mode. An attenuated total reflection (ATR) accessory with a germanium crystal was used to determine the FT-IR spectra. All photopolymerizations were conducted under air conditions using 419 nm light (2×10^{15} quant s^{-1}). The concentrations of dye and sulfonium salt were 0.2 mM and 20.0 mM, respectively.



Scheme 2. Two-component initiator system – coumarine dye and iodonium salt.



1

Dye	R_1	R_2
1a	H	H
1b	Br	H
1c	Cl	H

2

Dye	R	X
2a	H	Br
2b	CH_3	Br
2c	CH_3	Cl

Scheme 3. Structure of the studied dyes.

The conversion of each functional group was calculated by taking the ratio of the functional group absorbance at a given time (A_t) to the initial absorbance (A_0):

$$\text{Conversion } (\%) = 1 - A_t/A_0 \tag{1}$$

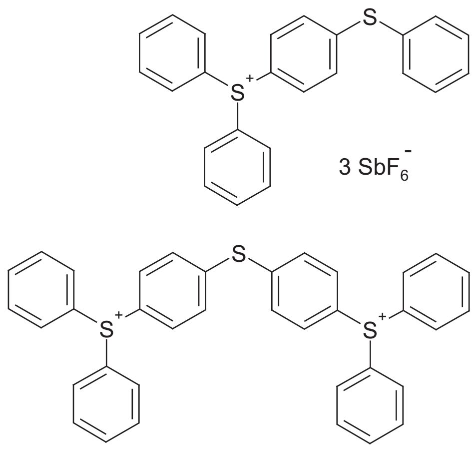
The kinetic parameter, R_p/M_0, was determined from the initial slopes of the irradiation time-conversion curves according to Eq. (2):

$$R_p/M_0 = ([\text{conversion}]_{t2} - [\text{conversion}]_{t1})/(t_2 - t_1) \tag{2}$$

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.

2.3. Coating formulation, curing procedure and film property test

The mixture of CADE and TMPTA (3:2 v/v) were poured onto a glass plate to form a layer ca. 0.3 mm thick, and then the samples were exposed to visible radiation for a given time. The concentration



Scheme 4. Mixed salts of triarylsulfonium hexafluoroantimonate.

Table 1
Spectroscopic, electrochemical and thermodynamic properties of the photoredox pairs.

Dye	λ_{max} [a] nm	E^{00} [b] kJ mol^{-1}	E_{ox} [c] V	Φ $^1O_2$ [b]	ΔG_{et} kJ mol^{-1} **3** ($E_{red} = -1.00$ V $\lambda_{max} = 276$ nm [d])
1a	416	267	0.21	0.08	−149.6
1b	418	264	0.24	0.65	−143.7
1c	414	266	0.25	0.25	−144.7
2a	408	273	0.47	0.50	−124.9
2b	413	271	0.41	0.31	−129.8
2c	413	273	0.34	0.19	−138.5

[a] in TMPTA.
[b] in 1-methyl-2-pyrrolidone from Refs. [19,20].
[c] in DMF from Refs. [19,20].
[d] in CH_2Cl_2.

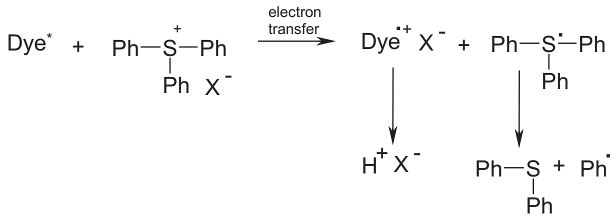
of dye and sulfonium salt was 0.2 mM and 20 mM, respectively. The photopolymerizations were conducted in air using 419 nm light with an intensity of 3.2×10^{17} quant s^{-1}. Pencil hardness was conducted to evaluate the surface and curing properties of the cured films according to the standard ASTM methods D3363–74. The gel content was determined on the cured films by measuring the weight loss after 24 h extraction in chloroform at room temperature according to the standard test method ASTM D2765–84. The mechanical properties of the films were characterized using NanoTest 600 with a Berkovich indenter tip. Five indentations were made in each sample, and the results presented are an average of these indentations.

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

In contrast to UV initiated hybrid polymerization, there are only a few initiator systems [15,18] that are able to initiate this photopolymerization under visible irradiation. Therefore, we designed a novel two component initiator system. These photosystems were composed of dyes **1**–**2** and triarylsulfonium salts **3**. The spectroscopic, photophysical and electrochemical properties of the dyes and sulfonium salt are presented in Table 1.

These 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 sulfonium salts [22] is presented in Scheme 5. Irradiation of the dye/sulfonium photoredox pair leads to electron transfer from the excited sensitizer (Dye*) to the sulfonium salt ($Ph_2S{-}Ph^+$). The resulting sulfonium salt radical ($Ph_2S{-}Ph^\bullet$) is then cleaved as depicted in Scheme 5. The rapid decomposition of the sulfonium salt radical retards any reverse electron transfer and renders the overall process irreversible. The phenyl radical Ph• may initiate free radical polymerization reactions, such as the polymerization of acrylate, while the radical cation Dye•$^+$ may initiate the cationic polymerization of appropriate monomers. Alternatively, the radical cation may interact with solvents or monomers resulting in the release of strong protic acid, which similarly initiates cationic polymerization.



Scheme 5. Dye-sensitized photodecomposition of sulfonium salts.

In such photoredox initiator systems, the Gibbs free energy change (ΔG_{et}) must be negative to facilitate the intermolecular photoinduced electron transfer from the excited dyes **1**–**2** to the sulfonium salt. In our study, values for ΔG_{et} were calculated from the Rehm–Weller equation (Eq. (3)) [23]:

$$\Delta G_{et}\left(\text{kJ mol}^{-1}\right) = 97\left[E_{OX}(S/S^{\bullet+}) - E_{red}(A^{\bullet-}/A)\right] - E^{00}(S) - Z_1Z_2/\varepsilon r_{12} \quad (3)$$

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 1. 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}. Because the neutral radical of the sulfonium compound is formed ($Z = 0$) in the electron transfer process this last term is negligible. E_{red} ($A^{\bullet-}/A$) is the reduction potential of the triarylsulfonium salts, which are presented in Table 1.

The calculated thermodynamic parameters listed in Table 1 indicate that all combinations of the dye/sulfonium salt systems studied here possess a high driving force ($-\Delta G_{et} > 120$ kJ mol^{-1}) upon exposure to light. This means that their photoelectron transfer process easily occurs through the excited state. It can be assumed then based on this calculation that the photodecomposition of the sulfonium salt caused by the dyes is initiated by a photoinduced intermolecular electron transfer from the dyes to the sulfonium compound.

These two component systems were examined for their usefulness as photoinitiators in the free-radical/cationic hybrid photopolymerization of a mixture of multifunctional monomers TMPTA and CADE. Fourier transform infrared spectroscopy was employed to monitor the kinetics of functional group disappearance in TMPTA and CADE. The polymerization kinetics were measured as percent loss of acrylate $CH{=}CH_2$ double bonds at 810 cm^{-1} [24] and epoxycyclohexyl groups at 748 cm^{-1} [25]. Fig. 1 shows an example of a conversion of the reactive groups during

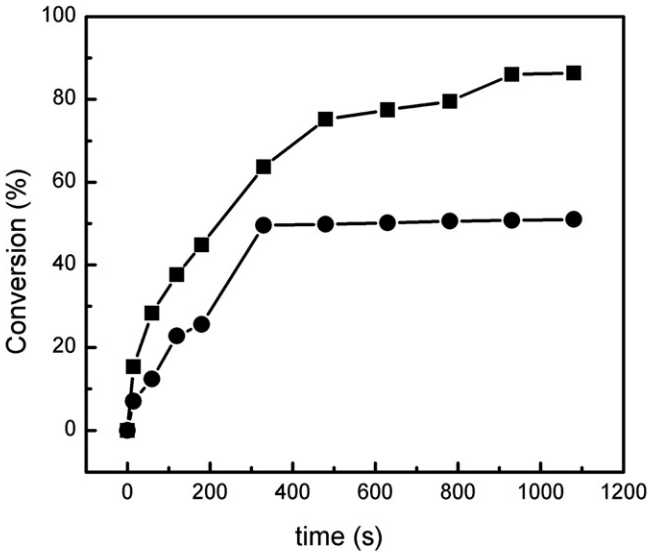


Fig. 1. Conversion of acrylate (circle) and epoxy (square) groups during photopolymerization initiated by **2b/3** photoredox pairs.

Table 2
Conversion (%) of monomers and FT-IR kinetic data (R_p/M_0).

Dye	Epoxy		Acrylate	
	R_p/M_0 s^{-1}	Conv %	R_p/M_0 s^{-1}	Conv %
1a	0.65	64	0.006	31
1b	1.42	80	0.057	55
1c	0.85	78	0.042	52
2a	0.43	86	0.19	51
2b	0.30	67	0.17	42
2c	0.22	49	0.11	34

photolysis of the TMPTA/CADE mixture. In this study, dyes **1**–**2** were used as photosensitizers and sulfonium salts were used as the initiator. As shown in Fig. 1 after photolysis, the conversion of the bands at 748 cm^{-1} and 810 cm^{-1} increase with time. The kinetic parameters R_p/M_0 were determined from the slopes of the initial portion of the conversion of the epoxide ring and acrylate double bond versus time curves and are presented in Table 2.

It is evident that photoredox pairs presented here composed of a dye and hexafluoroantimonate triarylsulfonium salts are able to simultaneously initiate cationic and radical polymerization. In all of the photosystems studied here, a higher conversion of epoxide ring compared to conversion of double bond was observed.

Among the studied dyes, the compounds **1b** and **2a** significantly accelerated the photopolymerization of triacrylate and epoxide monomers compared to dyes **1a** and **2c**. Dyes **1b** and **2a** also demonstrated higher quantum yields of singlet oxygen generation (Table 1) than dyes **1a** and **2c**. Thus, it is possible that electron transfer between these dyes and the triarylsulfonium salt occur via both singlet and triplet state. In air, the singlet state of the dye is involved in electron transfer, whereas electron transfer may occur via triplet state in an oxygen free atmosphere.

In industry, the physical properties of films and coatings must be tailored to the ultimate application. To analyze the properties of the photocured film, the mixture of TMPTA and CADE were photopolymerized in a photochemical reactor with a higher radiation intensity (3.2×10^{17} 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 μm thick with a gel content above 92% (Table 3) indicating the formation of a highly crosslinked network.

The thermal characterization of the films obtained upon the photopolymerization of the TMPTA/CADE mixture using dye/sulfonium photoredox pair is reported in Table 3. The thermogram of this film shows two glass transition temperatures around 54 °C and 225 °C, which indicates that visible curing of the TMPTA/CADE mixture produced an interpenetrating polymer network via both free radical and cationic mechanisms.

All coatings were tested by both pencil hardness and by nanoindentation. Nanoindentation is now commonly used to study mechanical properties of materials on the nanoscale [26]. Recent studies suggest that the ratio of hardness to elastic modulus (H/E) may be a more suitable parameter for predicting wear properties compared to evaluating hardness alone [27]. The effect of H/E on wear is based on the knowledge that materials with high H/E values are expected to have small accumulative strain and small accumulative strain energy in sliding, leading to high wear resistance [28]. Therefore, enhancing elasticity (i.e., to reduce E) may be a more suitable approach to improve wear resistance than enhancing the hardness of the material alone. 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.

Table 3
Properties of the VIS-cured films obtained in the presence of the presented photoredox pairs. [a]

Dye	Gel content (%)	$T_{g\ 1}$, $T_{g\ 2}$ DSC (°C)	Hardness MPa	Elastic modulus GPa	H/E	Pencil Hardness
1a	92	57, 229	334.9	4.2	0.079	F
1b	95	54, 225	144.9	2.6	0.055	3H
1c	93	56, 227	319.1	4.1	0.071	2H
2a	92	60, 229	247.1	3.8	0.065	3H
2b	93	57, 227	144.1	2.3	0.064	2H
2c	93	57, 228	373.0	4.3	0.087	F

[a] - Irradiated for 15 min with light intensity 3.2×10^{17} quant s^{-1}; properties were measured after 72 h.

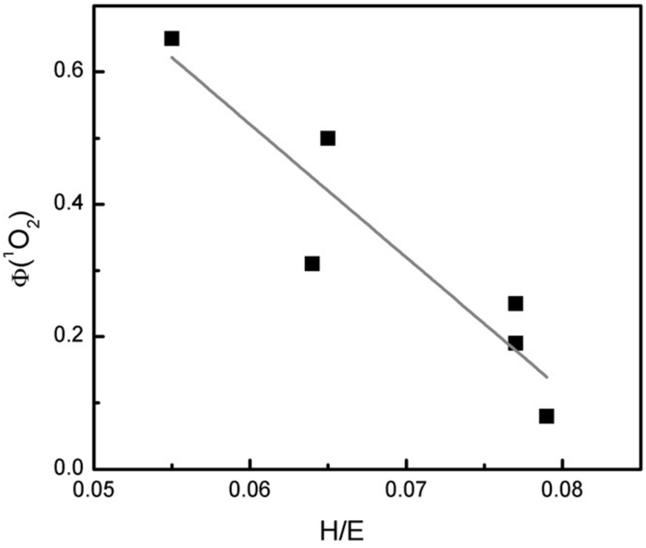


Fig. 2. The relationship between quantum yield of singlet oxygen generation and H/E ($R = 0.92$).

The results of these tests are presented in Table 3. The mechanical properties of the cured TMPTA/CADE were found to depend on the dye that was employed as the sensitizer. The coatings with the highest values of pencil hardness have were those obtained with aid of sensitizers **1b**, **1c**, **2a** and **2b**. These dyes demonstrate a higher $\Phi(^1O_2)$ then dyes **1a** and **2c**. Analyses of the data also revealed that there is a linear relationship between the quantum yield of singlet oxygen generation and the H/E value of the cured films (Fig. 2). At a depth of 1 μm, where O_2 can quench the radical and sensitizers' triplet state, electron transfer reaction between triarylsulfonium salt and dye (i.e., **1b, 1c, 2a, 2b)** may occur via a singlet state. Additionally, the cationic polymerization of the epoxide is responsible for surface curing. Therefore, films obtained during hybrid photopolymerization initiated by the photoredox pair **1a/3** and **2c/3** show the highest value of H/E. 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 TMPTA. The overall hardness of the coatings, measured as pencil hardness, is a result of these two polymerizations.

4. Conclusions

Dye derivatives of 5,12-dihydroquinoxalino[2,3-b]quinoxaline and 5,12-dihydroquinoxalino[2,3-b]pyridopyrazine composed of hexafluoroantimonate triarylsulfonium salt were employed as initiators for visible-light initiated free radical and cationic photopolymerization of an acrylate/epoxide hybrid system. The FT-IR data revealed that these photoredox pairs are able to simultaneously initiate both cationic and radical polymerization in the presence of air. The DSC measurements show that these initiator systems may produce an interpenetrating polymer network. A linear relationship was found between the quantum yield of singlet oxygen generation and the *H*/*E* value of the cured films. The observed mechanical properties of the coatings indicated that when combined with hexafluoroantimonate triarylsulfonium salts, dyes **1b**, **1c**, **2a** and **2b** may have practical applications as visible-light hybrid initiators.

Acknowledgments

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