ACS Macro Letters
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Panchromatic Photopolymerizable Cationic Films Using Indoline and Squaraine Dye Based Photoinitiating Systems

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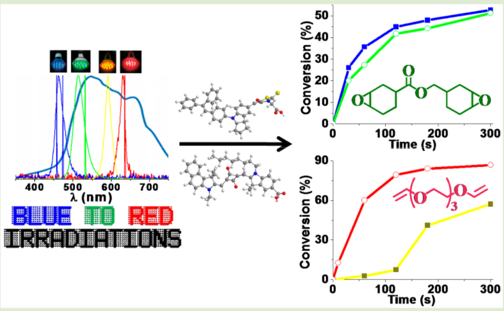
S *Supporting Information*

ABSTRACT: The photoinitiating abilities of indoline and squaraine dyes (D102 and SQ02) incorporated in multicomponent systems for the cationic polymerization of an epoxide or a vinyl ether have been investigated. The polymerizable films exhibit a panchromatic character as revealed by their photosensitivity to a halogen lamp (370−800 nm); household LED bulbs centered at 462 nm (blue), 514 nm (green), 591 nm (yellow), and 630 nm (red); and laser diodes at 457, 473, 532, and 635 nm. SQ02 is particularly efficient in the 520−700 nm range, while D102 exhibits a good efficiency in the 400−580 nm region. The radical photopolymerization of an acrylate can also be observed particularly at 635 nm or upon a halogen lamp. The photochemical mechanisms are studied by steady state photolysis, fluorescence, cyclic voltammetry, electron spin resonance spin trapping, and laser flash photolysis techniques.



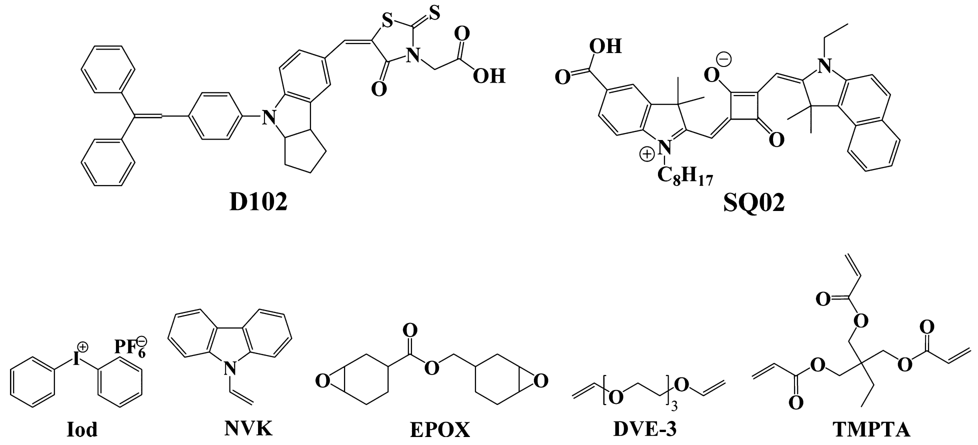
The development of novel dyes usable as photoinitiators (PIs) in photoinitiating systems (PISs) of polymerization working under soft visible light irradiations (e.g., household halogen lamps or fluorescent bulbs, household LEDs, sunlight, etc.) is an ongoing challenge attracting great attention in various fields ranging from radiation curing, imaging, and optic technologies to medicine, material science, or microelectronic areas.[1−8] Albeit examples of visible light induced radical polymerization are well-known (see a recent review in ref 1), the attempts for the design of photoinitiating systems for cationic polymerizations are actually more limited. Among other authors,[6−14] we have presented, in the very recent years, a lot of highly sensitive systems for cationic photopolymerization reactions under visible light irradiations,[5,15−27] and conjugated organic dyes that are used in the dye-sensitized solar cell (DSSC) area could be good PI candidates as they normally exhibit excellent absorption spectra in the visible wavelength range.[28,29] They should allow the preparation of panchromatic photopolymerizable films.

In the present paper, we have selected two dyes, i.e., an indoline dye (D102) and a squaraine dye (SQ02) (used in DSSC;[28−31] Scheme 1), to be incorporated into high-performance PISs (containing an iodonium salt and optionally *N*-vinylcarbazole) for the cationic polymerization of an epoxide and a vinyl ether under several blue-to-red visible light sources, i.e., a very low intensity household halogen lamp (370−800 nm) and LED bulbs (centered at 462 nm (blue), 514 nm (green), 591 nm (yellow), and 630 nm (red)), and laser diodes at 457, 473, 532 and 635 nm. Such families of dyes have been obviously somewhere mentioned in the patent literature, but rather few works using parent derivatives have been devoted to their polymerization ability (see, e.g., ref 32 where a squaraine dye/iodonium salt combination was used but in radical photopolymerization under a high intensity Xenon lamp irradiation). To the best of our knowledge, nothing has been published on their use in cationic photopolymerization under soft conditions. In this work, the photochemical mechanisms of the initiating species formation are investigated by steady state photolysis, fluorescence, cyclic voltammetry, electron spin resonance, and laser flash photolysis techniques (all these techniques are presented in detail in the Supporting Information and in refs 33−37).

The absorption spectra of the investigated dyes (D102 and SQ02) in acetonitrile and the emission spectra of different light sources are shown in Figure 1(A) and Figure 1(B), respectively. The absorption of D102 (maximum located at 500 nm with a molar extinction coefficient ε = 47 500 M^{-1} cm^{-1}) exhibits a

Received: June 17, 2013
Accepted: July 24, 2013
Published: July 29, 2013

Scheme 1. Chemical Structures of the Studied Dyes (D102 and SQ02), Additives, and Monomers



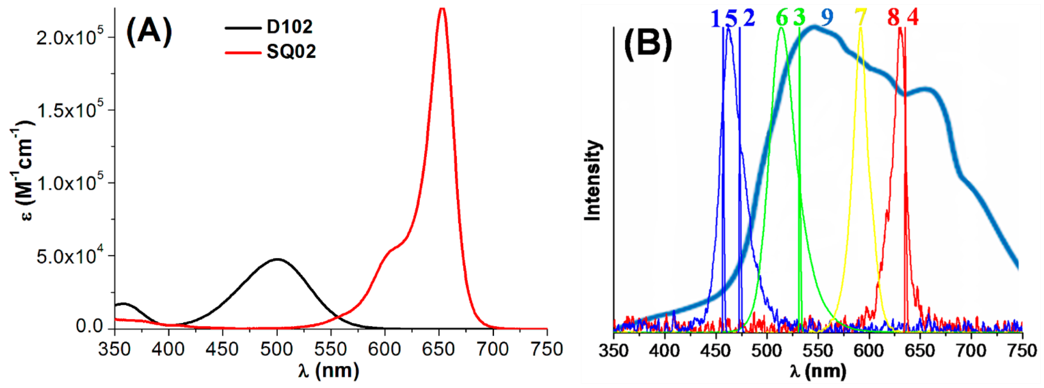


Figure 1. (A) UV−vis absorption spectra of D102 and SQ02 in acetonitrile. (B) Emission spectra of the laser diode at (1) 457 nm, (2) 473 nm, (3) 532 nm, and (4) 635 nm and LED bulbs centered at (5) 462 nm (blue), (6) 514 nm (green), (7) 591 nm (yellow), (8) 630 nm (red), and (9) halogen lamp.

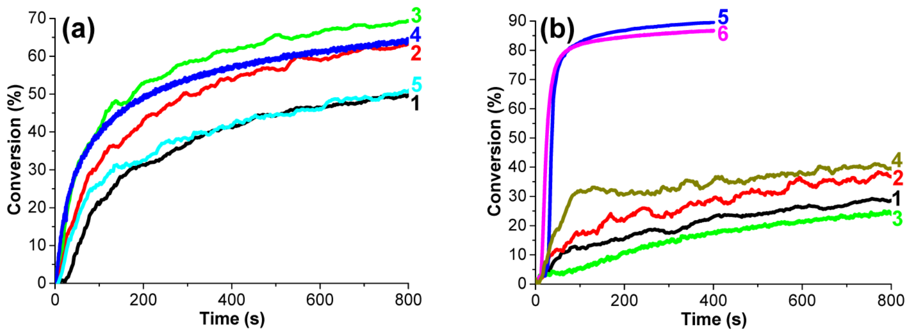


Figure 2. (a) Photopolymerization profile of EPOX under air in the presence of (1) D102/Iod (0.5%/2%, w/w) upon the halogen lamp exposure and D102/Iod/NVC (0.5%/2%/3%, w/w/w) under the (2) halogen lamp, (3) laser diode at 457 nm, (4) laser diode at 473 nm, and (5) laser diode at 532 nm exposure. (b) Photopolymerization profile of (i) EPOX under air in the presence of (1) SQ02/Iod (0.5%/2%, w/w) upon the halogen lamp exposure; (2) SQ02/Iod/NVC (0.5%/2%/3%, w/w/w) upon the halogen lamp exposure; (3) SQ02/Iod/NVC (0.5%/2%/3%, w/w/w) upon the laser diode at 635 nm exposure; and (4) SQ02/Iod/NVC/TTMSS (0.5%/2%/3%/3%, w/w/w/w) upon the halogen lamp exposure; (ii) DVE-3 in laminate in the presence of SQ02/Iod (0.5%/2%, w/w) upon the (5) halogen lamp and (6) laser diode at 635 nm exposure.

good overlapping with the emission spectra of the laser diodes at 457 nm (22 000 M^{-1} cm^{-1}), 473 nm (34 000 M^{-1} cm^{-1}), and 532 nm (26 800 M^{-1} cm^{-1}) and the LED bulbs at 462 nm (25 700 M^{-1} cm^{-1}) and 514 nm (42 800 M^{-1} cm^{-1}). As to the SQ02 spectrum, it presents a longer wavelength and more intense absorption maximum (653 nm; 221 100 M^{-1} cm^{-1}) and quite well matches the emission spectra of the laser diode at 635 nm (105 400 M^{-1} cm^{-1}) and the LED bulbs at 591 nm (35 800 M^{-1} cm^{-1}) and 630 nm (84 200 M^{-1} cm^{-1}). These dyes are also obviously suitable for an irradiation with a halogen lamp. High ε values (>1000 M^{-1} cm^{-1}) are available from λ = 400 to 585 nm for D102 and from λ = 519 to 701 nm for SQ02.

The photopolymerization profiles of EPOX in the presence of D102- or SQ02-based photoinitiating systems under air using several irradiation sources are given in Figure 2 and the final conversions summarized in Table 1. Upon the halogen lamp exposure, the D102/Iod combination initiates the

Table 1. EPOX (and DVE-3[a]) Final Conversions Obtained under Air upon Exposure to the Halogen Lamp and the Laser Diode at 457, 473, 532, and 635 nm at *t* = 800 s in the Presence of D102- or SQ02-Based PISs

PISs	halogen lamp	laser diode at 457 nm	laser diode at 473 nm	laser diode at 532 nm	laser diode at 635 nm
Iod	0	0	0	0	0
D102/Iod	50%	-	-	-	-
D102/Iod/NVC	63%	69%	64%	51%	-
SQ02/Iod	29%|90%[a]	-	-	-	87%[a]
SQ02/Iod/NVC	37%|40%[b]	-	-	-	24%

[a] DVE-3 final conversions obtained in laminate. [b] EPOX final conversion obtained in the presence of SQ02/Iod/NVC/TTMSS (TTMSS is tris(trimethylsilyl)silane).

polymerization of EPOX (final conversion (FC) of 50%; tack free coating; Figure 2(a), curve 1). No polymerization was observed in the presence of Iod alone as it can initiate the ring-opening cationic photopolymerization only under mid-UV irradiation, i.e., <300 nm.[34,38] The addition of NVC improved the EPOX conversion−time profiles (FC = 63%; Figure 2(a), curve 2 vs curve 1); NVC does not absorb visible light but is known as a suitable additive for cationic polymerization (see the chemical mechanisms below).[39] The D102/Iod/NVC system also initiates the polymerization of EPOX under laser diodes at 457 nm (FC = 69%; Figure 2(a), curve 3), 473 nm (64%; Figure 2(a), curve 4), and 532 nm (51%, Figure 2(a), curve 5). The SQ02-based photoinitiating systems also work upon the halogen lamp but to a lesser extent (Figure 2(b), curves 1−2; FC = 30% vs 60%); they operate, however, under red lights (laser diode exposure at 635 nm; relatively low FC: 25%). Tris(trimethylsilyl)silane (TTMSS) and NVC can play a role of additives and improve the polymerization profiles (Figure 2(b) curve 4 vs curve 1).[39] Changing EPOX for DVE-3 leads to excellent polymerization profiles in laminate upon the halogen lamp (SQ02/Iod combination; FC = 90%; Figure 2(b), curve 5) and the laser diode at 635 nm (FC = 87%; Figure 2(b), curve 6; tack free coating).

Interestingly, upon very soft LED bulb exposures (∼10 mW cm^{-2}), the D102/Iod/NVC combination exhibits good photoinitiating abilities for the cationic polymerization of EPOX under air (Figure 3(a) and Table S1 in the Supporting Information SI; blue LED, FC = 53%; green LED, FC = 51%; tack free coatings), whereas the SQ02/Iod photoinitiating system efficiently initiates the cationic polymerization of DVE-3 in laminate (Figure 3(b) and Table S1 in the Supporting Information; yellow LED, FC = 57%; red LED, FC = 87%; tack free coating). For yellow light (Figure 3b, curve 1), a slower polymerization profile is found in agreement with the lower light absorption properties of SQ02 at this wavelength (590 vs 630 nm).

Remarkably, the combination of D102 and SQ02 in a single formulation can lead to panchromatic photopolymerizable cationic films. Indeed, for a four-component initiating system (SQ02/D102/Iod/NVC), high conversions can be obtained for the polymerization of DVE-3 upon the different laser diode (457, 473, 532, and 635 nm) and the polychromatic halogen lamp exposures (tack free coatings can be obtained for all these different irradiation conditions). With this combination of the new proposed initiators, the film can be sensitive at any color within the visible spectrum: from blue to green with D102 and from green to red for SQ02, respectively.

The D102- or SQ02-based systems can also initiate the radical polymerization of TMPTA in laminate under soft irradiation conditions (Figure 4 and Table S2 in the Supporting Information SI): (i) FC = 52%; D102/Iod; halogen lamp exposure (Figure 4, curve 1), and (ii) FC = 38%; SQ02/Iod; halogen lamp (Figure 4, curve 4). The addition of NVC increases the polymerization rates but slightly decreases FC

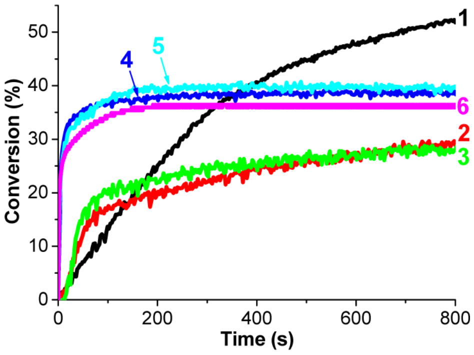


Figure 4. Photopolymerization profile of TMPTA in laminate: (i) in the presence of (1) D102/Iod (0.5%/2%, w/w) and (2) D102/Iod/NVC (0.5%/2%/3%, w/w/w) upon the halogen lamp exposure; (3) D102/Iod/NVC (0.5%/2%/3%, w/w/w) upon the laser diode exposure at 457 nm exposure; (ii) in the presence of (4) SQ02/Iod (0.5%/2%, w/w) and (5) SQ02/Iod/NVC (0.5%/2%/3%, w/w/w) upon the halogen lamp exposure; (6) SQ02/Iod/NVC (0.5%/2%/3%, w/w/w) upon the laser diode exposure at 635 nm exposure.

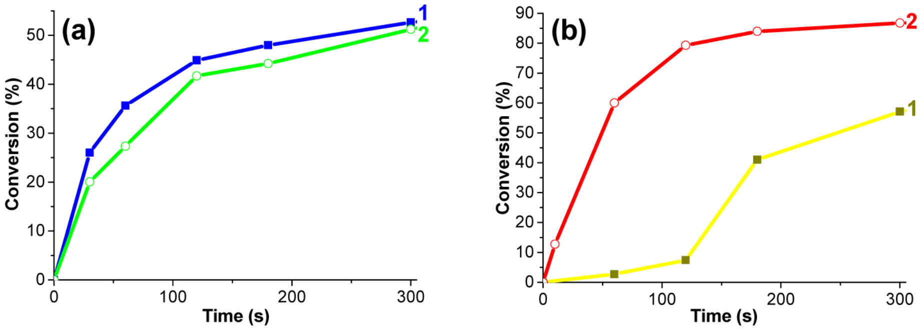


Figure 3. (a) Photopolymerization profile of EPOX under air in the presence of D102/Iod/NVC (0.5%/2%/3%, w/w/w) upon the (1) blue LED bulb and (2) green LED bulb exposure. (b) Photopolymerization profile of DVE-3 in laminate in the presence of SQ02/Iod (0.5%/2%, w/w) under the (1) yellow LED bulb and (2) red LED bulb exposure.

(Figure 4, curves 2 and 3). Upon exposure to the laser diode at 635 nm, a 38% conversion together with a very unusual high rate of polymerization (26% conversion within 10 s) is readily obtained with SQ02/Iod/NVC which appears as one of the rare efficient photoinitiating systems under red light reported so far.[40,41] TMPTA was selected as a multifunctional benchmark monomer; i.e., the photopolymerization process is associated with the formation of a polymer network.

In the absorption spectra recorded during the steady state photolysis of D102/Iod in acetonitrile (halogen lamp exposure; under air; Figure S1 in Supporting Information), the isosbestic points observed at 364 and 554 nm clearly demonstrate that no secondary reactions occurred during reaction 2; the decrease of the absorption at 500 nm is accompanied by the appearance of a band at 600 nm that can probably be ascribed to $D102^{\bullet+}$ or to an associated photoproduct (reactions 1 and 2). The photolysis of SQ02/Iod leads to a decrease of the 653 nm band and a small increase of the absorption at 450 nm. The bleaching is faster with SQ02/Iod compared to D102/Iod (within 30 vs 120 s). This fast bleaching of SQ02 is particularly interesting for the synthesis of colorless coatings with this initiating system.

$$\mathrm{Dye} \rightarrow {}^{1}\mathrm{Dye}(h\upsilon) \quad \text{and} \quad {}^{1}\mathrm{Dye} \rightarrow {}^{3}\mathrm{Dye} \tag{1}$$

$$\begin{aligned} {}^{1,3}\mathrm{Dye} + \mathrm{Ph_2I^+} &\rightarrow \mathrm{Dye}^{\bullet+} + \mathrm{Ph_2I}^{\bullet} \rightarrow \mathrm{Dye}^{\bullet+} + \mathrm{Ph}^{\bullet} \\ &+ \mathrm{Ph\text{-}I} \end{aligned} \tag{2}$$

$$\mathrm{Ph}^{\bullet} + \mathrm{NVC\ (or\ DVE\text{-}3)} \rightarrow \mathrm{Ph\text{-}NVC}^{\bullet}\ (\mathrm{or\ Ph\text{-}DVE\text{-}3}^{\bullet}) \tag{3}$$

$$\begin{aligned} &\mathrm{Ph\text{-}NVC}^{\bullet}\ (\mathrm{or\ Ph\text{-}DVE\text{-}3}^{\bullet}) + \mathrm{Ph_2I^+} \\ &\rightarrow \mathrm{Ph\text{-}NVC^+}\ (\mathrm{or\ Ph\text{-}DVE\text{-}3^+}) + \mathrm{Ph}^{\bullet} + \mathrm{Ph\text{-}I} \end{aligned} \tag{4}$$

The ^{1}D102/Iod and ^{1}SQ02/Iod interaction (reaction 2) rate constants were determined by fluorescence quenching experiments: $k_q = 2.4 \times 10^{10}\ M^{-1}\ s^{-1}$ and $>1.5 \times 10^{9}\ M^{-1}\ s^{-1}$ for D102 and SQ02, respectively. These high k_q values indicate that the processes are almost diffusion-controlled. The free energy changes ΔG for the ^{1}D102/Iod and ^{1}SQ02/Iod electron transfer reactions are highly negative and make the process favorable: −1.27 and −1.19 eV, respectively (E_{ox} of D102 and SQ02 = 0.77 and 0.47 V, respectively, as measured by cyclic voltammetry (Figure S2 in the Supporting Information (SI)); reduction potential $E_{red} = -0.2\ V^{1}$ for Iod; singlet state energy E_S (2.24 and 1.86 eV for D102 and SQ02, respectively) as extracted from the UV−vis absorption and fluorescence emission spectra as usually done[23]). In line with reaction 2, phenyl radicals were observed in ESR spin trapping experiments on irradiated D102/Iod (Figure S3(A) in the SI) and SQ02/Iod solutions (Figure S3(B) in the SI).

In laser flash photolysis experiments, a weak and very long-lived transient absorption at 540 nm was observed after laser excitation (355 nm) of D102 in nitrogen-saturated acetonitrile, which could probably be assigned to the tiny amount of the D102 radical cation arising from photoionization. No triplet state absorption was observed for D102, which likely implies a very low triplet quantum yield (for other squaraines, it has been already found that the triplet state cannot be directly populated and that the intersystem crossing quantum yields are poor[42,43]). As a consequence, the singlet route is the most important for reaction 2.

In the presence of NVC or DVE-3, reactions 3 and 4 occur as in other systems.[39] On the basis of the above investigations, the $D102^{\bullet+}$ and $SQ02^{\bullet+}$ radical cations (reaction 2) and Ph-NVC^{+} are the initiating species for the cationic photopolymerization of EPOX; the DVE-3^{+} cation (reactions 3 and 4) is likely the initiating species for the polymerization of the vinyl ether; the $Ph^{\bullet}$ radicals (reaction 2) initiate the radical polymerization of TMPTA.

Albeit examples of visible light induced radical polymerization are well-known (see refs 1−8,44), this work clearly demonstrates that dyes encountered in dye-sensitized solar cells remain an excellent choice for cationic polymerization, when incorporated in photoinitiating systems, due to their broad absorption spectra in the visible light range. The present systems allow the development of highly sensitive panchromatic cationic photopolymerizable films usable for very low light intensity (here: blue to yellow and green to red). Holographic recording or manufacture of holographic optical elements in radical, cationic, or radical/cationic media might also be possible under selected blue, green, or red laser beams. Moreover, these kinds of dyes should be inherently interesting for the sunlight curing of cationic matrices under air. The development of other dye-based systems is under way.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figure S1: Steady state photolysis of D102/Iod and SQ02/Iod solutions; Figure S2: Cyclic voltammograms of D102 and SQ02 in CH_2Cl_2; Figure S3: ESR spectra of the radicals generated in D102/Iod and SQ02/Iod solutions upon the halogen lamp exposure; Table S1: EPOX or DVE-3 final conversions obtained at t = 300 s upon exposure to different LED bulbs in the presence of D102 or SQ02 based PISs; Table S2: TMPTA final conversions obtained in laminate upon exposure to the halogen lamp, the laser diodes at 457 nm and 635 nm for t = 800 s in the presence of D102 or SQ02 based PISs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ ACKNOWLEDGMENTS

J.L. thanks the Institut Universitaire de France for the financial support.

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