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End capped polyenic structures as visible light sensitive photoinitiators for polymerization of vinylethers

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ABSTRACT

Nine new photoinitiating systems based on a combination of new and established dyes (having an end capped polyenic structure) with an iodonium salt have been synthesized and tested for the polymerization of divinylether and epoxy monomers upon a visible light exposure. They exhibit a strong absorption in the 350–650 nm range which well matches the visible light emission of different convenient visible light sources. Interestingly, very soft irradiation conditions can be employed. Excellent polymerization profiles have been obtained from selected dye iodonium salt combinations using a halogen amp or a laser diode à 457 nm. The chemical mechanisms associated with these novel photoinitiating systems are investigated by steady-state photolysis and ESR experiments.

1. Introduction

Dye photosensitized polymerization reactions (DPPR) occur in the presence of a colored molecule ("dye") incorporated into a visible light absorbing photoinitiating systems (vPIS) and being able to act as a photoinitiator (PI) or a photosensitizer (PS) [1,2]. DPPRs play an important role in many industrial applications within e.g. the radiation curing and imaging area [1,2] as they allow a rapid cure of a multifunctional monomer/oligomer matrix under exposure to visible light delivered by high intensity sources or soft irradiation devices. These DPPRs have been largely known for many years (see e.g. in Refs. [1,3]) in free radical polymerization (FRP) and, to a lesser extent (indeed, until the recent years, the available cationic (vPISs) were rather limited), in cationic polymerization. The search of colored molecules and visible light absorbing photoinitiating systems (vPISs) is continuously carried out and the proposal of novel systems still remains an exciting topic. In particular, there is still a need in (CP) and (FRPCP) as the synthesis of polymers based on cationic formulation can avoid the detrimental shrinkage of the film observed during FRP reactions.

Solvent-free formulations are based on acrylate monomers which are known to undergo a rapid FRP [4]. Vinyl ether monomers (VEs) (low-odor and non-irritating) have recently appeared as an environment friendly alternative to the widely used acrylate monomers which show a strong odor and may cause skin and eye irritation [5]. VEs are very reactive monomers and exhibit a fast cationic polymerization [6,7]. They are encountered in various UV-curing applications (in particular as protective coatings) where a

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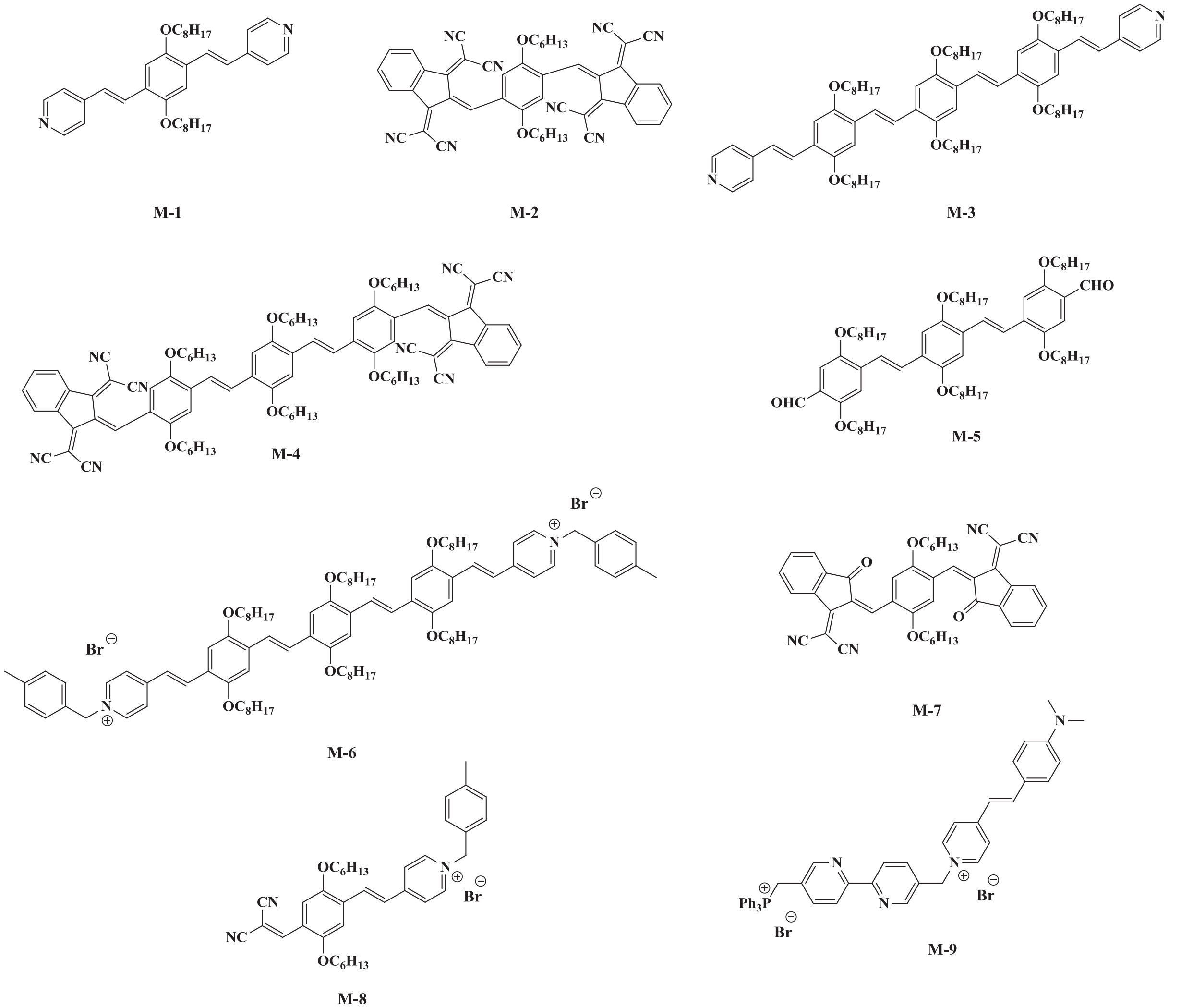
high speed and an extensive cure are desired, together with low shrinkage, great impact strength and high adhesion of the UV-cured polymer. They can also be used to reduce the formulation viscosity.

In this laboratory, we have recently launched a series of work aiming at designing vPIS for radical and cationic polymerizations. In the present paper, we look for compounds presenting an extended delocalization and being able, as part of vPISs, to initiate the cationic polymerization of vinyl ethers and epoxides upon visible light exposure under a soft irradiation source (e.g. household halogen lamp) or laser diodes. Nine new dyes (based on an end capped polyenic structure containing one or more 2,5-dioctyloxyphenyl units (**M-1** to **M-8**) or a pyridinium unit (**M-9**) in the main chain; see Scheme 1) will be synthesized and their polymerization initiation ability checked. The chemical mechanisms will be investigated by steady state photolysis and ESR experiments.

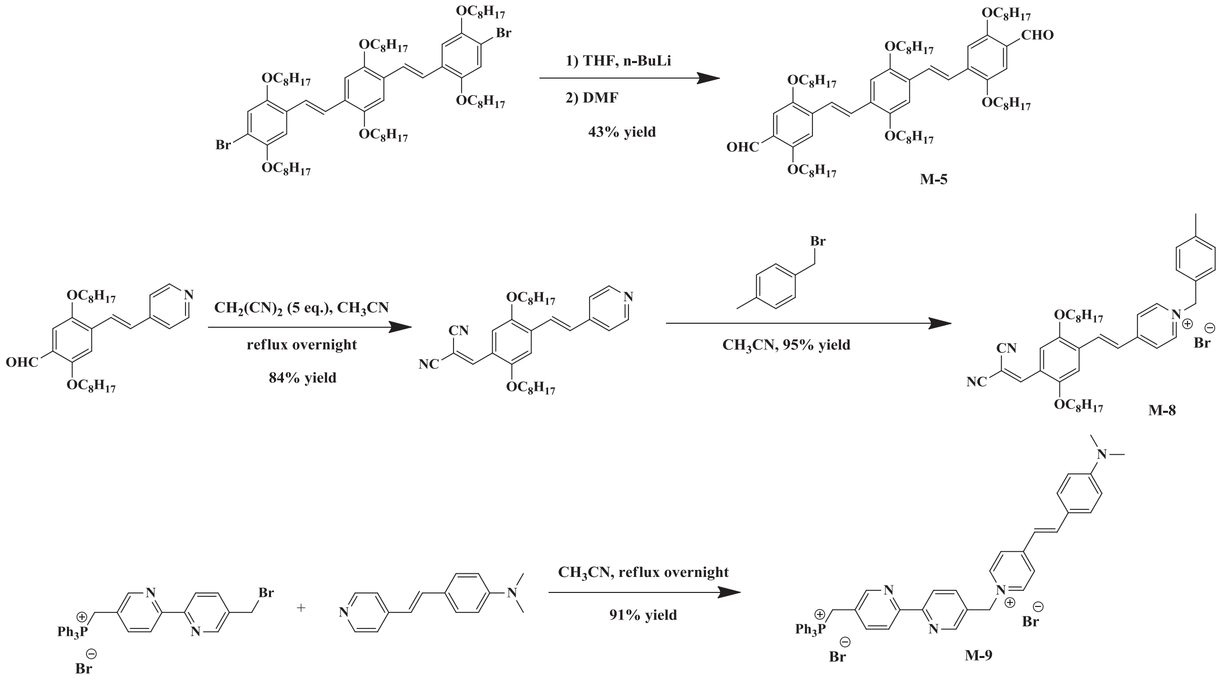
2. Experimental section

i) Synthesis of the different photoinitiators:

All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. Elemental analyses were recorded with a Thermo Finnigan EA 1112 elemental analysis apparatus driven by the Eager 300 software. ^{1}H and ^{13}C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole: ^{1}H (400 MHz) and ^{13}C (100 MHz). The ^{1}H chemical shifts were referenced to the solvent peak DMSO-d_6 (2.49 ppm), $CDCl_3$ (7.26 ppm) and the ^{13}C chemical shifts were referenced to the solvent peak DMSO-d_6 (39.5 ppm), $CDCl_3$ (77 ppm). (*E,E*)-2,5-Dioctyloxy-1,4-*bis*(2-[4]pyridyl-ethenyl)benzene **M-1**, 2,2′,2″,2‴-(((2,5-*bis*(hexyloxy)-1,4-phenylene)*bis*(methanylylidene))bis(1*H*-indene-3,2,1 (2*H*)-triylidene))tetramalononitrile **M-2**, 1,4-*bis*[2-(4-([4]pyridyl-ethenyl))-2,5-dioctyloxy-phenyl)ethenyl]-2,5-*bis*(octyloxy)benzene **M-3**, oligo(*p*-phenylene)vinylenes **M-4** and **M-6**, 2,2′-((2*Z*,2′*Z*)-((2,5-*bis*(hexyloxy)-1,4-phenylene)*bis*(methanylylidene))*bis*(3-oxo-2,3-dihydro -1*H*-indene-2,1-diylidene))dimalononitrile **M-7** were synthesized as previously reported [8]. 4,4′-((1*E*,1′*E*)-(2,5-*bis*(octyloxy)-1,4-phenylene)*bis*(ethene-2,1-diyl))*bis*-(2,5-*bis*(octyloxy)benzaldehyde) **M-5** was synthesized by a two-step formylation of 1,4-*bis*[2-(4-bromo-2,5-dioctyloxyphenyl) ethenyl]-2,5-*bis*(octyloxy)benzene [9] consisting in the lithiation



Scheme 1. Investigated compounds.



Scheme 2. Synthetic procedure.

with n-BuLi followed by treatment with DMF. (*E*)-2,5-*bis*(octyloxy)-4-(2-(pyridin-4-yl)vinyl)benzaldehyde used for the synthesis of **M-8** was synthesized as previously reported [10]. [[5′-(Bromomethyl)-2,2′-bipyridin-5-yl]methyl]phosphonium bromide [11] and (E)-*N,N*-dimethyl-4-(2-(pyridin-4-yl)vinyl)aniline [12] used as reagents for the synthesis of **M-9** was synthesized as previously reported, without modifications and in similar yields (Scheme 2).

2.1. Synthesis of 4,4′-((1E,1′E)-(2,5-bis(octyloxy)-1,4-phenylene) bis(ethene-2,1-diyl))bis(2,5-bis(octyloxy)benzaldehyde) *M-5*

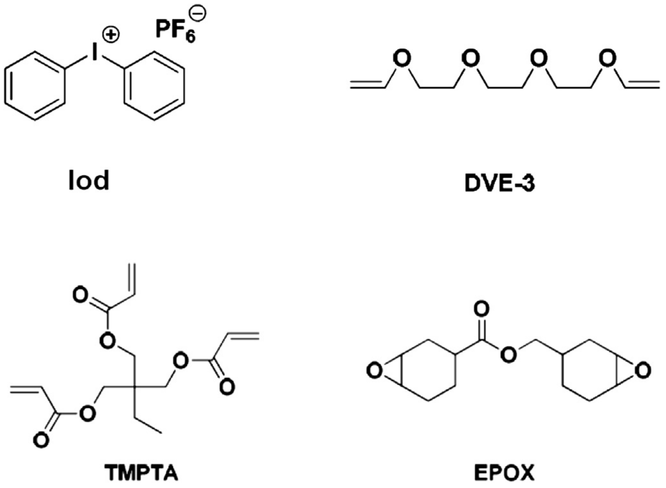
5,5′-((1*E*,1′*E*)-(2,5-*bis*(octyloxy)-1,4-phenylene)*bis*(ethene-2,1-diyl))*bis*(2-bromo-1,4-*bis* (octyloxy)benzene) (3 g, 2.48 mmol) was suspended in dry THF (100 mL) and the solution was cooled at −78 °C. n-BuLi (3.1 mL, 4.96 mmol, 2 eq.) was added and the reaction mixture was stirred at that temperature for 15 min. Dry DMF (1 mL) was added and the reaction mixture was allowed to warm to room temperature and stirred overnight. After addition of water, DCM was added. The water layer was washed several times with DCM. The organic phase was combined, dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The residue was chromatographed on silica gel (DCM/Hexanes as the eluent). Several fractions corresponding to the starting materials (0.51 g, 17% recovered starting materials) the monoaldehyde (0.7 g, 29%) and the dialdehyde (1 g, 43%) were separated. The last fraction was evaporated and addition of ethanol precipitated the dialdehyde. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.87–0.91 (m, 18H), 1.27–1.60 (m, 60H), 1.75–1.90 (m, 12H), 4.03–4.15 (m, 12H), 7.18 (s, 2H), 7.22 (s, 2H), 7.35 (s, 2H), 7.54 (d, 2H, J = 16.3 Hz), 7.62 (d, 2H, J = 16.3 Hz), 10.5 (s, 2H, CHO); ^{13}C NMR ($CDCl_3$) δ (ppm): 14.5, 23.1, 26.6, 26.7, 26.8, 29.64, 29.68, 29.70, 29.73, 29.76, 29.79, 31.2, 31.2, 32.21, 32.26, 32.27, 69.47, 69.55, 69.80, 110.5, 110.8, 111.2, 123.7, 124.5, 127.4, 127.9, 135.4, 151.1, 151.8, 156.6; HRMS (ESI MS) m/z: theor: 1106.8514 found: 1106.8513 ($M^{+\cdot}$ detected).

2.2. Synthesis of (E)-2-(2,5-bis(octyloxy)-4-(2-(pyridin-4-yl)vinyl) benzylidene)malononitrile

(*E*)-2,5-*bis*(octyloxy)-4-(2-(pyridin-4-yl)vinyl)benzaldehyde (2 g, 4.29 mmol) and malononitrile (1.42 g, 21.47 mmol, 5 eq.) were dissolved in acetonitrile (30 mL) and a few drops of piperidine were added. The reaction was refluxed overnight. After cooling, the solvent was removed under reduced pressure. The residue was dissolved in a minimum of acetone and addition of ethanol precipitated the product. It was filtered off, washed several times with ethanol and dried under vacuum (1.85 g, 84% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.91 (*t*, 6H, J = 6.9 Hz), 1.29–1.51 (m, 20H), 1.79–1.84 (m, 4H), 4.06 (*t*, 2H, J = 6.6 Hz), 4.11 (*t*, 2H, J = 6.6 Hz), 7.16 (d, 1H, J = 16.5 Hz), 7.17 (s, 1H), 7.34 (s, 1H), 7.39 (d, 2H, J = 6.0 Hz), 7.66 (d, 1H, J = 16.5 Hz), 8.26 (s, 1H), 8.61 (d, 2H, J = 6.0 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm): 14.0, 22.5, 26.0, 26.1, 29.07, 29.12, 29.16, 29.22, 29.55, 29.6, 31.7, 31.8, 69.0, 69.2, 110.1, 111.1, 113.6, 125.0, 127.4, 129.3, 132.5, 151.0, 155.9; HRMS (ESI MS) m/z: theor: 113.3355 found: 113.3353 ($M^{+\cdot}$ detected).

2.3. Synthesis of (E)-4-(4-(2,2-dicyanovinyl)-2,5-bis(octyloxy) styryl)-1-(4-methylbenzyl)pyridin-1-ium bromide *M-8*

(*E*)-2-(2,5-*bis*(octyloxy)-4-(2-(pyridin-4-yl)vinyl)benzylidene) malononitrile (1 g, 1.95 mmol) and α-bromo-p-xylene (360 mg, 1.95 mmol) were dissolved in acetonitrile (10 mL) and the reaction mixture was refluxed overnight. After cooling, addition of diethyl ether precipitated the product which was filtered off and washed with a mixture of ethanol/ether (1/5). The product was isolated as a powder (1.29 g, 95% yield). ^{1}H NMR (CD_3CN) δ (ppm): 0.87 (*t*, 6H, J = 6.5 Hz), 1.29–1.44 (m, 20H), 1.50–1.57 (m, 4H), 2.36 (s, 3H), 4.16 (*t*, 4H, J = 6.7 Hz), 5.59 (s, 2H), 7.30–7.37 (m, 4 H), 7.54 (d, 1H, J = 16.5 Hz), 8.00 (d, 2H, J = 5.4 Hz), 8.05 (d, 1H, J = 16.5 Hz), 8.57 (d, 2H, J = 7.1 Hz); ^{13}C NMR (CD_3CN) δ (ppm): 14.4, 21.2, 23.4, 26.9, 29.8, 29.9, 30.0, 32.6, 64.2, 70.4, 113.3, 125.3, 125.8, 128.2, 130.0, 131.0, 131.4, 136.7, 141.0, 144.8, 153.3, 155.3; HRMS (ESI MS) m/z: theor: 618.4054 found: 618.4050 ($M^{+\cdot}$ detected).



Scheme 3. Additives and Monomers.

2.4. *Synthesis of (E)-4-(4-(dimethylamino)styryl)-1-((5′-((triphenylphosphonio)methyl)-[2,2′-bipyridin]-5-yl)methyl)pyridin-1-ium bromide* ***M-9***

5′-(Bromomethyl)-2,2′-bipyridin-5-yl]methyl]phosphonium bromide (0.6 g, 0.993 mmol) and (E)-*N*,*N*-dimethyl-4-(2-(pyridin-4-yl)vinyl)aniline (0.27 g, 1.20 mmol) were suspended in acetonitrile (20 mL) and the reaction mixture was refluxed overnight. After cooling, the solvent was partially evaporated and addition of ether precipitated a solid which was filtered off and washed several times with ether. 750 mg of product were isolated (91% yield). ^{1}H NMR (DMSO-d$_6$) δ (ppm): 2.41 (s, 3H, Me), 5.47 (d, 2H, $J = 14.8$ Hz), 5.87 (s, 2H), 6.76 (d, 2H, $J = 8.7$ Hz), 7.22 (d, 1H, $J = 16.0$ Hz), 7.54 (d, 2H, $J = 8.7$ Hz), 7.57 (d, 2H, $J = 8.9$ Hz), 7.75–7.79 (m, 12H), 7.90–7.96 (m, 4H), 8.10–8.15 (m, 2H), 8.22 (d, 1H, $J = 8.3$ Hz), 8.32 (d, 2H, $J = 3.3$ Hz), 8.64 (d, 1H, $J = 6.2$ Hz), 8.92 (s, 1H), 9.03 (d, 2H, $J = 6.5$ Hz); ^{13}C NMR (DMSO-d$_6$) δ (ppm): 25.2 (d, $J = 47.2$ Hz), 39.5, 40.0, 58.7, 111.9, 117.0, 118.4, 120.5 (d, $J = 27$ Hz), 121.4, 122.7, 129.6, 130.2 (d, $J = 12$ Hz), 130.4, 134.0 (d, $J = 10.5$ Hz), 135.3, 137.7, 139.4 (d, $J = 5.3$ Hz), 142.8, 143.2, 143.5, 149.6, 151.0 (d, $J = 6$ Hz), 151.9, 154.1 (d, $J = 3.8$ Hz), 154.3, 154.9 (d, $J = 2.2$ Hz); HRMS (ESI MS) m/z: theor: 334.1529 ($M^+/2$) found: 334.1524 ($M^{+\cdot}$ detected).

ii) Chemical compounds:

Diphenyliodonium hexafluorophosphate (Ph_2I^+ or Iod) and Triethyleneglycol divinyl ether (DVE-3; as a representative of vinyl ether monomers) were obtained from Aldrich and used with the best purity available (Scheme 3). Trimethylolpropane triacrylate (TMPTA) and (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX; Uvacure 1500) were obtained from Cytec (Scheme 3). TMPTA, EPOX, and DVE-3 were selected as benchmark monomers: these monomers are well known in the photopolymerization field and represent excellent structures to evaluate the initiating ability of new photoinitiating systems.

iii) Irradiation sources:

Several lights were used: i) polychromatic light from a halogen lamp (Fiber-Lite, DC-950 – incident light intensity: $I_0 \approx 12$ mW cm^{-2}; in the 370–800 nm range); ii) monochromatic light delivered by a laser diode at 457 nm (MBL-III-BFIOPTILAS; $I_0 \approx 100$ mW cm^{-2}). The emission spectra of these several lights were already given in Ref. [13].

iv) Cationic Polymerization (CP) and Free Radical Promoted Cationic Polymerization (FRPCP):

The two-component photoinitiating systems are based on dye/iodonium salt (0.3%/2% w/w). The experimental conditions are given in the Figure captions. The residual weight content is related to the monomer. The photosensitive formulations (25 μm thick) were deposited on a BaF$_2$ pellet under air (or in laminate for DVE-3; DVE-3 is a very low viscosity monomer: polymerization must be carried out in laminate to avoid a change of thickness).

The evolution of the functional groups of the monomers – conversion C (%) – is determined by measuring the peak area A of the corresponding characteristic bands at each time: $C(\%) = (A_0 - A_t)/A_0 \times 100$ where C is the conversion at t time, A_0 the initial peak area before irradiation and A_t the peak area of the functional groups at t time. The evolution of the epoxy group (for EPOX) and the double bond (for vinyl ether monomer) contents were continuously followed by real time FTIR spectroscopy (JASCO FTIR 4100) at about 790 cm^{-1} and 1619 cm^{-1}, respectively.

v) Computational Procedure:

Molecular orbital calculations were carried out with the Gaussian 03 suite of programs. The electronic absorption spectra for the different compounds were calculated with the time-dependent density functional theory at B3LYP/6-31G* level on the relaxed geometries calculated at UB3LYP/6-31G* level.

vi) ESR spin trapping (ESR-ST) experiments:

The ESR-ST experiments were carried out using an X-Band spectrometer (MS 400 Magnettech). The radicals were produced at RT upon a halogen lamp exposure under N$_2$ and trapped by phenyl-N-tbutylnitrone (PBN) according to a procedure described in detail in Refs. [14,15]. The ESR spectra simulations were carried out with the PEST WINSIM program.

vii) Fluorescence experiments:

The fluorescence properties of the compounds were studied using a JASCO FP-750 spectrometer.

viii) Redox potentials:

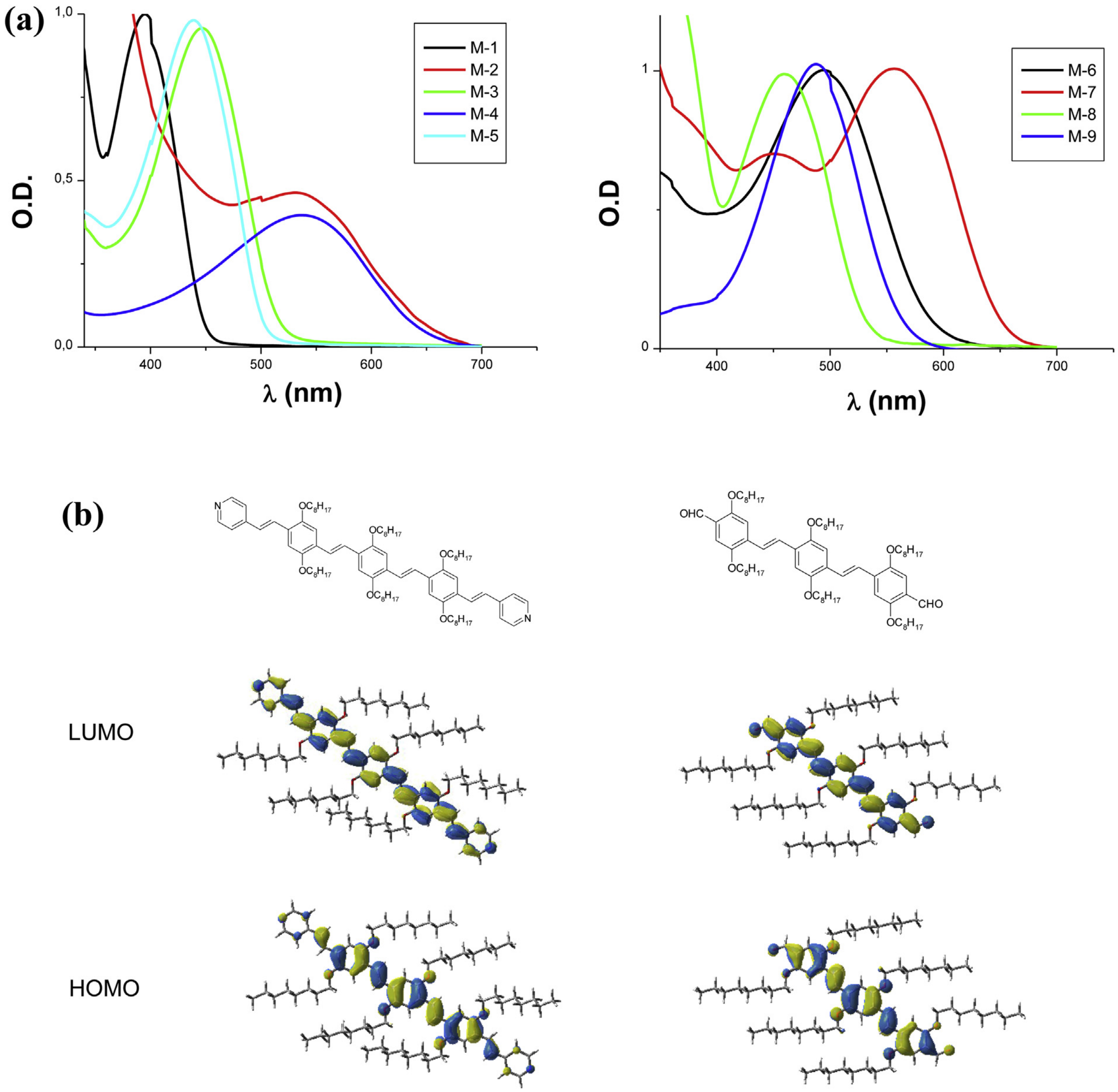


Fig. 1. (a) UV–visible absorption spectra of the different dyes in acetonitrile or toluene; (b) HOMO and LUMO for **M-3** and **M-5** at B3LYP/6-31G* level.

The redox potentials (E_{ox} vs. SCE) were measured in acetonitrile by cyclic voltammetry with tetrabutyl-ammonium hexafluorophosphate 0.1 M as a supporting electrolyte. The free energy change ΔG_{et} for an electron transfer reaction is calculated from the classical Rehm–Weller equation (Eq. (1)) [16] where E_{ox}, E_{red}, E_T and C are the oxidation potential of the donor, the reduction potential of the acceptor, the excited state energy and the coulombic term for the initially formed ion pair, respectively. C is neglected as usually done in polar solvents [17].

$$\Delta G_{et} = E_{ox} - E_{red} - E_T + C \quad (1)$$

3. Results and discussion

3.1. Absorption properties of the new dyes

The ground state absorption spectra of the new proposed dyes are depicted in Fig. 1. These dyes allow a large and efficient matching with different light source emission spectra (e.g. halogen lamp and laser diodes at 405, 457, 473, 532 or 635 nm; see Table 1). Remarkably, high molar extinction coefficients are determined at 457 nm (e.g. 21 200, 37 500 M^{-1} cm^{-1} for **M-3** and **M-5**, respectively).

Molecular orbital MO calculations, using the time-dependent density functional theory at B3LYP/6-31G* level on the relaxed geometries calculated at UB3LYP/6-31G* level, show that the lowest energy transition involves strongly delocalized MOs (see e.g. the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of **M-3** and **M-5** in Fig. 1(b)).

Remarkably for **M-3**, the most efficient dye in the photoinitiating system, the maximum absorption wavelength (λ_{max}) is red-shifted in the presence of the iodonium salt (Fig. 2); the change of λ_{max} for different [Iod] is given in Table 2. This shift can be likely explained by the formation of a ground state complex between **M-3** and Iod. For **M-5**/Iod, such a behavior is not observed (the UV–vis spectrum of **M-5** is affected by the presence of Iod).

Table 1
Maximum absorption wavelengths for the new proposed dyes.

Dye	λ_{max} (nm) [ε in M^{-1} cm^{-1}] absorption
M-1	395
M-2	534
M-3	446 [22 322]
M-4	536
M-5	438 [41 983]
M-6	495
M-7	557
M-8	460
M-9	487

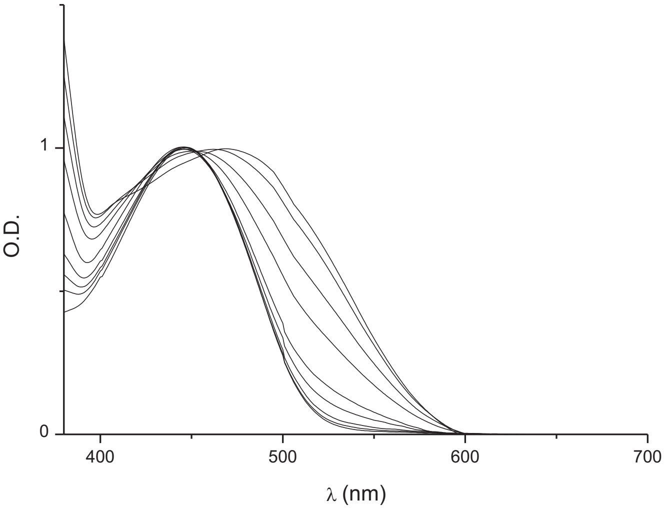


Fig. 2. Absorption spectra for **M-3** for different [Iod] (see Table 2) in acetonitrile/toluene.

Table 2
λ_{max} for **M-3** for different [Iod] in acetonitrile/toluene (50%/50%).

[Iod] M	λ_{max} (nm)
$0.5\ 10^{-3}$	446
$0.15\ 10^{-2}$	446
$0.37\ 10^{-2}$	446.8
$0.58\ 10^{-2}$	446.9
$0.79\ 10^{-2}$	449.3
$1.00\ 10^{-2}$	454.9
$1.27\ 10^{-2}$	460.5
$1.53\ 10^{-2}$	469.3

3.2. Cationic photopolymerization

The photopolymerization of DVE-3 was carried out in laminate upon visible lights (457 nm laser diode and halogen lamp). In the presence of the **M-3**/Iod two-component system, very high rates of polymerization and high final conversions are found (e.g. conversions of about 95% and 94% after 300 s of irradiation with the 457 nm laser diode and halogen lamp, respectively; Fig. 3(A)). The low intensity of the halogen lamp (12 mW cm^{-2}) being already enough (almost total conversion), a ~8 fold increase (using the laser diode) cannot obviously change anything in the polymerization profile. Tack free coatings are obtained. The bleaching of the polymer film under irradiation is quite remarkable (see below for the bleaching of the dye in presence of Iod upon irradiation); this can be useful for applications requiring colorless coatings. When using **M-5**/Iod (Fig. 3(B)), a final conversion of ~50% (laser diode) and ~80% (halogen lamp) is reached after 10 min irradiation; the polymerization rate is faster with the laser diode but a lower final conversion is reached, this can be ascribed to a too fast polymer network synthesis preventing a full conversion with the laser diode. The other dye/Iod systems are much less efficient (low final conversions are obtained < 15%) (Fig. 1 in supporting information).

The **M-3**/Iod system is also suitable for the ring opening polymerization of EPOX under air (~50% of conversion at $t = 800$ s; laser diode irradiation; Fig. 4). Therefore, **M-3** appears to be an efficient photosensitizer for the iodonium salt decomposition. Using the other dyes, poorer polymerization profiles are obtained (e.g. 20% conversion with **M-5**/Iod and <15% for the other dyes). The difference between the DVE-3 vs. the EPOX profiles should be ascribed to the better propagation rate constants of vinyl ethers rather than to a specific effect of the photoinitiating systems (as in Refs. [1,2]).

Although the irradiated **M-3**/Iod or **M-5**/Iod systems generate radicals (see below), no photopolymerization of TMPTA significantly occurs (i.e. final conversions <15%).

3.3. Chemical mechanisms observed in the dye/Iod systems

Because of their high efficiency in photopolymerization, the mechanistic study was focused on **M-3** and **M-5**. For the other dyes, a very low reactivity was found for polymerization, but also for photolysis (see Fig. 2 in supporting information). This can be ascribed to the low reactivity of theses dyes with Iod to generate initiating species for the polymerization reaction (see below for the structure/reactivity relationship). The free energy change ΔG_{et} for the expected **M-3**/Ph_2I^+ and **M-5**/Ph_2I^+ electron transfer eT

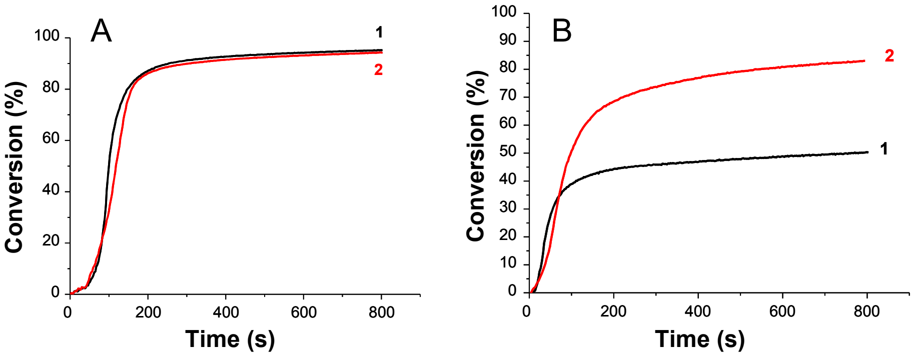


Fig. 3. Photopolymerization profiles of DVE-3 in laminate; in the presence of (A) **M-3**/Iod (0.3%/2%w/w) and (B) **M-5**/Iod (0.3%/2%w/w) upon exposure to: (1) laser diode at 457 nm; (2) halogen lamp.

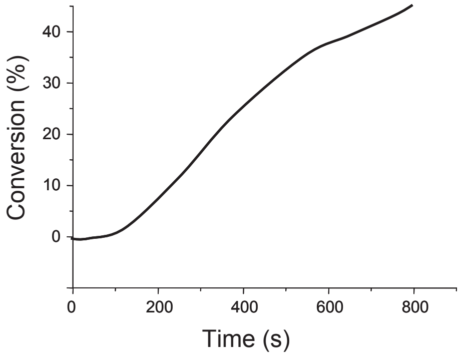


Fig. 4. Photopolymerization profiles of EPOX under air; upon a laser diode exposure at 457 nm in the presence of **M-3**/Iod (0.3%/2%w/w).

Table 3
Maximum emission wavelength experimentally obtained by fluorescence spectroscopy for **M-3** and **M-5**; singlet state energy level (E_{S1}) from Fig. 5(B); oxidation potential (E_{ox}) and ΔG for the electron transfer (^{1}dye/Iod).

Dye	λ_{max} (nm) emission	E_{S1} (eV)	E_{ox} (V vs. SCE)	ΔG (^{1}dye/Iod)(eV)
M-3	522	2.53	0.78	−1.55
M-5	516	2.54	0.9	−1.44

reaction is favorable ($\Delta G = -1.55$ and -1.44 eV, respectively; $E_{red}(Ph_2I^+) \sim -0.2$ V[1]; used parameters in Table 3; see Fig. 5(A) and Fig. 5(B)).

When exposed to the halogen lamp, a very fast bleaching of the **M-3**/Iod and **M-5**/Iod solution is found (Fig. 6). The radicals generated in these systems can be observed in ESR-spin trapping experiments. For the irradiation of **M-3**/Iod and **M-5**/Iod solutions upon a halogen lamp exposure under N_2, a phenyl radical $Ph^•$ (originating from the known r2[1]) is clearly observed (Fig. 7). It obviously results (r1a) from this eT process (oxidation of the dye by Iod) leading to PhI, dye $^{•+}$ and $Ph^•$. For the other investigated dyes, this bleaching is much slower or even not observed.

In the presence of radical inhibitors (oxygen, PBN), no polymerization occurs for the **M-3**/Iod and **M-5**/Iod initiating systems. This is in agreement with a free radical promoted cationic polymerization reaction (FRPCP) (r3, r4), Ph-DVE-3$^+$ being the main initiating structure. Indeed, Ph-DVE-3$^•$ is the free radical generated though the addition of $Ph^•$ onto the vinyl ether double bond (r3). This latter radical is electron rich and can be oxidized by Ph_2I^+ leading to Ph-DVE-3$^+$ (r4) as polymerization initiating structure.

$$\text{dye} \rightarrow {}^1\text{dye}\ (h\nu)$$

$$^1\text{dye} + Ph_2I^+ \rightarrow \text{dye}^{•+} + Ph_2I^• \quad (\text{r1a})$$

$$\text{dye}^{•+} + Ph_2I^• \rightarrow \text{dye} + Ph_2I^+ \quad (\text{r1b})$$

$$Ph_2I^• \rightarrow Ph^• + \text{Ph-I} \quad (\text{r2})$$

$$Ph^• + \text{DVE-3} \rightarrow \text{Ph-DVE-3}^• \quad (\text{r3})$$

$$\text{Ph-DVE-3}^• + Ph_2I^+ \rightarrow \text{Ph-DVE-3}^+ + Ph^• + \text{Ph-I} \quad (\text{r4})$$

3.4. *Structure/reactivity for the different investigated dyes*

The efficiency of the dyes decreases in the series **M-3** > **M-5** >> **M-1**, **M-2**, **M-4**, **M-6** to **M-9**: this trend can be ascribed to a strong interplay of different factors:

i) *the respective light absorption properties of these dyes*; this is probably not the driving factor i.e. the extinction coefficient is higher for **M-5** than for **M-3** at 457 nm despite a lower reactivity for **M-5** (36 700 vs. 20 700 M^{-1} cm^{-1} for **M-5** and **M-3**, respectively).
ii) *the reactivity of the dye for (r1a)*; with two favorable ΔG_{et} for r1a for **M-3**/Iod and **M-5**/Iod, a very different reactivity was found. This process is probably not the crucial one.
iii) *the yield in* $Ph^•$ *leading to a FRPCP process through r2-r4.* Indeed, a back electron transfer reaction (r1b) can decrease the yield in $Ph^•$; this latter parameter can hardly be extracted but the intensity of the free radical signals in ESR-spin trapping experiments roughly follows the reactivity trend (**M-3** > **M-5** >> **M-1**, **M-2**, **M-4**, **M-6** to **M-9**). Almost no radical was observed for the irradiation of **M-1** (or **M-2**, **M-4**, **M-6** to **M-9**)/Iod solutions in full agreement with the lack of reactivity of these dyes. These data suggest a strong influence of the yield in $Ph^•$ in the overall reactivity of the system.

4. Conclusion

In this paper, two-component photoinitiating systems containing an iodonium salt and various dyes involving a novel end capped polyenic skeleton have been proposed for the cationic polymerization of a vinylether (DVE-3) and a diepoxide under air either upon a very soft irradiation (halogen lamp) or a laser diode

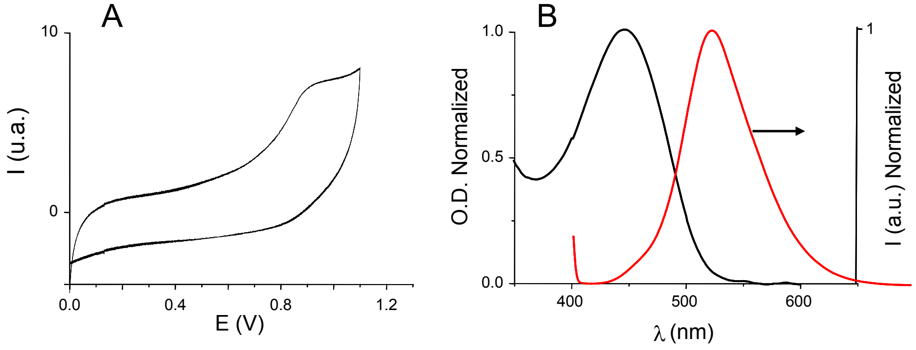


Fig. 5. (A) Cyclic voltammogram for **M-3** in acetonitrile/toluene (50%/50%) (B) (a) Absorption and (b) fluorescence spectra for **M-3** in acetonitrile/toluene (50%/50%).

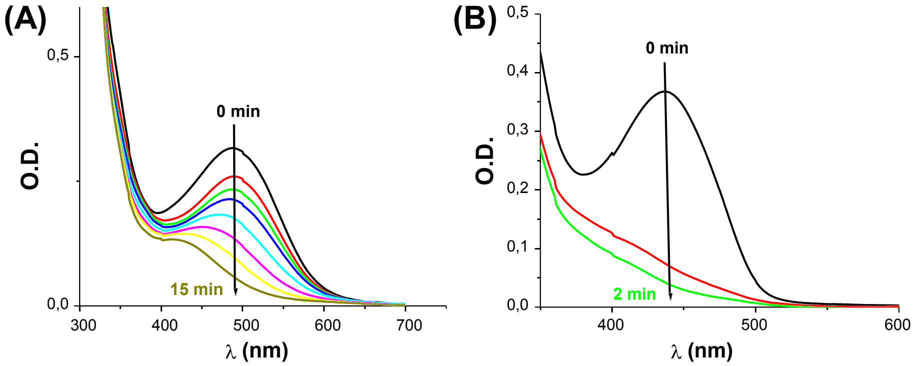


Fig. 6. Photolysis of **M-3**/Iod (A) and **M-5**/Iod (B) in acetonitrile/toluene (50%/50% w/w); under air; halogen lamp exposure; [Iod] = 0.02 M.

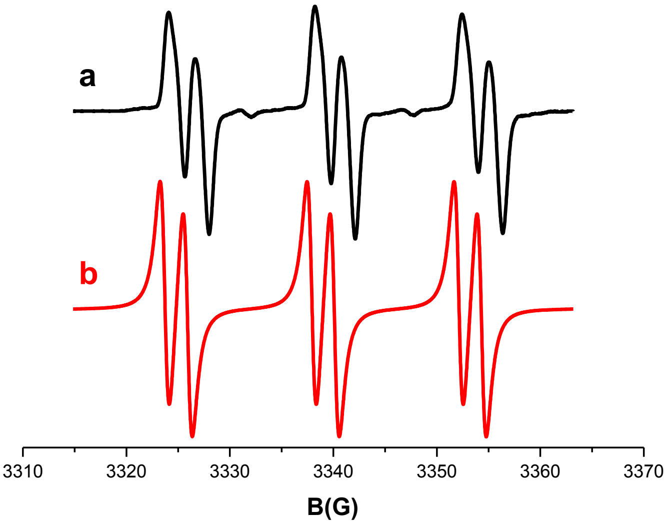


Fig. 7. ESR-Spin Trapping spectrum of **M-3**/Iod; [Iod] = 0.01 M; in tert-butylbenzene; halogen lamp exposure; under N2; experimental (a) and simulated (b) spectra. Phenyl-N-tert-butylnitrone (PBN) is used as spin trap. The hyperfine coupling constants *hfc* (a_N = 14.2 G; a_H = 2.2 G) agree with the known data for the PBN/Ph˙ adduct [14,15].

exposure. A remarkable tunable absorption is obtained over the 350–650 nm range. Excellent DVE-3 polymerization profiles were recorded using **M-3**/Iod at 457 nm. This system might be useful in holographic recording or holographic optical element manufacture (using e.g. the 488 nm line of the Ar^+ laser) where a high reactivity and a low shrinkage of the matrix are required.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2014.02.002

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