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Photoinitiators based on a phenazine scaffold: High performance systems upon near-UV or visible LED (385, 395 and 405 nm) irradiations

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ABSTRACT

Novel photoinitiators based on a phenazine scaffold are proposed for the ring opening polymerization of epoxy monomers as well as the free radical polymerization of (meth)acrylates. Good to excellent polymerization profiles can be obtained upon different easily accessible, energy saving and cheap LEDs (385, 395 and 405 nm) as well as a diode laser at 405 nm or halogen lamp opening new fields for polymer synthesis upon soft and convenient irradiations. These compounds can be particularly attractive as high performance photoinitiators in the 350–425 nm range. The initiation mechanisms are investigated in detail through fluorescence, cyclic voltammetry, steady state photolysis and electron spin resonance (ESR) experiments.

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1. Introduction

The photoinitiating systems PISs play an important role in free radical polymerization (FRP), thiol-ene polymerization (TEP), cationic polymerization (CP) or free radical promoted cationic polymerization (FRPCP) and interpenetrated polymer networks (IPN) synthesis (see e.g. in Refs. [1,2]). Huge efforts are devoted to the design of UV, visible and near IR sensitive PISs working upon exposure to monochromatic or polychromatic lights, under high or low intensity sources, in laminate, inert atmosphere or under air (Ref. [3] and references therein) The search for novel skeletons or novel derivatives of existing structures operating in more and more complicated experimental conditions required by the industrial applications is a fascinating topic. Particularly, the recent development of cheap, energy saving and easily accessible LEDs operating upon soft irradiations has opened new fields for polymer synthesis. In the frame of our works on the design of PISs, we propose here to develop phenazine derivatives as photoinitiators (PI) of FRP, CP and FRPCP upon highly attractive near UV or visible LED lights. Phenazines **PH**s are encountered in e.g. the medical area (see e.g. Ref. [4]), optics (see e.g. Ref. [5]), photoconductive materials (see e.g. Ref. [6]), solar cells and photovoltaics (see e.g. Refs. [7,8]). They have been mentioned in the photopolymerization area (in FRP as additives, see e.g. Refs. [9–11]; in CP as photosensitizers for the decomposition of onium salts, see e.g. Refs. [12–16]; in solid-state photopolymerization, see e.g. Ref. [17]). More recently, synthetized benzo [2,3-b]—phenazines were found to be quite efficient photosensitisers in radical as well as cationic polymerization processes [18] but upon high intensity Xenon lamp exposure.

In the present paper, we will revisit this kind of scaffold and synthesize new derivatives (Scheme 1), check their ability (when incorporated in various PISs) in photopolymerization reactions induced under soft lights delivered by near UV LEDs (385 and 395 nm). Additional lights (low intensity laser diode@405 nm and halogen lamp; higher intensity (~100 mW/cm²) LED@405 nm) will also be used. High performance initiating systems will be proposed for radical and cationic polymerizations and for the synthesis of interpenetrated polymer networks. The photochemical mechanisms of the initiation species formation will be investigated by steady state photolysis, fluorescence, cyclic voltammetry, and electron spin resonance spin trapping, and laser flash photolysis techniques.







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2. Experimental section

2.1. 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. ¹H and ¹³C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole: ¹H (400 MHz) and ¹³C (100 MHz). The ¹H chemical shifts were referenced to the solvent peak CDCl₃ (7.26 ppm) and the ¹³C chemical shifts were referenced to the solvent peak CDCl₃ (77 ppm). All these dyes were prepared with analytical purity up to accepted standards for new organic compounds (>98%) which was checked by high field NMR analysis. Diquinoxalino[2,3-a:2',3'-c]phenazine PH_1, [19] 2,3,8,9,14,15-hexamethyldiquinoxalino[2,3-a:2',3'-c]phenazine PH_2 [20] were synthesized according to literature procedures. Pyrene-4,5,9,10-tetraone used for the synthesis of PH_2 was synthesized as previously reported, without modification and in similar yield [21].

2.1.1. Synthesis of diquinoxalino[2,3-a:2',3'-c]phenazine-2,8,14triyltris(phenylmethanone) and diquinoxalino[2,3-a:2',3'-c] phenazine-2,8,15-triyltris(phenylmethanone) **PH_3**



Hexaketocyclohexane octahydrate (1 g, 3.2 mmol) and 3,4diaminobenzophenone (2.04 g, 9.6 mmol, 3 eq.) were refluxed in 1:1 glacial acetic acid/ethanol (50 mL) at 140 °C for 24 h. After cooling, the solution was concentrated until a precipitate formed. The reaction mixture was then filtered and the blue-violet solid was washed with water and pentane. The solid was then treated with refluxing 30% nitric acid (20 mL) for 3 h. Upon cooling, no precipitate formed. The solution was poured into water. The yellow solid was filtered off, and dissolved in DCM. The organic phase was dried over magnesium sulfate and the solvent removed under reduced pressure. The solid was purified by dissolution in a minimum of DCM and precipitation with pentane (1.92 g, 86% yield). ¹H NMR (CDCl₃) δ (ppm): 7.55–7.74 (m, 6H), 7.78–7.99 (m, 5H), 8.27–8.47 (m, 2H), 8.50–8.59 (m, 4H), 8.68–8.84 (m, 4H), 8.88–8.98 (m, 3H); HRMS (ESI MS) *m*/*z*: theor: 697.1983 found: 697.1981 ([M + H]⁺ detected); Anal. Calc. for C₄₅H₂₄N₆O₃ : C, 77.6; H, 3.5; O, 6.9; Found: C, 77.7; H, 3.4; O, 6.8%.

2.1.2. Synthesis of 6,7,15,16-tetramethylquinoxalino[2',3':9,10]phenanthro[4,5-abc]phenazine **PH_4**

Pyrene-4,5,9,10-tetraone (0.5 g, 1.91 mmol) and 4,5-dimethyl-1,2-diaminobenzene (0.65 g, 4.77 mmol, 2.5 eq.) were suspended in acetic acid (50 mL) and the solution was refluxed for 48 h. After cooling, the solvent was removed under reduced pressure. Water was added and the precipitate was filtered off, washed with water and pentane. The solid was dissolved in concentrated HNO₃ (10 mL) and the solution was refluxed overnight. After cooling, the orange precipitate was filtered off, washed with pentane and dried under vacuum (0.81 g, 92% yield). ¹H NMR (CDCl₃) δ (ppm): 2.59 (s, 12H), 7.99–8.10 (m, 6H), 9.53 (s, 4H); HRMS (ESI MS) *m/z*: theor: 458.2035 found: 458.2037 (M^{+.} detected); Anal. Calc. for C₃₆H₂₆ : C, 94.3; H, 5.7; Found: C, 94.5; H, 5.5%.

2.2. Chemical compounds

N-vinylcarbazole (NVK), diphenyliodonium hexafluorophosphate (Ph₂I⁺ or Iod), N-methyldiethanolamine (MDEA), phenacylbromide (R-Br), tris(trimethylsilyl)silane ((TMS)₃SiH) and 2,4,6-tris(trichloromethyl)-1,3,5-triazine (Tz or R'-Cl) were obtained from Aldrich with the best purity available and used as received (Scheme 2). (3,4-epoxycyclohexane)methyl 3,4epoxycyclohexylcarboxylate (EPOX; Uvacure and 1500) trimethylol-propane triacrylate (TMPTA) were obtained from Cytec (Scheme 2); these monomers were selected as benchmark multifunctional monomers for cationic and radical polymerizations, respectively. The formation of polymer networks at room temperature is expected preventing a full conversion of the reactive functions [1]. The polymerization of methacrylates was also investigated: bisphenol A-glycidyl methacrylate (Bis-GMA) and triethyleneglycol dimethacrylate (TEGDMA) were obtained from Aldrich and used with the highest purity available.

2.3. 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/





cm²; in the 370–800 nm range); ii) monochromatic light delivered by a laser diode at 405 nm ($I_0 \approx 2 \text{ mW/cm}^2$) and iii) LEDs @385 and 395 nm (ThorLabs; $I_0 \approx 10 \text{ mW/cm}^2$) and @405 nm (ThorLabs; $I_0 \approx 110 \text{ mW/cm}^2$).

2.4. Free radical photopolymerization (FRP) of acrylates

The experiments were carried out in laminated conditions or under air. The prepared formulations deposited on a BaF₂ pellet (25 μ m thick) were irradiated (see the irradiation devices). The evolution of the double bond content was continuously followed by real time FTIR spectroscopy (JASCO FTIR 4100) at about 1630 cm⁻¹ as in Ref. [22].

2.5. The ring opening polymerization of epoxy

The photosensitive formulations were deposited (25 μ m thick) on a BaF₂ pellet under air. The evolution of the epoxy group content was continuously followed by real time FTIR spectroscopy (JASCO FTIR 4100) at about 790 cm⁻¹, respectively [22].



Fig. 1. UV-visible absorption spectra of PH_1, PH2, PH_3, PH_4 in CHCl₃.

2.6. Computational procedure

All the molecular orbital (MO) 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 [23]. The geometries were frequency checked.

2.7. 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 light exposure (see the irradiation devices) under N₂ and trapped by phenyl-*N-tert*-butylnitrone (PBN) according to a procedure described in detail in Ref. [24]. The ESR spectra simulations were carried out with the PEST WINSIM program.

2.8. Fluorescence experiments

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

2.9. Redox potentials

The redox potentials (vs. SCE) were measured in acetonitrile by cyclic voltammetry with tetrabutyl-ammonium hexa-fluorophosphate 0.1 M as a supporting electrolyte. The free energy

Table 1
Molar extinction coefficients (in M^{-1} cm ⁻¹) of PH_1 to PH_4 at typical irradiation
device wavelengths (LEDs @365_385_395 or 405 nm or laser diode@405 nm)

	LED@365 nm	LED@385 nm	LED@395 nm	Laser diode or LED@405 nm
PH_1	16 300	19 000	17 900	19 100
PH_2	8100	9100	10 300	9980
PH_3	17 100	20 900	19 100	19 600
PH_4	10 300	14 100	20 050	15 300



Fig. 2. Molecular Orbitals involved in the lowest energy transition.

change ΔG_{et} for an electron transfer reaction is calculated from the classical Rehm-Weller equation (Eq. (1)) [25] where E_{ox} , E_{red} , E_{s} and C are the oxidation potential of the donor, the reduction potential of the acceptor, the excited state energy (singlet or triplet state) and

$$\Delta G_{\rm et} = E_{\rm ox} - E_{\rm red} - ES + C \tag{1}$$



Fig. 3. Photolysis of (A) **PH_2**/lod; (B) **PH_3**/lod; (C) **PH_4**/lod upon a laser diode@405 nm for irradiation times of 0, 1, 3 and 5 min; [lod] = 0.037 M in acetonitrile/chloroform 25 V/75 V.

Table 2

Oxidation potentials (E_{ox}); singlet state energy levels (E_{S1} from the UV and fluorescence spectra); triplet state energy levels (E_{T1} calculated at UB3LYP/6-31G* level) and free energy changes ΔG_{et} for the ¹PH/lod and ³PH/lod interactions.

PH	E _{S1} (eV)	E _{T1} (eV)	E _{ox} (V) SCE	$\Delta G_{\rm et}$ (¹ PH/ Iod) (eV)	$\Delta G_{\rm et}$ (³ PH/ Iod) (eV)
PH_1	3.01	2.39	a	а	а
PH_2	2.93	2.38	0.61	-2.12	-1.57
PH_3	2.96	2.25	0.32	-2.44	-1.73
PH_4	2.91	2.2	0.67	-2.04	-1.33

^a The solubility is poor in acetonitrile preventing accurate electrochemistry measurements.

3. Results and discussion

3.1. Light absorption properties of the different PHs

The UV–Vis absorption spectra of the proposed **PH**s are depicted in Fig. 1; the maximum absorption wavelengths are gathered in Table 1. All these proposed structures exhibit good to excellent light absorption properties in the 350–425 nm; their respective extinction coefficients for typical irradiation devices (LEDs @365, 385, 395, 405 nm or laser diode@405 nm) are gathered in Table 1.

Molecular orbital MO calculations show that the lowest energy transition exhibits a $\pi \rightarrow \pi^*$ character and involves strongly delocalized molecular orbitals (Fig. 2) in full agreement with the enhanced light absorption properties of these derivatives compared to the phenazine which exhibit only UV light absorption i.e. the associated absorption spectrum presents band at 365 nm with shoulders at 351 and 387 nm [27].

3.2. Photoreactivity for the PH/iodonium salt systems

The PH/Iod solutions are characterized by photolysis experiments upon light exposure; this behavior is clearly observed upon a diode laser@405 nm exposure in Fig. 3. For **PH_1**/Iod, no photolysis is detected. For a similar absorption at 405 nm, the photolysis rate follows the series **PH_3** ~ **PH_4** >> **PH_2** or **PH_1**. A similar trend is observed for the polymerization rate (see below) when using the PH/Iod based initiating systems.

This very fast photolysis is in agreement with a favorable reduction process (r1a). Accordingly, a strong ¹**PH_4**/lod fluorescence quenching is shown with a Stern–Volmer coefficient k_q , $\tau_0 = 16.5 \text{ M}^{-1}$ (Fig. 1 in supporting information; k_q and τ_0 stand for



Fig. 4. ESR-Spin Trapping spectrum of **PH_2/lod**; LED@395 nm exposure; experimental (a) and simulated (b) spectra. Phenyl-N-*tert*-butylnitrone (PBN) is used as spin trap; under N₂. The hyperfine coupling constants *hfcs* are $a_N = 14.2$ G; $a_H = 2.2$ G for the PBN adduct of phenyl radical in agreement with [28].

Table 3

Free Radicals observed in ESR spin-trapping experiments for different photoinitiating systems in *tert*-butylbenzene (spin trap = PBN).

Photoinitiating system	PBN radical adduct	Hyperfine coupling constants <i>hfcs</i>
PH/Iod	Ph	$a_{\rm N} =$ 14.2 G; $a_{\rm H} =$ 2.2 G
PH/Iod/NVK	Ph-NVK	$a_{\rm N} =$ 14.5 G; $a_{\rm H} =$ 2.5 G
PH/Iod/(TMS)₃SiH	(TMS)₃Si	$a_{\rm N} =$ 14.8 G; $a_{\rm H} =$ 5.5 G

the rate constant of interaction and the fluorescence lifetime, respectively). The electron transfer quantum yield Φ_{eT} for r1a calculated according to $\Phi_{eT} = k_q \tau_0 [\text{Iod}]/(1 + k_q \tau_0 [\text{Iod}])^1$ is high for ¹**PH_4**/Iod ($\Phi_{eT} \sim 0.5$ for [Iod] ~ 0.07 M in polymerization experiments – see below). The ΔG_{et} for r1a (Table 2) were evaluated according to the Rehm-Weller equation (Eq. (1)). A reduction potential of -0.2 V was used for Ph₂I⁺ according to the literature value [1]. A triplet state pathway can not be ruled out i.e. the associated $\Delta G_{et}(^{3}\text{PH}/\text{Iod})$ being also highly negative (see Table 2).



Fig. 5. Photolysis of a **PH_4**/MDEA solution upon a laser diode@405 nm for irradiation times of 0, 1, 3, 5 and 10 min; [MDEA] = 0.1 M in chloroform.



Fig. 6. ESR-Spin Trapping spectrum of **PH_2**/ethyldimethylaminobenzoate; LED@395 nm exposure; experimental (a) and simulated (b) spectra. Phenyl-N-*tert*-butylnitrone (PBN) is used as spin trap; under N₂. The hyperfine coupling constants are $a_{\rm N} = 14.3$ G; $a_{\rm H} = 2.4$ G for the PBN adduct of the aminoalkyl radical in agreement with [28].



Fig. 7. ESR-Spin Trapping spectrum of **PH_2**/phenacylbromide; LED@395 nm exposure; experimental (a) and simulated (b) spectra. Phenyl-N-*tert*-butylnitrone (PBN) is used as spin trap; under N₂. The hyperfine coupling constants are $a_N = 14.6$ G; $a_H = 4.4$ G for the PBN adduct of the phenacyl radical in agreement with [28].

(r1a) being favorable for all the **PH**s, the difference observed in their photolysis rates can be ascribed to a back electron transfer process (r1b) that is affected by the **PH** structure.

 ${}^{1,3}\mathbf{PH} + \mathbf{Ph}_{2}\mathbf{I}^{+} \rightarrow \mathbf{PH}^{*+} + \mathbf{Ph}_{2}\mathbf{I}^{*}$ (r1a)

 $\mathbf{PH}^{+} + \mathbf{Ph}_{2}\mathbf{I}^{-} \rightarrow \mathbf{PH} + \mathbf{Ph}_{2}\mathbf{I}^{+}$ (r1b)

 $Ph_2I' \rightarrow Ph' + Ph-I$ (r1c)

The processes r1a, r1c are also in agreement with the observation of phenyl radicals upon irradiation of the four **PH**/lod solutions in ESR-spin trapping experiments (Fig. 4).

In the PH/Iod/NVK three-component system, Ph-NVK[•] radicals are observed in agreement with (r1d) (Table 3). In PH/Iod/(TMS)₃₋ SiH, silyl radicals ((TMS)₃Si[•]) are formed (r1e) (Table 3).

$$Ph' + NVK \rightarrow Ph-NVK'$$
 (r1d)

$$Ph' + (TMS)_3SiH \rightarrow Ph-H + (TMS)_3Si'$$
(r1e)

3.3. Photoreactivity of the PH/amine systems

The **PH**/amine solutions are characterized by an efficient photolysis upon a diode laser@405 nm (Fig. 5). This photolysis is associated with the observation of aminoalkyl radicals in ESR-spin trapping experiments (Fig. 6) in agreement with r2. Accordingly, strong ¹**PH**/amine fluorescence quenchings are observed (Fig. 2 in supporting information) e.g. a Stern–Volmer coefficient k_q . $\tau_0 = 5.5 \text{ M}^{-1}$ is found for ¹**PH**_4/MDEA; the associated electron transfer quantum yield Φ_{eT} for r2 is very high (~0.6) for [MDEA] ~ 0.25 M in polymerization experiments.

$1,3$
PH + MDEA \rightarrow PH⁻ + MDEA⁺ \rightarrow PH-H⁻ + MDEA^(-H) (r2)

In the **PH**/amine/phenacylbromide (R–Br) three-component system, the phenacyl radical is also clearly observed in the ESR-spin trapping experiments (Fig. 7). This shows the occurrence of r3 in addition to r2. Using Tz (noted R'-Cl in Scheme 2) instead of R–Br, a similar behavior can be expected.

$$^{1,3}\mathbf{PH} + \mathbf{R} - \mathbf{Br} \text{ (or } \mathbf{R'} - \mathbf{Cl}) \rightarrow \mathbf{PH'}^+ + (\mathbf{R} - \mathbf{Br})^{\bullet-} \text{ (or } \mathbf{R'} - \mathbf{Cl}^{\bullet-})$$
(r3a)

PH-H' + R-Br (or R'-Cl)
$$\rightarrow$$
 PH + **H**⁺ + (R-Br)⁻ (or R'-Cl⁻) (r3b)

$$R-Br^{\bullet-} (or R'-Cl) \rightarrow R^{\bullet} + Br^{-} (or R'^{\bullet} + Cl^{-})$$
(r3c)

3.4. The initiation steps using the PH based photoinitiating systems

For the ROP of epoxides, PH^{+} can be considered as the initiating species when using the PH/lod combinations (see r1a). In the PH/



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Fig. 8. ROP profiles of **EPOX** under air upon (A) a LED@385 nm exposure in the presence of (1) **PH_3**/lod (0.5%/3% w/w); (2) **PH_4**/lod (0.5%/3%/3% w/w); (3) **PH_3**/lod/(TMS)₃SiH (0.5%/3%/3% w/w); (4) **PH_4**/lod/(TMS)₃SiH (0.5%/3%/3% w/w). (B) A LED@395 nm lamp exposure in the presence of (1) **PH_4**/lod (0.5%/3% w/w); (2) **PH_4**/lod/(TMS)₃SiH. Insert: conversion of Si–H for run (2).



Fig. 9. ROP profiles of EPOX under air upon a halogen lamp exposure in the presence of (A) (1) PH_4/lod (0.5%/3% w/w); (2) PH_4/lod/NVK (0.5%/3%/3% w/w); (B) conversion of NVK for run (2) in (A).

Iod/NVK and PH/Iod/(TMS)₃SiH three-component systems, Ph-NVK and (TMS)₃Si⁻ are oxidized by the iodonium salt to generate the Ph-NVK⁺ and (TMS)₃Si⁺ cations, respectively. These latter species are very efficient to initiate a ring opening polymerization (ROP). The relative efficiencies of the different **PH**/Iod/NVK (or (TMS)₃SiH) combinations (see below) should be affected by i) the relative **PH** light absorption properties, ii) the radical or radical cation formation quantum yields, iii) the possible back electron transfer (r1b) and iv) the relative ability of **PH**⁺⁺ to initiate a ROP process.

The aminoalkyl and phenacyl radicals generated in the **PH**/ amine or **PH**/amine/phenacylbromide systems through r2, r3 can initiate the FRP. The relative **PH** light absorption properties as well as the radical formation quantum yields in r2 and r3 will affect the performance of the **PH** in the different systems.

3.5. ROP of EPOX

The conversion-time profiles of EPOX under air under exposure to LEDs or a halogen lamp are shown in Figs. 8 and 9; the conversions reached after 1000 s of irradiation are gathered in Table 4.

When using the different **PH**/lod initiating systems, the polymerization does not occur (e.g. Fig. 8A curves 1 and 2; Table 4). This shows the low ability of **PH**⁺⁺ generated in r1a to initiate a ROP process. The presence of NVK or (TMS)₃SiH drastically improves the polymerization profiles (e.g. Fig. 8A curve 1 vs. curve 3 and Table 4) i.e. the cations Ph-NVK⁺ and (TMS)₃Si⁺ are now the initiating species. The consumption of the Si–H and NVK functions (Figs. 8B and 9B) in the course of the photopolymerization is in line with r1d and r1e. With **PH_3** (or **PH_4**)/lod/NVK (or (TMS)₃SiH), tack free

Table 4

Final conversion reached after 1000 s of irradiation using different photoinitiating systems.

PISs (0.5%/3% w/w or 0.5%/3%/3% w/w)	LED@385 nm	LED@395 nm	Laser diode @405 nm	Halogen lamp
PH_1/lod or PH_1/lod/ (TMS)₃SiH	np		np	np
PH_2/lod or PH_2/lod/ (TMS) ₃ SiH	np		np	np
PH_3/lod	np	np		np
PH_3/lod/(TMS)₃SiH	50%	52%		52%
PH_3/Iod/NVK	35%			
PH_4/lod	np	np	np	np
PH_4/Iod/(TMS)₃SiH	48%	57%	50%	60%
PH_4/Iod/NVK	38%			52%

np: No polymerization.

coatings are obtained. The efficiency of the different phenazine derivatives decreases in the series **PH_3~PH_4** >> **PH_1**, **PH_2**.

3.6. Free radical photopolymerization of acrylates and methacrylates

The conversion-time profiles of TMPTA in laminate under a diode laser@405 nm are shown in Figs. 10–12. Only the **PH_3** and **PH_4** based three-component systems (**PH**/MDEA/R–Br) lead to good polymerizations (Fig. 10 curves 5 and 6; final tack-free coating with **PH_4**/MDEA/RBr). The efficiency decreases in the series **PH_4** > **PH_3** >> **PH_2**, **PH_1**. Interestingly, in the PH/MDEA/alkyl halide three-component systems, the 2,4,6-*tris*(trichloromethyl)-1,3,5-triazine (Tz) is an additive better than the phenacylbromide (Fig. 11, curve 1 vs. curve 2; a tack free coating is obtained).

The **PH_**3/MDEA/Tz (0.5%/3%/3% w/w) system is also excellent to initiate radical polymerization of acrylates upon LED@405 nm (Fig. 12). The intensity of this latter LED (~110 mW/cm²) ensures excellent polymerization profiles. The performance of this **PH_**3/MDEA/Tz system for the polymerization of methacrylates (i.e. Bis-GMA/TEGDMA blend (70%/30%, w/w)) is also remarkable with a final conversion of ~60% under air (Fig. 12) i.e. this demonstrates the high performance of this initiating system to overcome the oxygen inhibition.



Fig. 10. FRP profiles of TMPTA in laminated conditions upon exposure to a laser diode@405 nm in the presence of (1) PH_1/MDEA/RBr; (2) PH_2/MDEA/RBr (0.5%/3%/ 3% w/w); (3) PH_3/MDEA; (4) PH_4/MDEA (0.5%/3% w/w); (5) PH_3/MDEA/RBr; (6) PH_4/MDEA/RBr (0.5%/3%/ w/w).

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Fig. 11. FRP profiles of TMPTA in laminate upon exposure to a laser diode@405 nm in the presence of (1) **PH_4**/MDEA/RBr or (2) **PH_4**/MDEA/Tz (0.5%/3%/3% w/w).

3.7. Synthesis of interpenetrated polymer networks (IPNs)

The synthesis of IPNs was also carried out (Fig. 13). High conversions for both the acrylate and the epoxide functions were obtained using the **PH_4** (or **PH_3**)/Iod/NVK system; tack free coatings). The formations of free radicals and cations (see above) ensure the simultaneous radical and ROP processes.

4. Conclusion

This paper shows that novel phenazine derivative based threecomponent photoinitiating systems allow efficient radical polymerization of TMPTA, cationic polymerization of EPOX and TMPTA/ EPOX interpenetrated polymer network synthesis upon exposure to easily accessible, energy saving and cheap LEDs at 385, 395 and 405 nm as well as a laser diode at 405 nm or a halogen lamp. Their photochemical reactivity toward the production of initiating species is rather good. Their excellent absorption properties in the 380–425 nm range resulting from the presence of strongly



Fig. 12. FRP profiles of TMPTA in laminate (1) or Bis-GMA/TEGDMA (70%/30%, w/w) under air (2) upon exposure to a LED@405 nm in the presence of **PH_3**/MDEA/Tz (0.5%/ 3%/3% w/w).



Fig. 13. Polymerization profiles of an EPOX/TMPTA blend (50%/50% w/w) upon a halogen lamp exposure in the presence of **PH_4**/lod/NVK (0.5%/3%/3% w/w); in laminate.

delocalized molecular orbitals are promising for the development of other derivatives exhibiting a red-shifted absorption.

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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.polymer.2014.04.005.

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