# Macromolecules

# New Cleavable Photoinitiator Architecture with Huge Molar Extinction Coefficients for Polymerization in the 340–450 nm Range.

Mohamad-Ali Tehfe,<sup>†</sup> Frédéric Dumur,<sup>‡</sup> Bernadette Graff,<sup>†</sup> Jean-Louis Clément,<sup>‡</sup> Didier Gigmes,<sup>\*,‡</sup> Fabrice Morlet-Savary,<sup>†</sup> Jean-Pierre Fouassier,<sup>§</sup> and Jacques Lalevée<sup>\*,†</sup>

<sup>†</sup>Institut de Science des Matériaux de Mulhouse IS2M, LRC CNRS 7228, UHA, 15, rue Jean Starcky, 68057 Mulhouse Cedex, France <sup>‡</sup>CNRS, Institut de Chimie Radicalaire, Aix-Marseille Université, UMR 7273, F-13397 Marseille, France <sup>§</sup>UHA-ENSCMu, 3 rue Alfred Werner 68093 Mulhouse, France

**S** Supporting Information

**ABSTRACT:** A new Type I photoinitiator **Tr\_DMPA** is described. It consists in three 2,2'-dimethoxy 2-phenyl acetophenone (DMPA) units grafted onto a truxene (**Tr**) scaffold. Compared to DMPA itself, the lowest electronic transition exhibits a  $\pi\pi^*$  character and the corresponding molar extinction coefficients  $\varepsilon$  are increased from about 400  $M^{-1}$  cm<sup>-1</sup> (at about 332 nm for DMPA) to 63 000  $M^{-1}$  cm<sup>-1</sup> (at 338 nm for **Tr\_DMPA**); such huge values are exceptional in Type I photoinitiators at this wavelength. **Tr\_DMPA** undergoes a fast cleavage and efficiently initiate an acrylate polymerization upon a Xe–Hg lamp, a halogen lamp or a laser diode exposure at 405 nm (upon very low light intensities: 2– 12 mW/cm<sup>2</sup>) in the 300–450 nm range. The polymerization



of epoxides or divinylethers is also feasible in the presence of an iodonium salt at 405 nm where reference photoinitiators cannot efficiently operate. The chemical mechanisms analyzed by ESR, fluorescence, steady state photolysis, and laser flash photolysis experiments are discussed.

# INTRODUCTION

The design of photoinitiator PI of free radical polymerization FRP, cationic polymerization CP, free radical promoted cationic photopolymerization FRPCP and to a lesser extent anionic polymerization, acid and base cross-linking has received a considerable attention in the last 50 years (see ref 1 (up-to-date situation) and other books<sup>2</sup>). Both the amount of light absorbed  $I_{abs}$  by PI (together with the absorption wavelength range) and the PI reactivity are obviously the crucial key points for the design of high performance systems, the quantity I<sub>abs</sub> depending on both the wavelength ( $\lambda$ ) and the molar extinction coefficients ( $\varepsilon$ ). Therefore, the search of new high performance compounds has been continuously considered as of prime importance for many years. Two directions were used:<sup>1</sup> (i) search for new structures and (ii) modification of starting structures. Today, many chemical families of PI with characteristic  $\lambda$  and  $\varepsilon$  have been developed and the discovery of really new structures (exhibiting novel cleavable bonds, chromophores or electron/hydrogen atom donors/acceptors...) with improved absorption properties remains a challenge. Some recent achievements include the proposal of novel systems, e.g., C-Ge<sup>3</sup> or C-Si, Si-Si bond<sup>4</sup> containing PIs, graphitic carbon nitride or fullerenes,<sup>5</sup> NHCboranes.<sup>6</sup>

On the opposite, the modification of starting structures is more easily accessible. Indeed, structural changes in existing classes of highly reactive PIs already allowed (to some extent) a red-shift of the absorption and/or an increase of the  $\varepsilon$ . They are usually realized,<sup>1</sup> and, as still exemplified in very recent papers, through, e.g., (i) the introduction of suitable substituents (e.g., in triazine,<sup>7</sup> thioxanthone,<sup>8</sup> coumarin,<sup>9</sup> xanthone,<sup>10</sup> disulfone,<sup>11</sup> benzophenone,<sup>12,13</sup> 1,4-naphtoquinone,<sup>14</sup> pyridinium salt,<sup>15,16</sup> ferrocenium salt,<sup>17</sup> pyrromethene derivatives,<sup>18</sup> in modified hydrocarbons,<sup>19</sup> titanocenes,<sup>20</sup> dyes,<sup>21–23</sup> metal carbonyls,<sup>24</sup> iridium,<sup>25</sup> and platinium<sup>26</sup> or zinc complexes;<sup>27</sup> the older complete investigation of electronic effects in the series of hydroxyl alkyl phenyl ketones HAP or morpholinoketones<sup>2d</sup> remains a nice example), (ii) the incorporation of substituents or spacers that can enhance the  $\pi$  electron delocalization (e.g., a double or triple bond between a phenyl and a carbonyl group,<sup>28</sup> a triple bond linked to a thioxanthone and a silane group,<sup>29</sup> a thioxanthone-diphenylanthracene,<sup>30</sup> modified thioxanthones,<sup>31</sup> sulfur containing benzophenones,<sup>32</sup> sulfides<sup>33</sup>), (iii) the synthesis of difunctional derivatives DfcPI (e.g., by coupling two HAP moieties with a very small spacer),<sup>34</sup> (iv) the construction of bifunctional compounds BfcPI (e.g., benzophenone–sulfonyl ketone,<sup>35</sup> thioxanthone–anthracene,<sup>36</sup> thioxanthone–fluorene

Received: November 26, 2012 Revised: December 29, 2012

#### Scheme 1



or –carbazole,<sup>37</sup> thioxanthonemethyl–carboxylate,<sup>38</sup> keto oxime ester–eosin,<sup>39</sup> triazine derivative-dye,<sup>40</sup> Ir complex–Ru complex,<sup>41</sup> Ir complex–coumarin moiety<sup>42</sup>) or double photochromic initiator,<sup>43</sup> and (v) the coupling of several conjugated units (e.g., multifunctional thiophene and related compounds).<sup>44,45</sup>

In all these examples, (i) the absorption is often red-shifted (up to 30-40 nm in some cases), (ii) the  $\varepsilon$  are often higher

(sometimes noticeably), (iii) the practical polymerization efficiency is usually better (as a consequence of a better light absorption), and (iv) the photochemical reactivity can be compared to that of the parent compounds (except in cases where the novel molecular orbitals arrangement induces a complete change of the excited state properties).

A fascinating question is the following: is it still possible (and how) to boost the  $\varepsilon$  and/or the  $\lambda$  red-shift of existing PIs? For example, let us consider the near UV-visible light (360-430 nm) induced FRP area. In a general way, PIs are based on small molecular structures (e.g., aromatic ketones) but macro PIs (oligomeric, polymeric or dendritic PIs) have also been mentioned. They are usually classified as Type I PIs (cleavable compounds), Type II PIs (PI/hydrogen donor couples) and multicomponent PIs (e.g., PI/electron or hydrogen donor/ additive). A very recent account has shown an interesting and promising achievement using a new trifunctional architecture TfcPI where the molecular orbitals MOs of the core are coupled with those of three PI moieties (in macroPIs, the coupling between the PI units is inexistent). The first examples of such TfcPIs involved (i) a truxene structure as the core and benzophenone (Tr BP) or thioxanthone (Tr TX)<sup>46</sup> as possible PI units or (ii) a trichloromethyl triazine substituted by three benzophenone, anthracene or pyrene moieties.<sup>47</sup> These TfcPIs give rise to Type II PIs.

In the present paper, we look for a possible Type I PI (i) being able to absorb in the near UV-visible range (typically 340-450 nm range) where particular LEDs, halogen lamps or laser diodes operate, (ii) exhibiting huge  $\varepsilon$  values, and (iii) potentially keeping a high photochemical reactivity (e.g., efficient cleavage process). We propose to modify the well-known PI referred as DMPA (2,2'-dimethoxy-2-phenyl acetophenone) which undergoes a fast  $\alpha$ -cleavage (within 100–200 ps)<sup>48</sup> and behaves as a very efficient PI in acrylate photopolymerization.<sup>2d</sup> This will be realized through a grafting of three DMPA units onto a truxene scaffold (Tr DMPA in Scheme 1; as seen below in Scheme 2, this compound rather consists in a mixture of four regioisomers). The ability of Tr DMPA as photoinitiator/photosensitizer for the FRP of acrylates and the cationic polymerization of epoxides and vinylethers under very soft irradiation conditions (Xe-Hg lamp, halogen lamp, laser diode, LED) as well as the associated excited state processes will be investigated by steady state photolysis, laser flash photolysis, fluorescence and ESR experiments.

# EXPERIMENTAL SECTION

i. Synthesis of Tr\_DMPA. 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. <sup>1</sup>H and <sup>13</sup>C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole: <sup>1</sup>H (400 MHz) and <sup>13</sup>C (100 MHz). The <sup>1</sup>H chemical shifts were referenced to the solvent peak DMSO- $d_6$  (2.49 ppm) and the <sup>13</sup>C chemical shifts were referenced to the solvent peak DMSO- $d_6$  (39.5 ppm). Monoacetal of aromatic diketone was synthesized by adapting a literature procedure.<sup>49</sup> 2,7,12-Tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahexyltruxene was prepared following a procedure previously reported in the literature without modification and with similar yields.<sup>50</sup> The new photoinitiator was synthesized by adapting a literature procedure.<sup>51</sup>

1-(4-Bromophenyl)-2-phenylethanone. A 5 g (36.7 mmol) sample of 2-phenylacetic acid was suspended in 20 mL of thionyl chloride, and a



few drops of DMF were added. The reaction was refluxed until no evolution of fumes evolves. Excess of thionyl chloride was removed under reduced pressure and 20 mL (190.4 mmol) of bromobenzene were added. The solution was diluted with 20 mL of chloroform and cooled to 0 °C. Then 5 g (37.5 mmol) of AlCl<sub>3</sub> was added in one portion, and the reaction mixture was stirred at room temperature for 1 h. The solution was then heated at 80 °C overnight. The solution was quenched onto ice, extracted several times with DCM. The residue was purified by column chromatography using DCM/pentane = 1/3 as the eluent. A brown oil was isolated in quantitative yield (10 g, 99% yield). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were consistent with those previously reported.<sup>52</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 4.24 (s, 2H), 7.20–7.34 (m, 5 H), 7.59 (d, 2H, J = 8.4 Hz), 7.85 (d, 2H, J = 8.4 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ (ppm): 45.5, 127.1, 128.2, 128.8, 129.4, 130.2, 132.0, 134.2, 135.3, 196.6; HRMS (ESI MS) m/z: theor, 275.0066; found, 275.0068 ([M + H]<sup>+</sup> detected).

1-(4-Bromophenyl)-2-phenylethane-1,2-dione. A 3 g (10.9 mmol) sample of 1-(4-bromophenyl)-2-phenylethanone was dissolved in 20



mL of DMSO, 10 mL of water, and 20 mL of HBr in acetic acid. The solution was heated at 90 °C overnight. After cooling, the solution was poured onto ice. The solution was extracted with ether several time, the organic phases were combined, washed with water, dried over magnesium sulfate and the solvent removed under reduced pressure providing black oil. The residue was purified by column chromatography (SiO<sub>2</sub>) using CH<sub>2</sub>Cl<sub>2</sub>:pentane = 1:3 as the eluent and yielded light brown oil (2.58 g, 82% yield). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were consistent with those previously reported. <sup>53</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 7.52 (t, 2H, *J* = 7.9 Hz), 7.65–7.68 (m, 3H), 7.85 (d, 2H, *J* = 8.6 Hz), 7.96 (d, 2H, *J* = 7.1 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 129.0, 129.8, 130.3, 131.1, 131.6, 132.3, 132.6, 134.9, 193.1, 193.7. HRMS (ESI MS) *m/z*: theor, 288.9859; found, 288.9855 ([M + H]<sup>+</sup> detected).

2-(4-Bromophenyl)-2,2-dimethoxy-1-phenylethanone and 1-(4-Bromophenyl)-2,2-dimethoxy-2-phenylethanone. A 3 g (10.4 mmol)



sample of 1-(4-bromophenyl)-2-phenylethane-1,2-dione was dissolved in 1.5 mL (2.47 g, 2 equiv) of thionyl chloride and the solution was cooled to 0 °C. Then 1.68 mL (1.33 g, 4 equiv) was added over 2 h. After addition, the solution was allowed to warm to room temperature and the solution was stirred at 50 °C for 1h30. The solution was diluted with 4 mL of 2-propanol and 0.26 g (1.88 mmol) of potassium carbonate and 0.1 mL of trimethylphosphite were added. The reaction was stirred at room temperature overnight. All volatiles were removed under reduced pressure and the residue was diluted with water, extracted with ether several times. The organic phases were combined, dried over magnesium sulfate and the solvent removed under reduced pressure. The residue was purified by column chromatography (SiO<sub>2</sub>) using a gradient of solvent from DCM:pentane = 1:1 to DCM:acetone = 1:1. Monoacetal of diketone was obtained as a mixture of two regioisomers (2.50 g, 72% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 3.21 (s, 12H), 7.28-7.38 (m, 6H), 7.42–7.49 (m, 5H), 7.59 (d, 2H, J = 7.8 Hz), 7.94 (d, 2J, J = 8.6 Hz), 8.04 (d, 2H, J = 7.5 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 50.0, 103.2, 103.4, 123.2, 126.7, 128.08, 128.13, 128.5, 128.6, 129.8, 131.4, 131.5, 131.7, 132.7, 133.0, 133.9, 136.0, 136.4, 194.0, 194.5. HRMS (ESI MS) *m*/*z*: theor, 357.0097; found, 357.0095 ([M + Na]<sup>+</sup> detected).

*Tr\_DMPA*. To a mixture of 1-(4-bromophenyl)-2,2-dimethoxy-2-phenylethanone and 2-(4-bromophenyl)-2,2-dimethoxy-1-phenylethanone (1.07 g, 3.2 mmol) and 2,7,12-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahexyltruxene (980 mg, 0.8 mmol) in THF (80



mL) were added Pd(PPh<sub>3</sub>)<sub>4</sub> (60 mg) and aqueous KOH solution (5 mL, 2 M). The mixture was refluxed for 48 h under nitrogen. Then the mixture was poured into water. The aqueous layer was extracted with CHCl<sub>3</sub>. The combined organic phase was washed with brine and dried  $(MgSO_4)$ . The residue was purified by column chromatography  $(SiO_2)$ using DCM:acetone = 1:1 as the eluent. During evaporation, a light brown solid formed. A yield of 1.13 g of photoinitiator was obtained as a mixture of four regioisomers (88% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 0.52-0.59 (m, 18H), 0.75-1.10 (m, 48H), 2.12-2.17 (m, 6H), 2.95-3.01 (m, 6H), 3.22-3.29 (m, 18H), 7.28-8.24 (m, 36H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ (ppm): 13.8, 22.18, 22.28, 22.35, 22.39, 23.8, 29.4, 31.3, 37.0, 50.0, 50.1, 55.8, 103.3, 103.6, 103.7, 120.4, 120.5, 123.3, 124.8, 124.9, 126.9, 126.7, 126.8, 126.9, 126.93, 127.1, 127.2, 127.5, 127.74, 127.80, 127.86, 128.04, 128.08, 128.16, 128.2, 128.48, 128.54, 128.7, 128.87, 128.9, 129.88, 129.94, 129.98, 130.0, 130.3, 130.6, 130.7; 131.5, 131.7, 132.64, 132.68, 132.8, 132.9, 133.0, 134.0, 134.2, 134.3, 136.0, 137.0, 137.6, 137.7, 137.9, 140.3, 145.42, 145.45, 145.48, 145.7, 154.3, 194.5, 194.7, 195.0, 195.1. HRMS (ESI MS) m/z: theor, 1631.9764; found,  $1631.9762 ([M + Na]^+ detected).$ 

The four expected regioisomers  $(I_1-I_4)$  resulting from the Suzuki cross coupling reaction of 2-(4-bromophenyl)-2,2-dimethoxy-1-phenyl-ethanone and 1-(4-bromophenyl)-2,2-dimethoxy-2-phenylethanone with 2,7,12-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-hexahexyltruxene are depicted in Scheme 2. Because of the lack of selectivity during the acetalization reaction of the diketones, an equimolecular amount of the two possible brominated DMPA was obtained as clearly evidenced by NMR spectroscopy. During the Suzuki cross-coupling reaction and based on a similar reactivity of the two brominated DMPA, a mixture of four unseparable regioisomers (1:3:3:1 ratio) was expected, two of these regioisomers corresponding to the photoinitiator with the three acetal functions close or far from the truxene core, the two others corresponding to mixture of position. Ratio of each of the regioisomers could not be experimentally established due to the superimposition of their respective NMR signals.

**ii. Other Chemical Compounds.** 2,2-Dimethoxy-2-phenylacetophenone (DMPA from Aldrich) and a bisacylphosphineoxide (BAPO from BASF) were used as reference Type I photoinitiators. Methyldiethanolamine (MDEA) was obtained from Aldrich and [methyl-4 phenyl(methyl-1-ethyl)-4-phenyl] iodonium tetrakis (penta fluorophenyl) borate<sup>54</sup> (Iod) from Bluestar Silicones-France. (3,4epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX; Uvacure 1500 from Cytec), (epoxycyclohexylcarboxylate (EPOX; Uvacure 1500 from Cytec), (epoxycyclohexylethyl)methylsiloxane– dimethylsiloxane copolymer (EPOX-Si; from Bluestar Silicones-France; Silcolease UV POLY 200), triethylene glycol divinyl ether (DVE-3 from Aldrich), and trimethylolpropane triacrylate (TMPTA from Cytec) were selected as representative monomers (Scheme 3).

iii. Irradiation Sources. Several light sources were used: (i) polychromatic light from a halogen lamp (Fiber-Lite, DC-950 - incident light intensity:  $I_0 \approx 12 \text{ mW cm}^{-2}$ ; in the 350–800 nm range; the

emission spectrum is given in Figure S1 in the Supporting Information); (ii) polychromatic light from a Xe–Hg lamp ( $\lambda > 300$  nm;  $I_0 = 2$  mW cm<sup>-2</sup>); (iii) monochromatic light delivered by a laser diode at 405 nm (cube, continuum;  $I_0 \sim 12$  mW cm<sup>-2</sup>).

iv. Free Radical Photopolymerization Experiments. Trimethylolpropane triacrylate (TMPTA from Cytec) was used as a low viscosity monomer. The film polymerization experiments were carried out in laminated conditions. The films (25  $\mu$ m thick) deposited on a BaF<sub>2</sub> pellet were irradiated (see the irradiation sources above). The evolution of the double bond content was continuously followed by real time FTIR spectroscopy (JASCO FTIR 4100) at about 1630 cm<sup>-1.55</sup>

**v. Cationic Polymerization (CP).** The photosensitive formulations  $(25 \,\mu\text{m} \text{ thick})$  were deposited on a BaF<sub>2</sub> pellet under air (or in laminated conditions for DVE-3). The evolution of the epoxy group (for EPOX, EPOX-Si) and the double bond (for vinyl ether monomer) contents were continuously followed by real time FTIR spectroscopy (JASCO FTIR 4100). The formation of the polyether was well characterized at 1080 cm<sup>-1.55</sup>

**vi. Computational Procedure.** Molecular orbital calculations were carried out with the Gaussian 03 suite of programs.<sup>56</sup> 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.

**vii. Laser Flash Photolysis.** Nanosecond laser flash photolysis (LFP) experiments were carried out using a Qswitched nanosecond Nd/YAG laser ( $\lambda_{exc}$  = 355 nm, 9 ns pulses; energy reduced down to 10 mJ) from Continuum (Minilite) and an analyzing system consisting of a ceramic xenon lamp, a monochromator, a fast photomultiplier and a transient digitizer (Luzchem LFP 212).<sup>55</sup>

viii. Electron Spin Resonance (ESR). ESR spectroscopy (X-band ESR spectrometer equipped with a continuous photolysis device) was used to study the radicals generated from Tr\_DMPA upon irradiation with a Xe–Hg lamp (Lumatec) under nitrogen. A X-band spectrometer (MS 400 Magnettech) was used for the ESR spin trapping (ESR-ST) experiments (a well-established technique for the identification of the radical centers).<sup>57a,b</sup> The radicals generated by a light irradiation (Xe–Hg lamp, Hamamatsu, L8252, 150 W;  $\lambda > 310$  nm) under argon were trapped by phenyl-*N-tert*-butylnitrone (PBN), 2,3,4,5,6-pentamethylnitrosobenzene (PMNB) or 1,3,5-tri-*tert*-butyl-2-nitrosobenzene (TBNB). The ESR spectra were simulated with the PEST WINSIM program.<sup>57c</sup>

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

#### RESULTS AND DISCUSSION

**1. Photochemical Properties of Tr\_DMPA.** *1-a. Absorption and Emission Properties.* **Tr\_DMPA** is characterized by light absorption characteristics much better than those of DMPA (Figure 1): absorption maximum  $\lambda_{max} \sim 338$  nm and a molar extinction coefficient  $\epsilon_{max}$  of 63 000 M<sup>-1</sup> cm<sup>-1</sup> vs 332 nm and



Figure 1. (A) UV-visible absorption spectra of Tr\_DMPA and DMPA in toluene. Inset: zoom for DMPA. (B) HOMO and LUMO of Tr\_DMPA (UB3LYP/6-31G\* level).

~400 M<sup>-1</sup> cm<sup>-1</sup>. Therefore, **Tr\_DMPA** allows a large and efficient covering of the emission spectra of (i) the halogen lamp that mostly delivers near UV/visible light, (ii) the Xe–Hg lamp that delivers a UV–visible light ( $\lambda > 300$  nm), and (iii) the laser diode at 405 nm or LED at 395 nm. At 365 nm, a typical emission band of Hg lamps,  $\varepsilon = 31500$  M<sup>-1</sup> cm<sup>-1</sup> for **Tr-DMPA** ( $\varepsilon \sim 170$  M<sup>-1</sup> cm<sup>-1</sup> for DMPA). The ground state absorption spectrum spreads up to 450 nm with noticeable  $\varepsilon$  values: e.g., 3900 (395 nm), 2600 (405 nm), 1100 (440 nm), and 1000 (450 nm). To the best of our knowledge, **Tr\_DMPA** might be considered as the cleavable PI that exhibits the never attained highest  $\varepsilon$  values (see, in Table 1, typical examples of ( $\lambda$ ,  $\varepsilon$ ) couples for known or recently proposed Type I PIs).

Molecular orbital calculations for  $I_1$  show that (i) the strong coupling of the MOs of the DMPA units to those of the truxene core in **Tr\_DMPA** results in largely delocalized HOMO and LUMO (Figure 1B) and (ii) the allowed lowest HOMO  $\rightarrow$ LUMO electronic transition ( $\lambda_{max} = 338$  nm; oscillator strength (f) =1.68) exhibits a  $\pi \rightarrow \pi^*$  character. This is in contrast with DMPA where the forbidden  $n \rightarrow \pi^*$  transition occurs at 332 nm. As a consequence, (i) when going from DMPA to **Tr\_DMPA**, the lowest energy level moves from a  $n\pi^*$  to a  $\pi\pi^*$  state and (ii) the  $\pi \rightarrow \pi^*$  transition of **Tr\_DMPA** (338 nm) can be considered as resulting from a strong coupling of the  $\pi$  and  $\pi^*$  orbitals of DMPA and truxene (**Tr**). These results are in line with the better light absorption properties of **Tr\_DMPA** compared to DMPA. For  $I_2-I_4$ , the other regioisomers of  $Tr_DMPA$  (Scheme 2), similar properties than  $I_1$  were calculated.

The fluorescence quantum yields  $\Phi_f$  of truxene **Tr** and **Tr\_DMPA** are in a 5.5 ratio (Figure S2 in the Supporting Information). As  $\Phi_f$  (**Tr**) = 0.07,<sup>46</sup>  $\Phi_f$  (**Tr-DMPA**) is around 0.01. Time resolved fluorescence experiments lead to a first excited singlet state S<sub>1</sub> lifetime of **Tr\_DMPA**:  $\tau \sim 1.4$  ns. The S<sub>1</sub> state is quenched by the iodonium salt ( $k_q \tau = 27.4$  M<sup>-1</sup> where  $k_q$  stands for the bimolecular quenching rate constant); therefore, the  $k_q$  value ( $\sim 1.9 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup>) is close to the diffusion limit. The oxidation potential is  $E_{ox} = 1.13$  V (this work) and the calculated free energy change is negative ( $\Delta G = -1.87$  eV; using  $E_S = 3.32$  eV (extracted from the fluorescence spectrum);  $E_{red}$  (iod) = -0.2 V<sup>1</sup>). This supports an electron transfer process (eq 1a where  $Ar_2I^+$  stands for Iod) followed by the usual and known decomposition of the iodonium salt , eq1b.

$${}^{1}\mathbf{Tr}\mathbf{DMPA} + \mathbf{Ar}_{2}\mathbf{I}^{+} \to \mathbf{Tr}\mathbf{DMPA}^{\bullet+} + \mathbf{Ar}_{2}\mathbf{I}^{\bullet}$$
(1a)

and

$$\operatorname{Ar}_{2}\operatorname{I}^{\bullet} \to \operatorname{Ar}^{\bullet} + \operatorname{Ar}\operatorname{I}$$
 (1b)

1-b. The Cleavage Process of Tr-DMPA. Interestingly, upon a UV (Xe-Hg lamp) or visible light (laser diode at 405 nm) exposure, a fast bleaching of the **Tr\_DMPA** solution is observed (Figure 2): this suggests a high photoreactivity.

ESR-ST experiments (where different spin trap agents are used: PBN, TBNB, PMNB) highlight a Norrish I cleavage of **Tr\_DMPA** leading to dimethoxybenzyl derived radicals (X-Ph- $C(OMe)_2^{\bullet}$ ) and benzoyl derived radicals (X-Ph- $C(O)^{\bullet}$ ) (see eq 2). In this equation, eq2, X represents the substituent of the DMPA moiety in **Tr\_DMPA** as four regioisomers are present (Scheme 2). In the ESR experiments, the hyperfine coupling constants (*hfcs*) for the different benzoyl (or dimethoxybenzyl) spin trap adducts can not be distinguished for the different regioisomers; i.e., the *hfcs* are probably weakly affected by the nature of X.

$$TrDMPA \rightarrow X-Ph-C(=O)^{\bullet} + X-Ph-C(OMe)_{2}^{\bullet}$$

$$(h\nu)$$
(2)

Indeed, the PBN radical adduct of a benzoyl type radical ( $a_N = 14.2 \text{ G}$ ;  $a_H = 4.4 \text{ G}$ ; Figure 3A; see reference  $hfcs^{58}$ ) is observed during the irradiation of **Tr\_DMPA** in *tert*-butylbenzene. Using TBNB as a spin trap, the hfcs ( $a_N = 9.9 \text{ G}$ ;  $a_H = 1.9 \text{ G}$ ; Figure 3B) of the adduct are also in agreement with the known data for a benzoyl radical.<sup>59</sup> The presence of the dimethoxybenzyl derived radical (Ph-C(OMe)<sub>2</sub><sup>•</sup>) is revealed in Figure 3C (PMNB as a spin trap;  $a_N = 13.52 \text{ G}$ ; see reference data in ref 59). No radicals are observed in the absence of irradiation.

Upon irradiation of a **Tr\_DMPA**/Iod solution in ESR-spin trapping experiments, the PBN radical adduct of an aryl radical is observed ( $a_{\rm N}$  = 14.2 G;  $a_{\rm H}$  = 2.2 G). The aryl can be formed through reactions 1 (see above) and 3 (as a result of the known oxidation of the dimethoxybenzyl radicals generated through 2).

$$R^{\bullet} + Ar_2 I^+ \to R^+ + Ar^{\bullet} + ArI$$
(3)

Remarkably, free radicals are directly observed in ESR upon direct steady-state photolysis at low temperature (Figure 3D). This confirms an efficient formation of free radicals upon light exposure in full agreement with the Type I character of  $Tr_DMPA$ . The associated ESR spectrum, however, is a superposition of the different radicals generated in 2 for the Table 1. Examples of Ground State Absorption Wavelengths  $\lambda$  and Molar Extinction Coefficients  $\varepsilon$  of Typical Cleavable Photoinitiators<sup>*a*</sup>

Photoinitiator	$\lambda$ (nm)	$\epsilon (M^{-1}cm^{-1})$
	300	13000
	365	70
SI-SI-SI	390	6000
TX-Si		
	384	3700
Ph(C=O)-Ge(CH <sub>3</sub> ) <sub>3</sub>	411	550
	380	32000
	450	800
Titanocene		
Cl-HABI	365	400

<sup>*a*</sup>From refs 1 and 2d.



Figure 2. Photolysis of Tr\_DMPA in acetonitrile/toluene (50%/50%) under air: UV-visible absorption spectra recorded at different irradiation times. Xe–Hg lamp exposure (very low light intensity: 1 mW/cm<sup>2</sup>).

different regioisomers (Scheme 2) and will not be investigated further.

The fast decomposition of **Tr\_DMPA** in laser flash photolysis experiments prevents any systematic studies. A strong bleaching together with a partial recovery of the ground state absorption is observed at 360 nm (Figure 4) in line with the cleavage reaction 2. No triplet or radical absorption is recorded on the investigated time scale and wavelength range.

The cleavage process of **Tr\_DMPA** in the triplet state is expected to be exothermic according to the calculations (at the UB3LYP/6-31G\* level) of the triplet state energy level ( $E_T$  is 57.5 kcal/mol) and the C–C bond dissociation energy (BDE = 54.5 kcal/mol). A singlet state cleavage cannot be ruled out as the singlet state energy level is higher than  $E_T$  rendering the dissociation process more exothermic. This is in contrast with DMPA where the cleavage is considered as exclusively triplet (indeed, the  $E_T$  of DMPA is noticeably higher (experimental value, 66.2 kcal/mol;<sup>60</sup> calculated value, 68.2 kcal/mol; see in ref 1) whereas the BDE has almost the same value (56 kcal/mol)<sup>61</sup>). The lower  $E_T$  of **Tr\_DMPA** can be associated with a lower reactivity of this compound for the cleavage from the triplet state.

In the presence of Iod  $(3 \times 10^{-2} \text{ M})$  as in the polymerization experiments (see below), the quenching of S<sub>1</sub> by Iod competes  $(k_q[\text{Iod}] \sim 10^9 \text{ s}^{-1})$  with the intersystem crossing  $k_{\text{isc}}$ , the internal conversion  $k_{\text{ic}}$  and the possible S<sub>1</sub> cleavage  $k_c$  processes  $(k_{\text{isc}} + k_{\text{ic}} + k_c \sim 10^9 \text{ s}^{-1})$ . On these kinetic grounds, both **Tr\_DMPA^•+** 1a



**Figure 3.** ESR spin-trapping experiments for the irradiation of **Tr\_DMPA** solution with different spin trap agents: (A) phenyl-*N-tert*-butylnitrone (PBN); (B) 1,3,5-tri-*tert*-butyl-2-nitrosobenzene (TBNB) and (C) 2,3,4,5,6-pentamethylnitrosobenzene (PMNB). (D) Steady-state ESR spectrum for the irradiation of **Tr\_DMPA** at 223 K. In *tert*-butylbenzene (experimental (a) and simulated (b) spectra).



**Figure 4.** Kinetic observed at 360 nm after laser excitation of **Tr\_DMPA** at 355 nm.

and  $R^+$  species 3 are present. They should be able to initiate a cationic polymerization (see below). The crowded and delocalized structure of **Tr\_DMPA**<sup>++</sup>, however, might probably make more difficult its addition to the epoxide.

**2.** Tr\_DMPA as a New Type I Photoinitiator. 2-a. Free Radical Photopolymerization FRP of TMPTA. The best typical conversion—time profiles for the photopolymerization of trimethylolpropane triacrylate (TMPTA) under a polychromatic light exposure (Xe–Hg lamp) in laminated conditions are displayed in Figure 5. They outline the high efficiency of Tr\_DMPA compared to DMPA using a very low light intensity  $(2 \text{ mW/cm}^2)$  as well as a low photoinitiator content  $(0.1\% \text{ w/w;} [\text{Tr_DMPA}] = 6.4 \times 10^{-4} \text{ M}, [DMPA] = 5 \times 10^{-3} \text{ M})$ , i.e., a tack

free coating is only obtained for **Tr\_DMPA** as the final conversion is about 10% higher to that obtained for DMPA – Figure 5A. The calculated amount of energy absorbed  $I_{abs}$  (evaluated as presented in ref 62) being in a ratio 1/10 for DMPA and **Tr\_DMPA** and the polymerization rates  $(R_ps)$  almost similar (Figure 5A), the initiation quantum yields are in the same ratio. Therefore, the photochemical/chemical reactivity of **Tr\_DMPA** (expressed by  $\Phi_{isc}$  cleavage rate constants, addition rate constants of the radicals to the acrylate double bond) appears lower than that of DMPA. Its lower reactivity is largely counterbalanced by its higher  $I_{abs}$ . The extractability of the initiator from the synthesized polymers (evaluated as presented by us in<sup>29</sup>) is found to be very low i.e. this highlights that the fragments (X-Ph-C(=O)• and X-Ph-C(OMe)<sub>2</sub>•) are directly linked to the polymer network.

Interestingly, when using a halogen lamp exposure, the efficiencies of both compounds decrease (the light distribution of this source is less favorable than for the Xe–Hg lamp) but the difference is larger (35% vs <10% conversion at 300 s for Tr\_DMPA and DMPA, respectively). When adding MDEA to Tr\_DMPA, higher  $R_p$ s and final conversions (~50%) of TMPTA are obtained (Figure 5B, curve 2); the final coating is tack-free e.g. within 3 min of irradiation. The acceleration of the polymerization in the presence of an amine (MDEA) can result from the reduction of the oxygen inhibition. Using DMPA/MDEA, the conversion reaches a maximum of ~30%, the  $R_p$  is low and the inhibition time is much more important (Figure 5B, curve 1). This trend of reactivity is in agreement with the light absorption properties of the different PIs at  $\lambda$  > 370 nm: Tr\_DMPA  $\gg$  DMPA—see Figure 1A. Under the laser diode at



Figure 5. Photopolymerization profiles of TMPTA in laminated conditions: (A) upon the Xe–Hg lamp exposure in the presence of (1) DMPA (0.1% w/w) and (2) Tr\_DMPA (0.1% w/w); (B) upon the halogen lamp exposure in the presence of (1) DMPA/MDEA (0.5%/2% w/w) and (2) Tr DMPA/MDEA (0.5%/2% w/w).



Figure 6. (A) Photopolymerization profiles of EPOX, upon halogen lamp irradiation in the presence of (1) DMPA/Iod (0.5%/3% w/w), (2) Tr\_DMPA/Iod (0.5%/3% w/w), and (3) BAPO/Iod (0.5%/3% w/w). (B) Photopolymerization profiles of EPOX-Si, upon halogen lamp irradiation in the presence of (1) DMPA/Iod (0.5%/3% w/w) and (2) Tr\_DMPA/Iod (0.5%/3% w/w); inset, IR spectra recorded during the photopolymerization of curve 2 (a) before and after (b) light irradiation. (C) Photopolymerization profiles of EPOX, upon the laser diode exposure at 405 nm in the presence of (1) DMPA/Iod (0.5%/3% w/w) and (2) Tr\_DMPA/Iod (0.5%/3% w/w). (D) Photopolymerization profiles of EPOX-Si, upon laser diode exposure at 405 nm in the presence of (1) DMPA/Iod (0.5%/3% w/w) and (2) Tr\_DMPA/Iod (0.5%/3% w/w), upon laser diode exposure at 405 nm in the presence of (1) DMPA/Iod (0.5%/3% w/w) and (2) Tr\_DMPA/Iod (0.5%/3% w/w), upon laser diode exposure at 405 nm in the presence of (1) DMPA/Iod (0.5%/3% w/w) and (2) Tr\_DMPA/Iod (0.5%/3% w/w), upon laser diode exposure at 405 nm in the presence of (1) DMPA/Iod (0.5%/3% w/w) and (2) Tr\_DMPA/Iod (0.5%/3% w/w), under air.

405 nm, **Tr\_DMPA** obviously works contrary to DMPA (final conversion 40% vs <10% at 300 s for **Tr\_DMPA** and DMPA, respectively). For LED at 395 nm, an efficient process is also only observed for **Tr\_DMPA**.

2-b. Cationic Photopolymerization of EPOX and EPOX-Si. The photopolymerizations of EPOX and EPOX-Si using Tr DMPA/Iod under the halogen lamp and the laser diode irradiation were carried out under air (Figure 6). The induction period can be ascribed to the presence of inhibitors e.g. the free radicals must be oxidized by iodonium salt for the formation of the polymerization initiating cations. Therefore, the oxygen must be first consumed, i.e., the free radicals react with oxygen (with formation of peroxyl radicals) preventing their oxidation by iodonium salt. In Figure 6, low light intensities are used and the polymerization starts when the oxygen concentration is low. Remarkably, the new proposed system is very efficient for the selected very soft irradiations conditions. An increase of the IR band at  $1080 \text{ cm}^{-1}$  is concomitantly observed due to the formation of the polyether network. Quite excellent conversiontime profiles are noted compared to those recorded in the presence of DMPA/Iod (no ring-opening photopolymerization occurs) or BAPO/Iod (Figure 6A, curve 2 vs curves 1 and 3). Final conversions (about 60%) are reached after 13 min of irradiation and tack free coatings are obtained (Figure 6 curves 2). This is still in line with the strongly red-shifted absorption of Tr DMPA compared to DMPA (Figure 1) which allows a good matching with the emission spectra of the light sources.

2-c. Cationic Photopolymerization of DVE-3. The photopolymerization of DVE-3 was carried out in laminated conditions using the laser diode (405 nm) irradiation. In the presence of the **Tr\_DMPA**/Iod system, an excellent polymerization is noted with a conversion ~90% after 2 min of irradiation (Figure 7). No



Figure 7. Photopolymerization profiles of DVE-3 in laminated conditions. Upon the laser diode exposure at 405 nm in the presence of (1) DMPA/Iod (0.5%/3% w/w) and (2) Tr\_DMPA/Iod (0.5%/3% w/w).

polymerization is observed when using DMPA/Iod in the same experimental conditions. This is in full agreement with the higher efficiency of **Tr\_DMPA** to initiate cationic polymerizations (see above for epoxy).

#### CONCLUSIONS

In this paper, the coupling of the MOs of three 2,2'-dimethoxy 2-phenyl acetophenone (DMPA) units linked to a truxene (**Tr**) scaffold leads to the design of a one-component trifunctional

photoinitiator **Tr\_DMPA** whose the fast Norrish I cleavage is similar to that of DMPA. The high molar extinction coefficients of **Tr\_DMPA** ( $\varepsilon_{max} > 60\,000 \text{ M}^{-1} \text{ cm}^{-1}$ ) have never been reported for PIs in the near UV wavelength range and probably in any cleavable PIs described so far. The most striking performance is undoubtedly observed in the polymerization of an epoxide and a divinylether under air at 405 nm where PIs such as DMPA or BAPO are almost inefficient.

This present work suggests that the incorporation of PI units into a truxene structure can be the starting point for the design of a new high performance class of Type I or Type II PIs being able to behave as light harvesting systems and to work in the near UV/ visible range under "extreme" experimental conditions (low viscosity media, low intensity light sources) as radical PIs in free radical and cationic polymerizations. The synthesis of **Tr\_DMPA** is relatively easy; its shell life stability is good and its solubility in organic formulations is excellent. The introduction of PI units onto a triazine skeleton was also recently achieved.<sup>47</sup> Other cores for the development of trifunctional TfcPIs (or even difunctional DfcPIs) architectures as well as new strongly coupled bifunctional structures BfcPIs can probably be proposed in the future.

# ASSOCIATED CONTENT

#### **Supporting Information**

Figure S1, emission spectrum for the halogen lamp, and Figure S2, emission spectra for **Tr** and **Tr\_DMPA**. This material is available free of charge via the Internet: http://pubs.acs.org.

### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: (J.L.) jacques.lalevee@uha.fr; (D.G.) didier.gigmes@ univ-amu.fr.

#### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

This work was partly supported by the "Agence Nationale de la Recherche" grant ANR 2010-BLAN-0802. J.L. thanks the Institut Universitaire de France for the financial support. The authors thank Jean Marc Frances (Bluestar Silicones-France) for the gifts of Iod & EPOX-Si. M.A.T., J.L., and D,G, thank the "TGE Renard" for the help for ESR experiments.

### REFERENCES

(1) Fouassier, J. P.; Lalevée, J. Photoinitiators for Polymer Synthesis: Scope, Reactivity and Efficiency; Wiley-VCH: Weinheim, Germany, 2012. (2) (a) Fouassier, J. P. Photoinitiation, Photopolymerization, Photocuring; Hanser: Munich, Germany, 1995. (b) Radiation Curing in Polymer Science and Technology; Fouassier, J. P., Rabek, J. F., Eds.; Chapman & Hall: London, 1993. (c) Crivello, J. V.; Dietliker, K. Photoinitiators for Free Radical, Cationic and Anionic Photopolymerization; Surface Coatings Technology Series; Bradley, G., Ed., Wiley: New York, 1999; Vol. III. (d) Dietliker, K. A Compilation of Photoinitiators Commercially Available for UV Today: Sita Technology Ltd.: London, 2002. (e) Photoinitiated Polymerization; Belfied, K. D., Crivello, J. V., Eds.; ACS Symposium Series 847; American Chemical Society: Washington DC, 2003;. (f) Photochemistry and Photophysics of Polymer Materials, Allen, N. S., Ed., Wiley: Hoboken, NJ, 2010. (g) Photopolymerization: Fundamentals and Applications; Scranton, A. B., Bowman, A., Peiffer, R. W., Eds.; ACS Symposium Series 673; American Chemical Society: Washington DC, 1997. (h) Green, W. A. Industrial Photoinitiators; CRC Press: Boca Raton, FL, 2010. (i) Handbook of Vinyl Polymers, Mishra, M. K.; Yagci, Y., Eds.; CRC Press: Boca Raton, FL, 2008.

(3) Ganster, B.; Fischer, U. K.; Moszner, N.; Liska, R. Macromol. Rapid Commun. 2008, 29, 57–62.

(4) Lalevée, J.; Fouassier, J. P. In *Encyclopedia of Radicals in Chemistry, Biology and Materials*; Studer, A.; Chatgilialoglu, C., Eds.; Wiley: New York, 2012; Vol. 1, Chapter 2.

(5) (a) Kiskan, B.; Zhang, J.; Wang, X.; Antonietti, M.; Yagci, Y. ACS *Macro Lett.* **2012**, *1*, 546–549. (b) Gilmaz, G.; Iskin, B.; Yilmaz, F.; Yagci, Y. ACS Macro Lett. **2012**, *1*, 1212–1215.

(6) Lalevée, J.; Telitel, S.; Tehfe, M. A.; Fouassier, J. P.; Curran, D. P.; Lacote, E. *Angew. Chem., Int. Ed.* **2012**, *51*, 5958–5961.

(7) Jiang, M.; Wang, K.; Ma, G.; Jian, L.; Juan, X.; Yu, Q.; Nie, J. J. Appl. Polym. Sci. 2011, 121, 2013–2017.

(8) Keskin Dogruyol, S.; Dogruyol, Z.; Arsu, N. J. Polym. Sci., Part A: Polym. Chem. 2011, 49, 4037–4040.

(9) Yin, R.; Wang, K.; Liu, J.; Nie, J. J. Appl. Polym. Sci. 2012, 125, 2371–2375.

(10) Asvos, X.; Siskos, M. G.; Zarkadis, A. K.; Hermann, R.; Brede, O. J. Photochem. Photobiol. A: Chem. 2011, 219, 255–264.

(11) Chen, H.; Yang, J.; Guo, D.; Wang, L.; Nie, J. J. Photochem. Photobiol. A: Chem. 2012, 232, 57–63.

(12) Wang, K.; Jiang, S.; Liu, J.; Nie, J.; Yu, Q. Prog. Org. Coatings 2011, 72, 517–521.

(13) Temel, G.; Enginol, B.; Aydin, M.; Karaca Balta, D.; Arsu, N. J. Photochem. Photobiol. A: Chem. 2011, 219, 26–31.

(14) Marzena Szymczak, A.; Podsiadły, R.; Podemska, K.; Sokołowska, J. Color. Technol. **2012**, *128*, 378–386.

(15) Czech, Z.; Kowalczyk, A.; Gąsiorowska, M.; Soroka, J.; Kabatc, J. J Adhes. Adhes. 2011, 31, 634–638.

(16) Tehfe, M. A.; Zein-Fakih, A.; Lalevée, J.; Dumur, F.; Gigmes, D.; Morlet-Savary, F.; Hamieh, T.; Fouassier, J. P. *Eur. Polym. J.* **2012**, DOI: 10.1016/j.eurpolymj.2012.10.010.

(17) Chen, Y.; Li, G.; Han, J.; Wang, T. J. Photochem. Photobiol. A: Chem. 2011, 222, 330-335.

(18) (a) Telitel, S.; Lalevée, J.; Blanchard, N.; Kavalli, T.; Tehfe, M. A.; Morlet-Savary, F.; Graff, B.; Fouassier, J. P. *Macromolecules* **2012**, *45*, 6864–6868. (b) Telitel, S.; Blanchard, N.; Schweitzer, S.; Morlet-Savary, F.; Graff, B.; Fouassier, J. P.; Lalevée, J. *Polymer*, to be publ.

(19) (a) Tehfe, M. A.; Lalevée, J.; Morlet-Savary, F.; Graff, B.; Blanchard, N.; Fouassier, J. P. ACS Macro Lett. 2012, 1, 198–203.
(b) Tehfe, M. A.; Lalevée, J.; Morlet-Savary, F.; Graff, B.; Blanchard, N.; Fouassier, J. P. Macromolecules 2012, 45, 1746–1752. (c) Tehfe, M. A.; Dumur, F.; Contal, E.; Graff, B.; Gigmes, D.; Morlet-Savary, F.; Fouassier, J. P.; Lalevée, J. Polym. Chem. 2012, DOI: 10.1039/ c2py20950k.

(20) Lalevée, J.; Tehfe, M. A.; Morlet-Savary, F.; Graff, B.; Fouassier, J. P. *Macromolecules* **2012**, *45*, 356–361.

(21) Tehfe, M. A.; Lalevée, J.; Dumur, F.; Zein-Fakih, A.; Gigmes, D.; Morlet-Savary, F.; Fouassier, J. P. *Polymer* **2012**, DOI: 10.1016/ j.polymer.2012.08.067.

(22) Kabatc, J.; Jurek, K. Polymer 2012, 53, 1973-1980.

(23) Podemska, K.; Podsiadły, R.; Szymczak, A. M.; Sokołowska, J. *Dyes Pigm.* **2012**, *94*, 113–119.

(24) Lalevée, J.; Tehfe, M. A.; Gigmes, D.; Blanchard, N.; Fouassier, J. P. *Macromolecules* **2010**, *43*, 6608–6615.

(25) Lalevée, J.; Peter, M.; Dumur, F.; Gigmes, D.; Blanchard, N.; Tehfe, M. A.; Morlet-Savary, F.; Fouassier, J. P. *Chem., Eur. J.* **2011**, *17*, 15027–15031.

(26) Tehfe, M. A.; Ma, L.; Morlet-Savary, F.; Graff, B.; Fouassier, J. P.; Zhao, J.; Lalevée, J. *Macromol. Chem. Phys.* **2012**, *213*, 2282–2286.

(27) Tehfe, M. A.; Lalevée, J.; Dumur, F.; Zein-Fakih, A.; Gigmes, D.; Contal, E.; Bertin, D.; Fouassier, J. P. To be published.

(28) Rosspeintner, A.; Griesser, M.; Pucher, N.; Iskra, K.; Liska, R.; Gescheidt, G. *Macromolecules* **2009**, *42*, 8034–8038.

(29) Lalevée, J.; Blanchard, N.; Fries, C.; Tehfe, M. A.; Morlet-Savary, F.; Fouassier, J. P. *Polym. Chem.* **2011**, *2*, 1077–1084.

(30) Karaka-Balta, D.; Temel, G.; Okal, N.; Yagci, Y. *Macromolecules* **2012**, *45*, 119–125.

(31) Sevinc Esen, D.; Karasu, F.; Arsu, N. Prog. in Org. Coat. 2011, 70, 102–107.

Article

(32) (a) Pietrzak, M.; Wrzyszczyński, A. J. Appl. Polym. Sci. 2011, 122, 2604–2608. (b) Wei, J.; Wang, B. Macromol. Chem. Phys. 2011, 212, 88–95.

(33) Gil, M.; Gawdzik, B.; Podkościelna, B. J. Appl. Polym. Sci. 2012, 125, 2839–2845.

(34) (a) Visconti, M. In *Photochemistry and UV Curing: New Trends*; Fouassier, J. P., Ed.; Research Signpost: Trivandrum, India, 2006; pp 153–163. (b) Dietlin, C.; Lalevée, J.; Allonas, X.; Fouassier, J. P.; Visconti, M.; Li Bassi, G.; Norcini, G. *J. Appl. Polym. Sci.* **2008**, 107, 246– 252.

(35) Lalevée, J.; Allonas, X.; Fouassier, J. P.; Visconti, M.; Li Bassi, G. In *Photochemistry and UV Curing: new trends*; Fouassier, J. P., Ed.; Research Signpost: Trivandrum, India, 2006; pp 79–90.

(36) (a) Yilmaz, G.; Tuzun, A.; Yagci, Y. J. Polym. Sci., Part A: Polym. Chem. 2010, 48, 5120–5125. (b) Balta, D. K.; Arsu, N.; Yagci, Y.; Jockusch, S.; Turro, N. J. Macromolecules 2007, 40, 4138–4141. (c) Yagci, Y.; Jockusch, S.; Turro, N. J. Macromolecules 2010, 43, 6245– 6260.

(37) Tunc, D.; Yagci, Y. Polym. Chem. 2011, 2, 2557-2563.

(38) Gilmaz, G.; Acik, G.; Yagci, Y. Macromolecules 2012, 45, 2219–2224.

(39) (a) Burget, D.; Fouassier, J. P.; Amat-Guerri, F.; Mallavia, R.; Sastre, R. *Acta Polym.* **1999**, *50*, 337–346. (b) Xu, J.; Ma, G.; Wang, K.; Gu, J.; Jiang, S.; Nie, J. *J. Appl. Polym. Sci.* **2012**, *123*, 725–731.

(40) Kawamura, K. J. Photochem. Photobiol. Part A: Chem. 2004, 162, 329-338.

(41) Lalevée, J.; Tehfe, M. A.; Dumur, F.; Gigmes, D.; Blanchard, N.; Morlet-Savary, F.; Graff, B.; Fouassier, J. P. ACS Macro Lett. **2012**, *1*, 286–290.

(42) Tehfe, M. A.; Lalevée, J.; Telitel, S.; Sun, J.; Zhao, J.; Morlet-Savary, F.; Graff, B.; Fouassier, J. P. *Polymer* **2012**, DOI: 101016/ j.polymer.2012.05.009.

(43) Kreutzer, J.; Dogan Demir, K.; Yagci, Y. *Eur. Polym. J.* 2011, 47, 792–799.

(44) (a) Aydogan, B.; Yagci, Y.; Toppare, L.; Jockusch, S.; Turro, N. J. *Macromolecules* **2012**, *45*, 7829–7834. (b) Aydogan, B.; Durmaz, Y. Y.; Kahveci, M. U.; Uygun, M.; Tasdelen, M. A.; Yagci, Y. *Macromol. Symp.* **2011**, 308, 25–34. (c) Aydogan, B.; Gunbas, G. E.; Durmus, A.; Toppare, L.; Yagci, Y. *Macromolecules* **2010**, *43*, 101–106. (d) Bulut, U.; Gunbas, G. E.; Toppare, L. J. Polym. Sci., Part A: Polym. Chem. **2010**, *48*, 209–213. (e) Bulut, U.; Balan, A.; Caliskan, C. J. Polym. Sci., Part A: Polym. Chem. **2011**, *49*, 729–733. (f) Yagci, Y.; Jockusch, S.; Turro, N. J. Macromolecules **2007**, *40*, 4481–4485.

(45) Telitel, S.; Lalevée, J.; Fouassier, J. P.; Detrembleur, C. To be published.

(46) Lalevée, J.; Tehfe, M.-A.; Dumur, F.; Gigmes, D.; Graff, B.; Morlet-Savary, F.; Fouassier, J.-P. *Macromol. Rapid Commun.* **2012**, DOI: 10.1002/marc.201200578.

(47) Tehfe, M. A.; Dumur, F.; Morlet-Savary, F.; Graff, B.; Fouassier, J. P.; Gigmes, D.; Lalevée, J. *Macromolecules* **2012**, *45*, 8639–8647.

(48) Morlet-Savary, F.; Allonas, X.; Fouassier, J. P. in *Photochemistry* and UV curing: new trends; Fouassier, J. P., Ed., Research Signpost: Trivandrum, India, 2006; pp 69–81.

(49) Brunisholz, J.; Kirchmayr, R. US patent 4,190,602 (1980).

(50) Wang, J.-L.; Chan, Y.-T.; Moorefield, C. N.; Pei, J.; Modarelli, D. A.; Romano, N. C.; Newkome, G. R. *Macromol. Rapid Commun.* **2010**, *31*, 850–855.

(51) Tehfe, M. A.; Lalevée, J.; Telitel, S.; Contal, E.; Dumur, F.; Gigmes, D.; Bertin, D.; Nechab, M.; Graff, B.; Morlet-Savary, F.; Fouassier, J. P. *Macromolecules* **2012**, *45*, 4454–4460.

(52) Wong, Y.-C.; Parthasarathy, K.; Cheng, C.-H. Org. Lett. 2010, 12, 1736–1739.

(53) Ren, W.; Xia, Y.; Ji, S.-J.; Zhang, Y.; Wan, X.; Zhao, J. Org. Lett. **2009**, *11*, 1841–1844.

(54) (a) Castellanos, F.; Fouassier, J. P.; Priou, D.; Cavezzan, A. US Pat. 5668192, 16/9/1997, Rhone Poulenc. (b) Castellanos, F.; Fouassier, J. P.; Priou, C.; Cavezzan, J. *J. Appl. Polym. Sci.* **1996**, *60*, 705–713.

(55) (a) Lalevée, J.; Blanchard, N.; Tehfe, M.-A.; Morlet-Savary, F.; Fouassier, J. P. *Macromolecules* **2010**, *43*, 10191–10195. (b) Lalevée, J.; Blanchard, N.; Tehfe, M. A.; Peter, M.; Morlet-Savary, F.; Gigmes, D.; Fouassier, J. P. *Polym. Chem.* **2011**, *2*, 1986–1991. (c) Lalevée, J.; Blanchard, N.; Tehfe, M. A.; Peter, M.; Morlet-Savary, F.; Fouassier, J. P. *Macromol. Rapid Commun.* **2011**, *32*, 917–920. (d) Lalevée, J.; Blanchard, N.; Tehfe, M. A.; Peter, M.; Morlet-Savary, F.; Fouassier, J. P. *P. Polym. Bull.* **2011**, *68*, 341–347.

(56) (a) Gaussian 03, Revision B-2, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; , Jr., Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.: Farkas, O.: Tomasi, I.: Barone, V.: Cossi, M.: Cammi, R.: Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J.J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; M. A. Al-Laham, Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; M. Head-Gordon, Replogle, E. S.; Pople, J. A., Gaussian, Inc.: Pittsburgh PA, 2003. (b) Foresman, J. B.; Frisch, A. In Exploring Chemistry with Electronic Structure Methods, 2nd ed., Gaussian. Inc.: Pittsburgh, PA, 1996.

(57) (a) Tordo, P. Spin-trapping: recent developments and applications. In Atherton, N. M., Davies, M. J., Gilbert, B. C. *Electron Spin Resonance;* Cambridge, The Royal Society of Chemistry; 1998; Vol 18. (b) Lalevée, J.; Dumur, F.; Mayer, C. R.; Gigmes, D.; Nasr, G.; Tehfe, M. A.; Telitel, S.; Morlet-Savary, F.; Graff, B.; Fouassier, J. P. *Macromolecules* **2012**, 45, 4134–4141. (c) Duling, D. R. J. Magn. Reson., Ser. B **1994**, 104, 105–110.

(58) Baumann, H.; Timpe, H. J.; Zubarev, V. E.; Fok, N. V.; Mel'nikov, M. V. J. Photochem. **1985**, 30, 487–500.

(59) Terabe, S.; Kuruma, K.; Konaka, R. J.Chem.Soc., Perkin Trans.II 1973, 1252–1256.

(60) Rutsch, W.; Berner, G.; Kirchmayr, R.; Husler, R.; Rist, G.; Buhler, N. In *Organic Coatings Science and Technology*; Parfit, G. D., Patsis, A. V., Eds.; 1986; Vol. *8*, 175–192, Marcel Dekker: N.Y.

(61) Lalevée, J.; Allonas, X.; Fouassier, J. P. J. Photochem. Photobiol. A: Chem 2003, 159, 127–133.

(62) Lalevée, J.; Blanchard, N.; Chany, A. C.; Souane, R.; El-Roz, M.; Graff, B.; Allonas, X.; Fouassier, J. P. *Macromolecules* **2009**, *42*, 6031–6037.