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## ARTICLE

# Quaternary ammonium salts of phenylglyoxylic acid as photobase generators for thiol-promoted epoxides photopolymerization

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A novel series of photobase generators (PBG), quaternary ammonium salts of phenylglyoxylic acid (PA) having the ability to generate highly strong bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) or 1,1,3,3-tetramethylguanidine (TMG) was synthesized. The photochemistry of these PBG was studied by photolysis, pH measurements and spin trapping ESR experiments. It is shown that the PBG underwent a photodecarboxylation process leading to the release of the base under irradiation. These photobase generators were successfully applied to the crosslinking of an epoxide monomer without any post thermal treatment. By adding thiols in the photocatalyst system, an improvement on the polymerization efficiency was observed due to the formation of a highly reactive initiating thiolate anion.

## INTRODUCTION

Photolabile initiators which generate active species such as free radicals or ionic species find an important developed in a wide range of applications such as triggering bioactivity,<sup>1</sup> drug<sup>2</sup> or fragrance<sup>3</sup>, in coatings, microelectronics applications...<sup>4-8</sup> In the field of polymer science and technologies, photoinitiators releasing free radicals under exposure have been extensively studied and are still the most common photolabile reactants used in industry for free radical photopolymerization.<sup>4-5</sup> However, free radical photopolymerization suffers from inhibition by atmospheric oxygen<sup>9-11</sup> which can affect the final properties of the polymer network structure. By contrast, cationic photopolymerization offers several advantages, among those the possibility to polymerize monomers unworkable by radical pathway, such as epoxide resins. However, there is only a limited set of photoacid generator (PAG) that are commercially available, and some of them have poor solubility in solvent or monomer which limited their use.<sup>12</sup>

Photopolymerization catalyzed by photobase generator (PBG), most often amines, is free from these disadvantages.<sup>13-15</sup> Since the first report of a PBG in 1987,<sup>16</sup> many different photochemically base-generating systems have been documented such as carbamates, O-acyloximes, aminimides or ammonium salts.<sup>14</sup> Used as photocatalyst systems for polymer crosslinking or polymer modification, PBG systems can find applications for the photocuring of epoxy resins,<sup>17-19</sup> in base-catalyzed Michael reactions,<sup>20</sup> as catalysts for the imidization reactions,<sup>21</sup> polythiourethane formation<sup>22</sup> or sol-gel hydrolysis-

condensation processes.<sup>23</sup> The photoresist industry was found to be a quite suitable application of PBG.<sup>24-26</sup>

Most of the works reported in the literature describes PBG which release weakly reactive primary or secondary amines. Therefore, a post-exposure baking is necessary to complete the polymerization reaction, a fact which represents one of the most important drawbacks in the use of photolabile base. Only a few PBG systems able to release tertiary amine as strong bases have been reported so far in the literature. For example, quaternary ammonium salt or benzyl bicyclic amidines PBG lead to the release of highly reactive tertiary amine.<sup>20-32</sup> These strong bases have been found to be quite effective for ring-opening polymerization and crosslinking of polymeric materials. However, it is known that photobase generators generally suffer from thermal instability.

Herein, we report the development of new series of PBG which are easily synthesized as quaternary ammonium salts of phenylglyoxylic acid (PA). PA is known to undergo a photodecarboxylation process with a high quantum yield.<sup>33</sup> It is then anticipated that the corresponding quaternary ammonium salts of PA could release amines under UV exposure. The base released comprised cyclohexylamine (CHA), 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), and 1,1,3,3-tetramethylguanidine (TMG). In order to gain insight into the chemical processes of free amine photogeneration, detailed investigation by electron spin resonance-spin trapping (ESR-ST) experiments were performed. Finally, the catalytic ability

of these photoreleased bases was applied to the crosslinking of an epoxide resin in the absence and in the presence of thiol as promoting agent.

## RESULTS AND DISCUSSION

### Synthesis of quaternary ammonium salts of phenylglyoxylic acid.

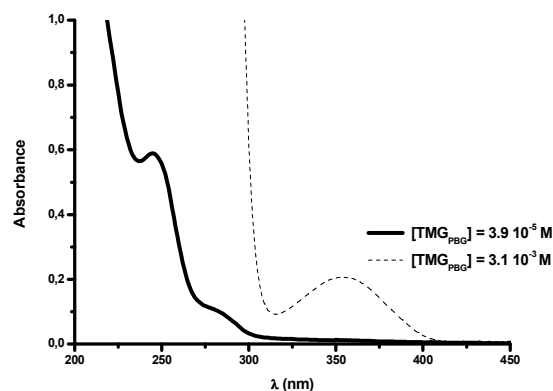
A series of photobase generators  $\text{TMG}_{\text{PBG}}$ ,  $\text{DBN}_{\text{PBG}}$ ,  $\text{DBU}_{\text{PBG}}$ ,  $\text{DABCO}_{\text{PBG}}$ ,  $\text{CHA}_{\text{PBG}}$  was successfully prepared (Table 1) using an adapted procedure from.<sup>34-35</sup> An equimolar amount of phenylglyoxylic acid and corresponding amine (TMG, DBN, DBU, DABCO or CHA) was simply mixed overnight at room temperature in chloroform and precipitated in diethyl ether. The crystals obtained were recrystallized twice in diethyl ether. The reaction yields are considerably high, and exceed 70 % for each synthesis. The analysis of the different  $^1\text{H}$  NMR spectra allows the identification of the ammonium protons. This result indicates the base protonation to form the quaternary ammonium salts of phenylglyoxylic acid, which are expected to release different bases (whose pKa values are reported in Table 1).<sup>36-37</sup> It was chosen to synthesize the DABCO monosalt, as it is known that the monoprotonated form of DABCO behave as a quite weak base.<sup>38</sup> Therefore, the presence of the free amino group in  $\text{DABCO}_{\text{PBG}}$  does not affect the stability of the resin.

**Table 1.** Structures and abbreviations of the PBG. pKa values of the conjugate acids for each amine released.

PBG	Base released	pKa <sup>36-37</sup>
$\text{CHA}_{\text{PBG}}$		10.6
$\text{DABCO}_{\text{PBG}}$		8.2
$\text{DBU}_{\text{PBG}}$		12.1
$\text{DBN}_{\text{PBG}}$		13.5
$\text{TMG}_{\text{PBG}}$		13.6
$\text{REF}_{\text{PBG}}$		9.3

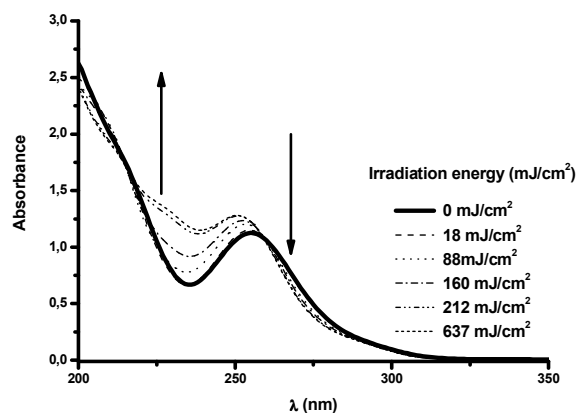
### Photochemical study

It has been reported that phenylglyoxylic acid undergoes a photodecarboxylation process with high efficiency quantum yield ( $\Phi_{366\text{nm}}=0.72$ ).<sup>33</sup> Hence, the photolysis of the quaternary ammonium salts described here involve presumably a photodecarboxylation reaction leading to the base releasing. This mechanism was studied on the basis of  $\text{TMG}_{\text{PBG}}$  in methanol as a typical PBG system. Figure 1 shows that the absorption spectrum of  $\text{TMG}_{\text{PBG}}$  exhibit two peaks with maxima at 246 and 357 nm, assigned respectively to  $\pi-\pi^*$  and  $n-\pi^*$  electronic transitions and with molar extinction coefficients ( $\epsilon$ ) of  $11,400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  and  $64 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ , respectively. These values are very close to those of phenylglyoxylic acid.



**Figure 1.** Absorption spectra of  $\text{TMG}_{\text{PBG}}$  in methanol at different concentrations ( $3.9 \cdot 10^{-5} \text{ M}$  and  $3.1 \cdot 10^{-3} \text{ M}$ ).

Irradiation of methanol solution of  $\text{TMG}_{\text{PBG}}$  ( $1.0 \cdot 10^{-4} \text{ M}$ ) at 313 nm induces changes in the absorption spectrum (Figure 2). A decrease of the peak at 254 nm and the appearance of a new band at 228 nm when the UV dose exposure increases can be observed.

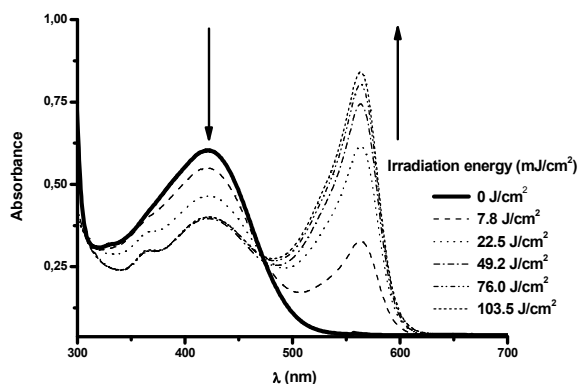


**Figure 2.** Absorption spectra changes of  $\text{TMG}_{\text{PBG}}$  in methanol after irradiation at 313 nm with different irradiation energies.

The decrease of the 254 nm band could be ascribed to phenylglyoxylate photodecarboxylation reaction<sup>39</sup> which leads to carbon dioxide and benzaldehyde. Then, the appearance of the new 228 nm band is tentatively attributed to benzaldehyde photoproduct.

The generated CO<sub>2</sub> was detected by using a procedure described elsewhere.<sup>40</sup> 1 mL of a methanol solution of TMG<sub>PBG</sub> (2.6 10<sup>-2</sup>M) was placed in Pyrex tube which was connected to another tube containing an aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (3.0 10<sup>-3</sup>M) and phenol red (4.5 10<sup>-4</sup>M). The TMG<sub>PBG</sub> solution was irradiated at the same time with Hg–Xe lamp (510 mW/cm<sup>2</sup>). The pink color of phenol red disappeared after 20 minutes due to the release of CO<sub>2</sub>. The absorption spectra obtained for the phenol red solution before and after irradiation indicate an absorption decrease of the basic form of the phenol red at 558 nm. Further, the appearance of a new band at 428 nm, which is associated to the acid form of phenol red, was observed.<sup>41</sup> Thus, this result indicates an efficient photodecarboxylation reaction, which suggests that a free base generation could occur from TMG<sub>PBG</sub> irradiation.

The formation of free base can also be evidenced by colorimetric method. Different methanol solutions of TMG<sub>PBG</sub> (5.2 10<sup>-3</sup> M) were irradiated with increasing doses of light (0, 7.8, 22.5, 49.2, 78.0 and 103.5 J/cm<sup>2</sup>). After 15 min of Ar bubbling, 25 μL of an aqueous solution of phenol red (3.4 10<sup>-5</sup> M) was added to each sample and the absorption spectra were recorded (Figure 3). No spectral change in the phenol red solution spectrum was observed in the dark (0 J/cm<sup>2</sup>), suggesting no premature base release in the absence of light. This underlines the good thermal stability of the TMG<sub>PBG</sub>. Increasing the dose light increases the characteristic absorption band at 565 nm of the deprotonated form of phenol red, as a consequence of the increasing release of base under irradiation.

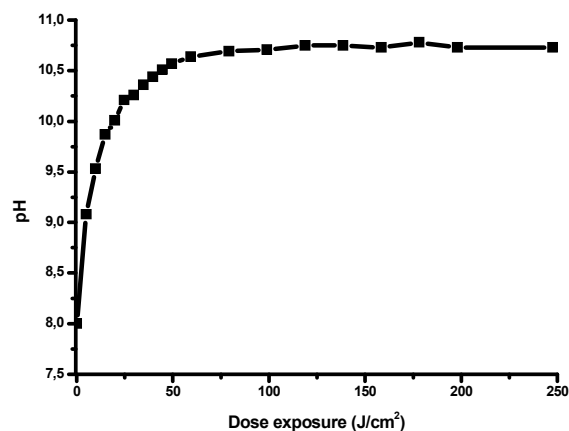


**Figure 3.** Absorption spectra changes in phenol red solution upon addition of TMG<sub>PBG</sub> solution irradiated with an Hg–Xe lamp at several doses.

The change in the basicity of the medium was also probed by pH monitoring. Before UV irradiation, the solution is recorded with a pH of 8.0, although this value does not represent the actual pH in the organic medium. After irradiation, the solution turned immediately to highly basic value. The pH of the irradiated solution gradually increased with the irradiation dose

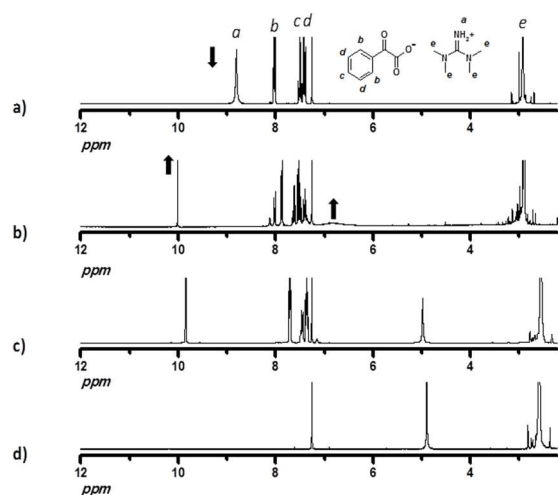
exposure (up to 10.8, Figure 4). Then, the value reached a plateau when the irradiation dose exposure was more than 60 J/cm<sup>2</sup>. This result indicates that most of the basic species were already released after 60 J/cm<sup>2</sup>.

TMG<sub>PBG</sub> photolysis was monitored by <sup>1</sup>H NMR spectroscopy (Figure 5). After photolysis, aromatic fragments were observed (Hb, Hc, Hd) arising from the starting material. This shows that the photolysis was not complete. Furthermore, a new peak appears at 10 ppm, as well as several aromatic peaks around 7.5–8.0 ppm. In comparison with the NMR spectra of a mixture of TMG and benzaldehyde, these changes can be assigned to the formation of benzaldehyde photolysis byproduct.



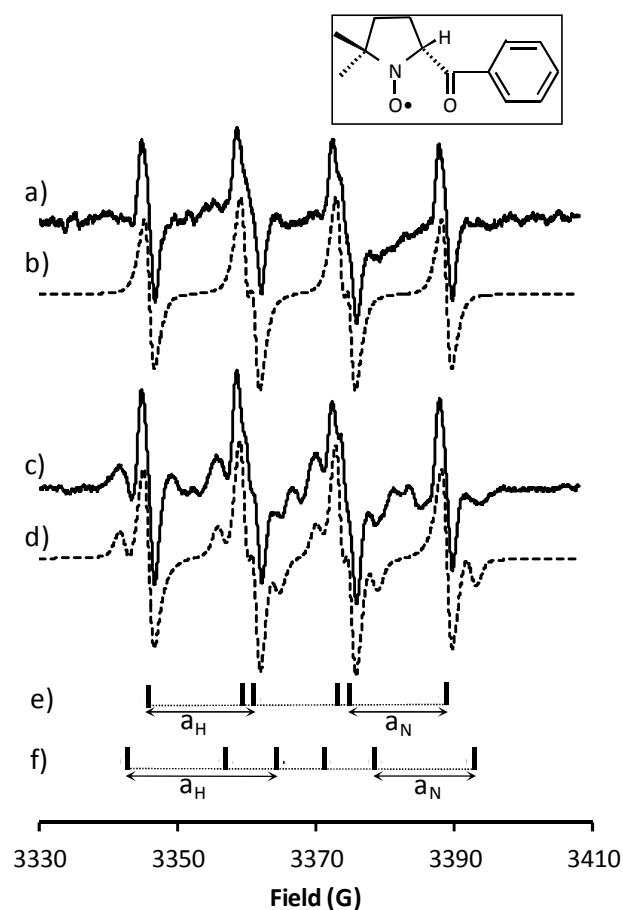
**Figure 4.** pH monitoring of a solution of TMG<sub>PBG</sub> upon UV irradiation at different light doses.

Protons Ha (8.9 ppm) associated to guanidinium NH<sub>2</sub><sup>+</sup> completely disappeared after UV irradiation. The residual NH<sub>2</sub><sup>+</sup> protons are expected to be displaced, as the signal depends on the relative basicity of the medium. Indeed, these protons can be observed as a new broad singlet at 6.5 ppm appears which is attributed to a mixing of NH<sub>2</sub><sup>+</sup>/NH due to the change in the basicity of the medium. Further increase in the basicity of the medium would displace this signal around 5, as shown in Figure 5d for neat TMG.



**Figure 5.**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ) of  $\text{TMGPBG}$  a) before and b) after irradiation UV irradiation with a dose of  $92 \text{ J/cm}^2$ , c) mixture of benzaldehyde and TMG and d) TMG.

The literature suggests that the photolysis mechanism of PA occurs by a photodecarboxylation reaction involving the formation of benzoyl radicals.<sup>39</sup> Then, the photodecomposition of PA was monitored by electron spin resonance using 5, 5-dimethyl-1-pyrroline-*N*-oxide (DMPO) as spin-trap in *t*-butylbenzene. The formation of benzoyl radical during the irradiation of PA in *t*-butylbenzene solution is clearly observed in Figure 6. Indeed, the hyperfine coupling constants found ( $a_{\text{N}} = 13.81 \text{ G}$  and  $a_{\text{H}} = 15.37 \text{ G}$ ) are in very good agreement with the published data in benzene ( $a_{\text{N}} = 13.99 \text{ G}$  and  $a_{\text{H}} = 15.57 \text{ G}$ ).<sup>42</sup> The same methodology was applied to irradiated solution of  $\text{TMGPBG}$ . The ESR experiment evidenced the formation of two different radical species (Figure 6) during irradiation which both contribute to the detected signal. The main one (93%) is assigned to the benzoyl radical ( $a_{\text{N}} = 13.81 \text{ G}$  and  $a_{\text{H}} = 15.48 \text{ G}$ ). The minor radical population is not yet assigned ( $a_{\text{N}} = 14.17 \text{ G}$  and  $a_{\text{H}} = 21.63 \text{ G}$ ). These results undoubtedly evidenced the Norrish I C-C bond cleavage for both PA and  $\text{TMGPBG}$ , leading to benzoyl radical formation.

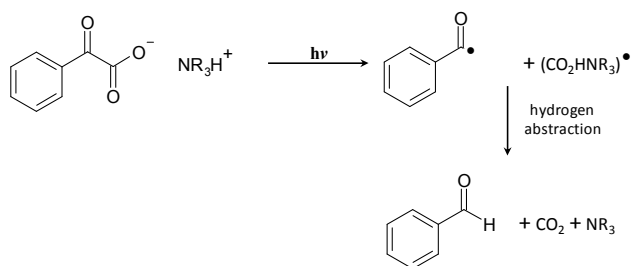


**Figure 6.** ESR spectra obtained a) after irradiation of 30 mM PA with b) corresponding simulated spectrum, and c) after irradiation of 30 mM of  $\text{TMGPBG}$  with d) corresponding simulated spectra. e) Peak assignment to the benzoyl radical adduct and f) peak attribution to the minor radical adduct population. Insert: structure of the benzoyl radical adduct.  $[\text{DMPO}] = 6.08 \text{ mM}$  in *t*-butylbenzene.

Thus, a base releasing mechanism involving quaternary ammonium salts of phenylglyoxylic acid can be proposed (Scheme 1). Under irradiation, an initial C-C homolytic bond cleavage occurs, affording benzoyl radical and  $(\text{CO}_2\text{HNR}_3)^{\bullet}$ . After a rearrangement step, involving H-transfer to the benzoyl radical, the amine is released and  $\text{CO}_2$  is extruded. It was not possible to detect accurately  $\text{HCO}_2^{\bullet}$ , which was only scarcely reported.<sup>43-44</sup>

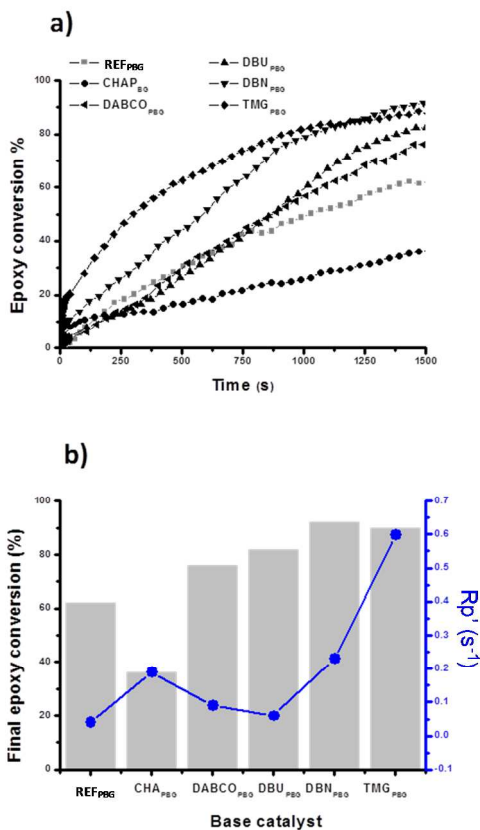
#### Photocrosslinking of an epoxide resin catalyzed by PBG

The catalytic ability of the amines generated during the photolysis of PA quaternary ammonium salts was evaluated in the crosslinking reaction of an epoxide resin (Epalloy 5000). It should be noted that the PBG were found to be stable for more than 10 months in the fridge, and for more than one day when mixed with the resin at RT. In spite of the ionic character of the compounds, no dissolution issue was encountered up to 8 wt% in the resin.



Scheme 1. Mechanism of photolysis of ammonium phenylglyoxylate salts.

The time evolution of the photopolymerization profiles were systematically compared with the performances of photogenerated N-isopropylmorpholine. This latter was obtained as the photoproduct of the Norrish 1 reaction of 2-Methyl-4'-(methylthio)-2-morpholinopropiophenone used as reference REF<sub>PBG</sub> (see Table 1).<sup>23</sup>



**Figure 7.** a) Kinetic profiles of epoxide crosslinking reactions catalyzed by the different PBG. b) Final epoxide conversion and maximum rate of polymerization.

Figure 7a shows the kinetics of crosslinking reactions catalyzed by 8 wt% of PBG at room temperature, as monitored by real time Fourier transform InfraRed spectroscopy (RT-FTIR). Table 2 collects the corresponding conversion rates  $R_p'$  and conversions  $C_{1500s}$  as recorded after 1500s of irradiation. As can be seen, apart DABCO<sub>PBG</sub>, all the PBG behave more efficiently than the reference compound REF<sub>PBG</sub>.

**Table 2.** Conversion after 1500 s photolysis  $C_{1500s}$  (%) and rates of conversion  $R_p'$  (s<sup>-1</sup>) of epoxide using the different PBG in the absence and in the presence of thiol.

	Without thiol		With thiol		
	$R_p'$ (s <sup>-1</sup> )	$C_{1500s}$ (%)	$R_p'$ (s <sup>-1</sup> )	$R_{p2}'$ (s <sup>-1</sup> )	$C_{1500s}$ (%)
CHA <sub>PBG</sub>	0.19	43	1.14	0.1	100
DABCO <sub>PBG</sub>	0.07	81	1.2	0.08	100
DBU <sub>PBG</sub>	0.06	86	1.23	0.05	100
DBN <sub>PBG</sub>	0.23	95	1.7	0.08	100
TMG <sub>PBG</sub>	0.6	90	1.9	0.09	100
REF <sub>PBG</sub>	0.04	60	0.13	/	82

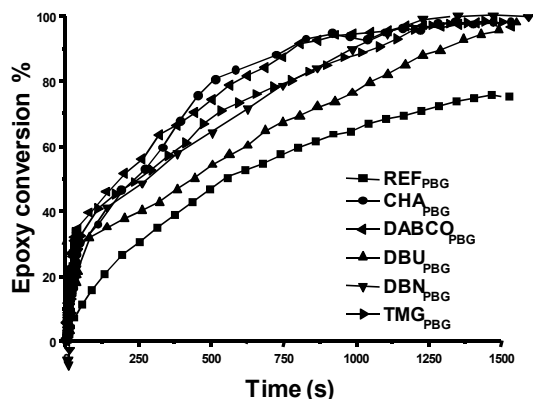
Roughly, higher the pKa is, faster is the photopolymerization process (Figure 7b). This is even more clear when looking at the final conversion, where a nice trend is observed over the new series of PBG. The different behavior of REF<sub>PBG</sub> is merely attributed to a different mechanism of photolysis that affects the amount of base released and therefore the conversion rate.<sup>23</sup> High pKa values, such as DBN and TMG, lead to great performances, the final epoxy conversion reaching almost 90%, with high conversion rates ( $R_p'$ ) and tack free polymer films. TMG<sub>PBG</sub> is 15 times faster than REF<sub>PBG</sub> (0.9 and 0.04 \*100/[M]<sub>0</sub> s<sup>-1</sup>, respectively).

It can be noticed that DABCO<sub>PBG</sub> (pKa 8.1) allows better epoxy conversion than CHA<sub>PBG</sub> (pKa 10.6). This result could be interpreted by the fact that tertiary amine are more powerful photocatalysts than primary amine due to a higher nucleophilicity. Indeed, the pKa value does not take into account the nucleophilicity of the base. However, in the framework of this paper, and as no mechanistic study was performed on the polymerization reaction itself, pKa is taken as a representative guess for the strength of the base.

#### PBG catalyzed thiol/epoxide systems

Thiol species are known to enhance the epoxide crosslinking process in base catalyzed reaction, due to the formation of very strong nucleophilic thiolate anions able to initiate efficiently the epoxide polymerization.<sup>45-46</sup> Nevertheless, only a few articles describing epoxy/thiol crosslinking catalyzed by photolabile amine species have been reported.<sup>47-51</sup>

Therefore, glycol dimercaptopropionate (GDMP, 8 wt%) was used in addition to PBG for the curing of epoxide. Figure 8 presents the kinetics of thiol/epoxide polymerization catalyzed by the different PBG, and Table 2 collects the corresponding values of  $R_p'$  and final conversion.



**Figure 8.** Conversion curves for thiol/epoxide polymerization catalyzed by the different PBG in the presence of GDMP.

The GDMP addition leads to an enhancement of both conversion rate and final epoxide conversion for all the systems studied. PBG based on PA allow the final epoxide conversion to reach 100% without any post backing treatment.

Kinetic profiles shown in Figure 8 exhibit a two-stage mechanism. The fast stage may correspond to the initiation process and depends on the pKa value as discussed above. The amine is rapidly consumed in the formation of thiolates which initiate the reaction. Moreover, it should be noted that for all PA based PBG the conversion rates  $R_{p1}$  can be nicely correlated with the pKa of the released amine, as a consequence of the proton transfer reaction from the thiol to the amines which depends on the amine basicity.

The second step is attributed to alkoxide propagation reaction. As it can be seen from Table 2, the corresponding maximum conversion rates  $R_{p2}$  for this second stage are very similar whatever the PBG used. This is attributed to the propagation reaction which depends only on the epoxide ring opening by an alkoxide propagating anion. The difference between the rate for the first and second stage is related to the relative efficiency of thiolate and alkoxide to open the ring of an epoxide. This difference in reactivity has been already demonstrated for the relative rate of nucleophilic displacement which was found three times higher for thiolate species compared to alkoxides.<sup>52</sup>

## CONCLUSION

A new series of highly performing photobase generators (PBG) was synthesized. It was demonstrated via different experimental methods that these PBG have the ability to release amine through a photodissociation mechanism. These compounds were successfully applied to the photopolymerization of an epoxide without any post baking. Moreover, it was shown that the pKa value of the released base determines the reactivity of the catalyst when applied to epoxide crosslinking. The same PBG were applied to catalyze thiol/epoxide polymerization. It was observed an improvement on the polymerization

performances for all of the systems studied, due to highly reactive nucleophilic thiolate generation.

## EXPERIMENTAL SECTION

**Materials.** Phenylglyoxylic acid (PA), cyclohexylamine (CHA), 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,1,3,3-tetramethylguanidine (TMG), phenol red, 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO), anhydrous chloroform, spectroscopic grade methanol, spectroscopic grade acetonitrile and tert-butylbenzene for ESR spectroscopy were purchased from Alpha Aesar. CHA, DBU, DBN, TMG and the different solvents were dried over 3Å molecular sieve prior use. Glycol dimercaptopropionate (GDMP) was supplied by Bruno Bock. 2-Methyl-4'-(methylthio)-2-morpholinopropiophenone ( $REF_{PBG}$ ) was a gift from Ciba Specialty Chemicals. The epoxide resin was the diepoxide of the cycloaliphatic alcohol, hydrogenated Bisphenol A (Epalloy 5000) obtained from CVC Chemicals.

**Instruments.** <sup>1</sup>H NMR spectra were measured in CDCl<sub>3</sub> using a Bruker instrument at 300 MHz. UV-Vis spectra were measured on a Beckman DU 640 spectrophotometer. The pH of the PBG solutions was measured by Eutech instrument pH700 in methanol. The polymerization experiments were carried out by real-time FTIR technique using a Vertex 70 FTIR spectrometer (Bruker Optik), equipped with MIR and NIR light sources, and a MCT detector working in the rapid scan mode, allowing an average of 4 scans/s collection rate (4 cm<sup>-1</sup> resolution).<sup>53</sup>

**Synthesis of photobase generators.** All the photobase generators were synthesized from a chloroform solution (40 ml) of the corresponding base (0.013 mol) and PA (1.3 g, 0.013 mol). The mixture was stirred overnight at room temperature, and then the solvent was evaporated. The resulting compound was further purified by recrystallization twice from diethyl ether. **CHA<sub>PBG</sub>**, white crystals in 83% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ(ppm) 7.43–8.50 (br s, 3H, NH<sub>3</sub><sup>+</sup>), 8.36–8.10 (d, *J*=8 Hz, 2H, Ar-H), 7.71–7.57 (t, *J*=7.3Hz, 1H, Ar-H), 7.55–7.43 (t, *J*=7.5 Hz, 2H, Ar-H), 3.27–2.84 (m, 1H, CH), 2.09–1.95 (m, 2H, CH<sub>2</sub>), 1.94–1.65 (m, 3H, CH<sub>2</sub>), 1.56–1.34 (m, 2H, CH<sub>2</sub>), 1.33–1.13 (m, 3H, CH<sub>2</sub>). **DABCO<sub>PBG</sub>**, white crystals in 63% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ(ppm) 8.27–7.36 (br s, 1H, NH<sup>+</sup>), 8.20–7.98 (m, 2H, Ar-H), 7.62–7.49 (m, 1H, Ar-H), 7.49–7.35 (m, 2H, Ar-H), 4.13–2.17 (s, 12 H, CH<sub>2</sub>). **DBU<sub>PBG</sub>**, white crystals in 73% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ(ppm) 12.55–11.7 (s, 1H, NH<sup>+</sup>), 8.05–7.87 (m, 2H, Ar-H), 7.54–7.45 (m, 1H, Ar-H), 7.45–7.36 (m, 2H, Ar-H), 3.61–3.26 (m, 6H, CH<sub>2</sub>), 3.00–2.72 (br s, 2H, CH<sub>2</sub>), 2.09–1.87 (m, 2H, CH<sub>2</sub>), 1.85–1.50 (m, 6H, CH<sub>2</sub>). **DBN<sub>PBG</sub>**, white crystals in 71% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ(ppm) 12.55–12.12 (s, 1H, NH<sup>+</sup>), 8.13–8.04 (m, 2H, Ar-H), 7.60–7.50 (m, 1H, Ar-H), 7.50–7.40 (m, 2H, Ar-H), 3.71–3.56 (t, *J*=7.80Hz, 7.80 Hz, 2H, CH<sub>2</sub>), 3.55–3.46 (t, *J*=4.86 Hz, 4.86 Hz, 2H, CH<sub>2</sub>), 3.45–3.36 (t, *J*=5.64 Hz, 5.64 Hz, 2H, CH<sub>2</sub>),

3.22–3.04 (t,  $J=7.80$  Hz, 7.80 Hz, 2H, CH<sub>2</sub>), 2.27–1.95 (m, 4H, CH<sub>2</sub>). **TMG<sub>PBG</sub>**, white crystals in 81% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 9.01–8.62 (s, 2H, NH<sub>2</sub><sup>+</sup>), 8.07– 7.96 (d,  $J = 5.23$  Hz, 3.27 Hz, 2H, Ar–H), 7.54–7.46 (m, 1H, Ar–H), 7.45–7.36 (m, 1H, Ar–H), 2.96–2.86 (br s, 12 H, CH<sub>3</sub>).

**Electron spin resonance spin-trapping (ESR–ST).** The ESR experiments were carried out using a X–Band spectrometer (MS 200 from Magnostech) at room temperature. The radicals were generated through photolysis (Hg–Xe lamp) under argon in tert–butylbenzene (used instead of benzene for safety reasons) and trapped by 5,5–dimethyl–1–pyrroline–*N*–oxide.<sup>54–55</sup>

**Real-time FTIR.** Polymerization profiles were recorded during 1500 seconds irradiation using Hg–Xe lamp with a reflector at 254 nm (Hamamatsu, L8252, 150 W), which was adapted to the FTIR spectrometer by means of a light guide. The incident light intensity was adjusted to 510 mW/cm<sup>–2</sup>. The formulation was prepared by mixing 8 wt% of PBG. The formulation was deposited on a silicon wafer support using a calibrated bar coater about 40  $\mu$ m thickness. The polymerization kinetics were measured by following the disappearance of the epoxy band at 915 cm<sup>–1</sup>. The conversion C%, directly related to the decrease in IR absorbance  $A_{915}$ , was calculated as:

$$C\% = \frac{(A_{915})_0 - (A_{915})_t}{(A_{915})_0} \times 100$$

Where  $(A_{915})_0$  and  $(A_{915})_t$  are the absorbance at 915cm<sup>–1</sup> at time zero and time  $t$ , respectively. The time derivation of experimental conversion curves allows the calculation of the conversion rate  $R_p' = dC\%/dt$ , which is related to the rate of polymerization  $R_p$  by  $R_p' = R_p \times 100/[M_0]$  where  $[M_0]$  is the initial monomer concentration (i.e. before exposure). According to this linear relationship, the values of conversion rate  $R_p'$  are reported in this work.<sup>56</sup>

## Notes and references

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