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# Photoinitiators with Functional Groups 9: New Derivatives of Covalently Linked Benzophenone-amine Based Photoinitiators

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# Photoinitiators with Functional Groups 9: New Derivatives of Covalently Linked Benzophenone-amine Based Photoinitiators

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As it had been shown that some covalently bound benzophenone (**BP**)—phenylglycine derivatives act as remarkable monomolecular Type II photoinitiators for radical polymerization, structural variations were investigated. The influence of the linking position between **BP** and the coinitiator and the coinitiator structure itself were considered. Furthermore, water soluble monomolecular BP-glycine based PIs were developed. While in UV-spectroscopy similar absorption behavior were found for all compounds, photo-DSC experiments revealed that derivative **2** has the most effective constitution.

**Keywords:** Radical polymerization, photopolymerization, low migration

## 1. Introduction

In UV-curable systems, the photoinitiator (PI) generates the reactive species, free radicals or ions and subsequently initiates the polymerization of diverse multifunctional monomers, oligomers or prepolymers (1). Usually, the initiator plays the key role by influencing the curing rate and –depth, the double bond conversion (DBC) and the final polymer properties.

Benzophenone (**BP**) derivatives in combination with tertiary amines as coinitiators are well-known bimolecular Type II photoinitiating systems for radical polymerization of acrylate based formulations (2). After electron transfer from the lone pair of the amine to the excited ketone, these PI systems suffer from a deactivation by back electron transfer (BET), preferentially in the solvent cage (3). To overcome these limitations, it is possible to use N-phenyl glycine (**NPG**) as coinitiator. **NPG** has the ability to react by spontaneous decarboxylation after electron transfer to the excited ketone and therefore BET is prevented (Scheme 1) (4).

Moreover, bimolecular systems suffer from diffusion controlled limitation of reactivity in highly viscous resin formulations, and especially at higher conversions (5, 6). To keep the coinitiator in close vicinity to the PI, the coinitiator can be bound to the chromophore. The resulting effect has recently been shown by using a thiol derivative of thioxanthone as a PI (7). A significantly higher reactivity has been observed in comparison to a physical mixture of the components, which has been related to its one component nature. Generally, heterosubstitution of the PI chromophore can alter the photochemical and photophysical properties. Alternatively, the functional group can be bound to the chromophore via an aliphatic linker. Several covalently bonded **BP**-amine systems have been investigated and an enhanced photo-reduction quantum yield was obtained by the introduction of a spacer between the moieties.(8, 9) Therefore, phenyl glycine derivatives were covalently bound to **BP** via a methylene spacer (**2E** and **2A**, Fig. 1), recently (10, 11).

These covalently bound PI systems were compared with the physical mixtures of the components and the industrially applied mixture of **BP**/triethanol amine (**TEA**). For [(4-benzoylbenzyl)phenylamino] acetic acid (**2A**), the polymerization rate ($R_p$) has been tripled compared to both reference initiators (10). As the ester **2E** has also given remarkable photoactivity, the decarboxylation step can not be the only responsible mechanism. Recent steady state photolysis experiments gave some indications of a $\beta$-phenylogous type of cleavage.

Based on these surprising results, we were interested to investigate the influence of different structural modifications on the performance of the PI. In all cases, the free acids (**A**) and also the esters (**E**) should be investigated to see the extent of a decarboxylation reaction.

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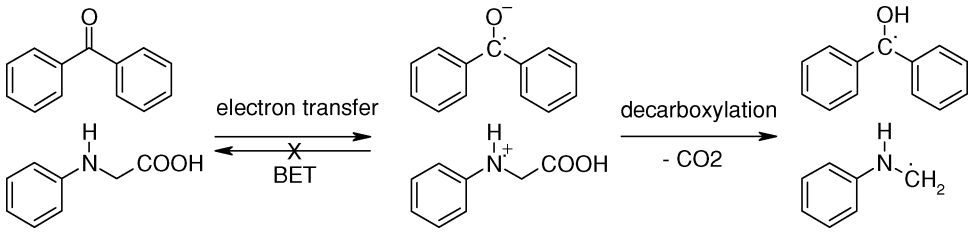



**Sch. 1.** Decarboxylation of N-phenyl glycine.

First, the influence of the substituent position at **BP** was of interest (**3E**, **3A**) (Fig. 1). Based on these investigations, the aromatic ring (**4E**, **4A**, **5E**, **5A**) and the carboxyl group (**2N**, **2K**, **2Q** (12) and **6**) of the glycine coinitiator moiety was modified or removed.

## 2. Experimental

### 2.1. *Materials*

All reagents were purchased from Sigma-Aldrich and were used without further purification. The solvents were dried and purified by standard laboratory methods. Thin-layer chromatography (TLC) was carried out with Alugram Sil-G/UV 254 sheets (Macherey Nagel). Column chromatography was performed on Merck silica gel 60 (0.063–0.200 mm).

For photo-DSC experiments, 2-(2-ethoxyethoxy) ethyl acrylate (EEEA, Miramer 170, Rahn) and N[3-(aryloyl ethyl amino) propyl]-N-ethyl acryl amide (DEBAAP, Ivoclar Vivadent AG) were used as monomers. **BP** or 3-(4-benzoylphenoxy)-2-hydroxy-N,N,N-trimethyl-1-propanaminium chloride (**QBPQ**, Quantacure BPQ, Great Lakes) were applied as reference initiators and a equimolar amount of triethanolamine (TEA) was used as coinitiator.

### 2.2. *Characterization*

$^1$H- and $^{13}$C-NMR spectra were recorded on a Bruker AC-E-200 FT-NMR-spectrometer, and deuterated chloroform ($CDCl_3$), dimethyl sulfoxide (DMSO-$d_6$) and deuterium oxide ($D_2O$) were used as solvents. The UV absorption was measured with a Hitachi U-2001 spectrometer with spectrophotometric-grade acetonitrile as solvent. Melting points were determined with a Kofler hot-stage-type microscope and are uncorrected. Elemental microanalysis was carried out with an EA 1108 CHNS-O analyzer from Carlo Erba at the microanalytical laboratory of the Institute for Physical Chemistry at the University of Vienna.

### 2.3. *Syntheses*

N-Methyl-N-phenylamino acetic acid (**1A**) (13), N-methyl-N-phenylglycine ethyl ester (**1E**) (14), [(4-benzoyl-benzyl)-phenyl-amino]-acetic acid ethyl ester (**2E**) (10), [(4-benzoyl-benzyl)-phenyl-amino]-acetic acid (**2A**) (10) and 3- and 4-(bromomethyl)-benzophenone (15) were synthesized according to procedures described in the literature. All spectral data were in agreement with the reported data.

### 2.4. *General procedure for preparation of 3E, 4E and 6*

3- or 4-(Bromo methyl)-benzophenone (3.07 g, 11.2 mmol) was dissolved in 3 mL of dry DMF under reflux.

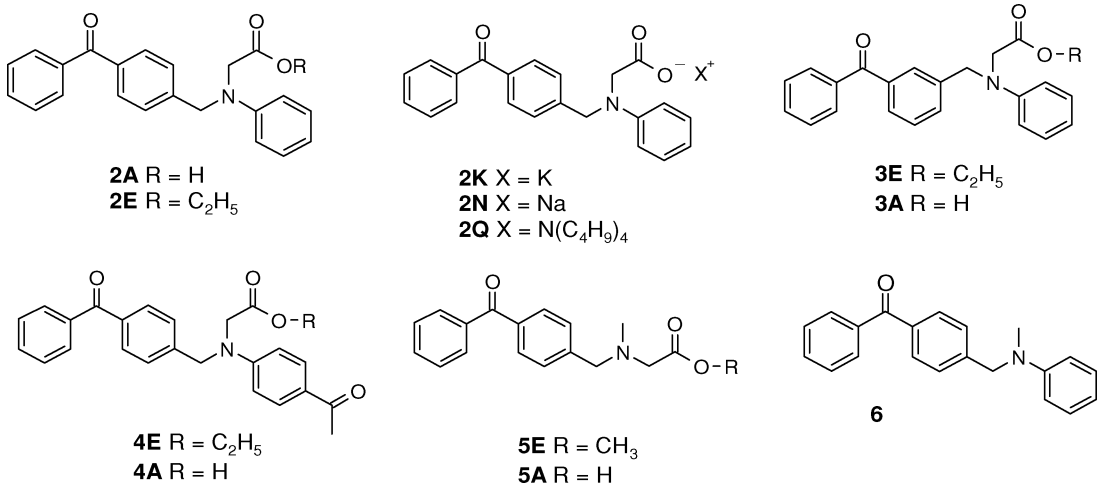



**Fig. 1.** Benzophenone based glycine related PIs.

Subsequently, this solution was added to a mixture of the corresponding secondary amine (N-Phenylglycine ethylester, (4-acetylphenylamino)-acetic acid ethylester, N-methylaniline) (11.2 mmol) and 2 equivalents of $K_2CO_3$ in 3 mL of dry DMF. The mixture was stirred for 6 h at 120°C. After cooling to ambient temperature, the salts were filtered off and washed with diethyl ether. The solvent was distilled from the filtrate and the residue was dissolved in 100 mL of chloroform (for **3E**, **6**) or acetic acid ethyl ester (for **4E**). After threefold extraction with water (3 × 80 mL), the organic layer was dried over $Na_2SO_4$ and concentrated *in vacuo* to obtain the crude product as a dark, highly viscous oil. The resulting residue was purified by column chromatography (petroleum ether/acetic acid ethyl ester).

*[(3-Benzoyl-benzyl)-phenyl-amino]-acetic acid ethyl ester (**3E**)*

Pale yellow highly viscous oil; Yield: 63%; $^1$H-NMR ($CDCl_3$, $\delta$ ppm): 7.81–7.69 (m, 4H), 7.57–7.43 (m, 5H), 7.28–7.20 (m, 2H), 6.84–6.68 (m, 3H), 4.75 (s, 2H), 4.22 (q, J = 7.1 Hz, 2H), 4.13 (s, 2H), 1.27 (t, J = 6.8 Hz, 3H); $^{13}$C-NMR ($CDCl_3$, ppm): 196.3, 170.9, 148.2, 143.7, 137.6, 136.5, 130.6, 130.0, 129.3, 128.2, 126.5, 118.0, 112.6, 61.1, 55.8, 52.9, 14.2; Elem. Anal. Calcd: C 77.19, H 6.21, N 3.75; Found: C 76.95, H 6.30, N 3.65.

*[(4-Acetyl-phenyl)-(4-benzoyl-benzyl)-amino]-acetic acid ethyl ester (**4E**)*

Yellow waxy compound; Yield: 24%; $^1$H-NMR ($CDCl_3$,$\delta$ ppm): 7.79–7.69 (m, 6H), 7.44–7.38 (m, 5H), 6.59–6.48 (m, 2H), 4.74 (s, 2H), 4.03–3.87 (m, 4H), 2.43 (s, 3H), 1.24 (t, J = 6.7 Hz, 3H); $^{13}$C-NMR ($CDCl_3$, ppm): 196.5, 196.4, 170.3, 150.8, 145.6, 137.6, 136.7, 132.4, 130.8, 130.4, 130.0, 128.3, 126.4, 113.7, 111.7, 64.6, 61.5, 45.0, 26.0, 14.2; Elem. Anal. Calcd: C 75.16, H 6.06, N 3.37; Found: C 74.97, H 6.18, N 3.48.

*{4-[(Methyl-phenyl-amino)-methyl]-phenyl}-phenyl-methanone(**6**)*

Pale yellow crystals; Yield: 78%; m.p. 41–42.5°C; $^1$H-NMR ($CDCl_3$,$\delta$, ppm): 7.84–7.78 (m, 4H), 7.62–7.24 (m, 7H), 6.81–6.77 (m, 3H), 4.65 (s, 2H), 3.10 (s, 3H); $^{13}$C-NMR ($CDCl_3$, ppm): 170.8, 144.5, 141.7, 137.6, 136.4, 132.2, 130.7, 130.0, 129.3, 128.4, 126.5, 118.2, 113.0, 61.0, 41.7; Elem. Anal. Calcd: C 83.69, H 6.35, N 4.65; Found: C 83.92, H 6.50, N 4.62.

*[(4-Benzoyl-benzyl)-methyl-amino]-acetic acid methyl ester (**5E**):*

Sarcosine methyl ester hydrochloride (2.54 g, 18.17 mmol) was dissolved in dry DMF (15 mL). After warming to 60°C, 3 equiv. of triethyl amine and a solution of 4-(bromo methyl)-benzophenone (3.07 g, 11.2 mmol) in hot dry DMF (15 mL) were added. The mixture was stirred for 24 hours at 80°C. After cooling to ambient temperature the salts were filtered off and the DMF was removed *in vacuo*. The crude product was dissolved in acetic acid ethyl ester (100 mL). After twofold extraction with water (2 × 60 mL), the organic layer was dried over $Na_2SO_4$ and concentrated *in vacuo*. The dark, highly viscous oil was purified by column chromatography (petroleum ether/ acetic acid ethyl ester 10:1) to give **5E** as a yellow highly viscous oil.

Yield: 47%; $^1$H-NMR ($CDCl_3$,$\delta$ ppm): 7.78–7.65 (m, 4H), 7.54–7.18 (m, 5H), 3.75 (s, 2H), 3.67 (s, 3H), 3.27 (s, 2H), 2.35 (s, 3H); $^{13}$C-NMR ($CDCl_3$, ppm): 196.3, 171.2, 143.4, 137.6, 136.5, 132.3, 130.2, 130.0, 129.9, 128.7, 128.2, 60.7, 57.5, 51.5, 42.3; Elem. Anal. Calcd.: C 72.71, H 6.44, N 4.71; Found: C 72.52, H 6.48, N 4.57.

### 2.5. *General procedure for preparation of acids 3A, 4A and 5A*

13.4 mmol of the ester **3E**, **4E** or **5E** were dissolved in ethanol (30 mL) and an aqueous solution of 3.5 equiv. of KOH (4 mL) was added. The reaction mixture was stirred at ambient temperature for 96 h under light protection. Ethanol was removed *in vacuo* at ambient temperature by aceotropic distillation with water (3 × 30 mL). Water was added to the remainder (total volume 120 mL) and the aqueous suspension was extracted with acetic acid ethyl ester (3 × 70 mL). Hydrochloric acid (0.5 M) was added to the aqueous solution until pH 2–3 was achieved. The cloudy liquid was extracted with acetic acid ethyl ester several times (5 × 100 mL). The combined organic layers were dried over $Na_2SO_4$ and the solvent was removed under *vacuo* at ambient temperature.

*[(3-Benzoyl-benzyl)-phenyl-amino]-acetic acid (**3A**)*

Yellow crystalls; Yield: 83%; m.p 98.5–100 °C; $^1$H-NMR ($CDCl_3$,$\delta$, ppm): 7.80–7.67 (m, 4H), 7.54–7.41 (m, 5H), 7.76–7.21 (m, 2H), 6.82–6.63 (m, 3H), 4.72 (s, 2H), 4.10 (s, 2H); $^{13}$C-NMR ($CDCl_3$, ppm): 196.4, 174.8, 138.0, 137.4, 132.5, 131.7, 130.2, 129.4, 128.9, 128.5, 128.1, 118.7, 112.8, 61.1, 55.9; Elem. Anal. Calcd.: C 76.50, H 5.54, N 4.06; Found: C 76.45, H 5.73, N 3.94.

*[(4-Acetyl-phenyl)-(4-benzoyl-benzyl)-amino]-acetic acid (**4A**)*

Yellow crystals; Yield: 83%; decompsition: 204–209°C, $^1$H-NMR ($CDCl_3$, $\delta$ ppm): 7.82–7.71 (m, 6H), 7.47–7.39 (m, 5H), 6.72–6.50 (m, 2H), 4.74 (s, 2H), 4.27 (s, 2H), 2.47 (s, 3H); $^{13}$C-NMR ($CDCl_3$, ppm): 196.5, 196.4, 176.1, 147.9, 145.6, 137.6, 136.7, 132.4, 130.8, 130.4, 130.0, 128.3, 126.4, 113.7, 111.7, 55.7, 52.4, 26.0; Elem. Anal. Calcd.: C 74.40, H 5.46, N 3.62; Found: C 74.63, H 5.68, N 3.48.

*[(4-Benzoyl-benzyl)-methyl-amino]-acetic acid (**5A**)*

Pale brown waxy substance; Yield: 73%; $^1$H-NMR (DMSO, $\delta$ ppm): 7.78–7.70 (m, 4H), 7.54–7.41 (m, 5H), 4.29 (s, 2H), 3.62 (s, 2H), 2.74 (s, 3H); $^{13}$C-NMR (DMSO, ppm): 196.3, 176.4, 143.4, 137.5, 136.3, 132.4, 130.4, 130.2,

130.1, 128.7, 128.0, 60.6, 57.4, 42.3; Elem. Anal. Calcd.: C 72.07, H 6.05, N 4.94; Found: C 72.35, H 6.28, N 4.74.

### 2.6. *General procedure for preparation of salts 2K, 2N and 2Q*

To a suspension of 2 g (5.79 mmol) of **2A** in 10 mL of water, an equimolar amount of 40% aqueous solution of the corresponding hydroxide was added under light protection. After 36 h of stirring at ambient temperature, the solvent was removed under *vacuo*. The product remains as a yellow solid in quantitative yield.

*[(4-Benzoyl-benzyl)-phenyl-amino]-acetate potassium salt (**2K**)*

$^1$H-NMR (DMSO,$\delta$ ppm): 7.77–7.67 (m, 5H), 7.61–7.53 (m, 4H), 7.14–7.06 (m, 2H), 6.58–6.54 (m, 3H), 4.72 (s, 2H), 3.94 (s, 2H); $^{13}$C-NMR (DMSO, ppm): 196.3, 171.2, 149.1, 145.9, 137.6, 135.7, 132.9, 130.3, 130.0, 129.9, 128.9, 127.0, 115.2, 112.2, 55.8, 55.1; Calcd.: C 68.90, H 4.73, N 3.65; Found: C 69.20, H 4.62, N 3.22.

*[(4-Benzoyl-benzyl)-phenyl-amino]-acetate sodium salt (**2N**)*

$^1$H-NMR (DMSO,$\delta$ ppm): 7.73–7.66 (m, 5H), 7.59–7.52 (m, 4H), 7.13–7.03 (m, 2H), 6.55 (m, 3H), 4.65 (s, 2H), 3.78 (s, 2H); $^{13}$C-NMR (DMSO, ppm): 196.3, 171.2, 149.1, 145.9, 137.6, 135.7, 132.9, 130.3, 130.0, 129.9, 128.9, 127.0, 115.2, 112.2, 55.8, 55.1; Element Anal. Calcd.: C 71.93, H 4.94, N 3.81; Found: C 71.80, H 5.11, N 3.49.

*[(4-Benzoyl-benzyl)-phenyl-amino]-acetate tetrabutyl-ammonium salt (**2Q**):*

$^1$H-NMR ($D_2O$, $\delta$ ppm)): 7.22–6.88 (m, 11H), 6.41–6.37 (m, 3H), 4.49 (s, 2H), 3.79 (s, 2H), 2.91 (m, 8H), 1.38 (m, 8H), 1.14 (m, 8H), 0.75 (t, J=7.1 Hz, 9H); $^{13}$C-NMR ($D_2O$, ppm): 197.0, 178.2, 148.3, 145.5, 136.8, 135.0, 132.4, 130.2, 129.6, 129.1, 128.1, 126.4, 116.1,111.7, 57.9, 54.9, 23.0, 19.1, 12.8; Element Anal. Calcd.: C 77.77, H 9.27, N 4.77; Found: C 77.61, H 8.98, N 4.38.

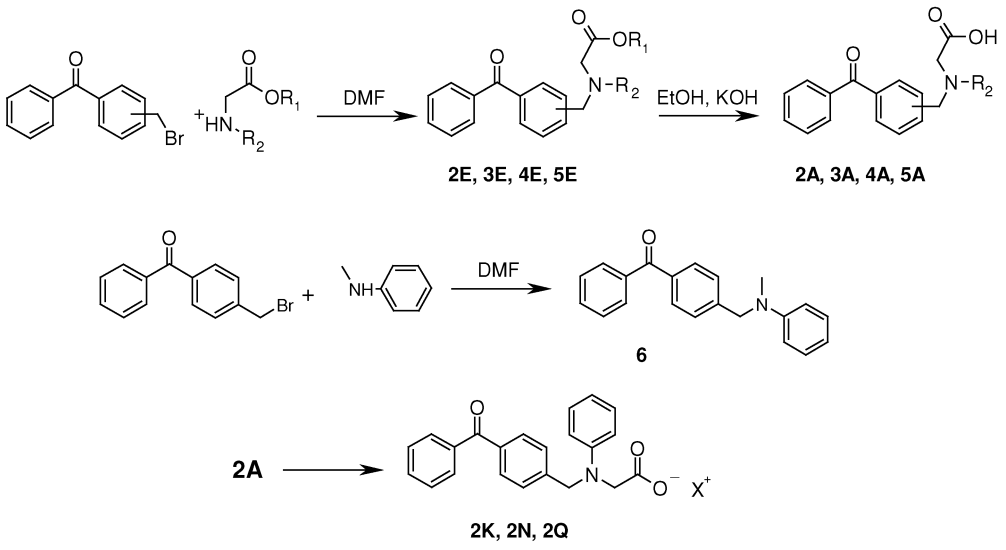
## 3. Results and discussions

### 3.1. *Syntheses*

Generally, the glycine ester derivatives **3E**, **4E** and **5E** (Scheme 2, Table 1) and compound **6** were obtained in an analogous way to a procedure already described (10, 16) by a coupling reaction of brominated *para*- and *meta*-methyl benzophenone and a suitable secondary amine (Scheme 2). The corresponding acids **3A**, **4A**, **5A** were prepared in 73 to 83% yield via saponification and subsequent acidification. (10) These steps had to be done at ambient temperature to avoid thermal decarboxylation. By stirring **2A** with an equimolar amount of an aqueous solution of alkali hydroxides and tetrabutyl ammonium hydrochloride (12), the salts **2N**, **2K** and **2Q** were synthesized in nearly quantitative yield.

### 3.2. *UV-Vis spectroscopy*

UV-Vis spectra of the new PIs were recorded in acetonitrile. The type of transition is of prime importance since electron transfer easily occurs with $\pi - \pi^*$ and n-$\pi^*$ transitions whereas only the n-$\pi^*$ excited states are efficient in hydrogen abstraction. A typical UV-Vis spectrum of **2A** and **2E** has been discussed recently (10). The $\varepsilon_{max}$ and the wavelength of maximum absorption ($\lambda_{max}$) of all initiators are summarized in Table 2.




**Sch. 2.** Syntheses of esters, acids and salts of BP based PIs.

**Table 1.** Substituents and functional groups of BP based PIs

| *Compound* | *Substituent position* | *R1* | *R2* | *X* | *Yield [%]* |
|---|---|---|---|---|---|
| **2A** | Para | — | $-C_6H_5$ | — | 82 |
| **2E** | Para | $-CH_2CH_3$ | $-C_6H_5$ | — | 77 |
| **2N** | Para | — | $-C_6H_5$ | Na | Quant. |
| **2K** | Para | — | $-C_6H_5$ | K | Quant. |
| **2Q** | Para | — | $-C_6H_5$ | $N(C_4H_9)_4$ | Quant. |
| **3E** | Meta | $-CH_2CH_3$ | $-C_6H_5$ | — | 63 |
| **3A** | Meta | — | $-C_6H_5$ | — | 79 |
| **4E** | Para | $-CH_2CH_3$ |  | — | 24 |
| **4A** | Para | — |  | — | 83 |
| **5E** | Para | $-CH_3$ | $-CH_3$ | — | 47 |
| **5A** | Para | — | $-CH_3$ | — | 73 |

Two characteristic absorption bands were found: A strong absorption for the $\pi - \pi^*$ transition at approx. $253 \pm 2.5$ nm and a broad shoulder in the range of 320 to 380 nm for the spin forbidden n-$\pi^*$ transition. The molar extinction coefficients ($\varepsilon_{max}$) of all presented PIs are in a similar order of magnitude.

### 3.3. *Photo-DSC*

To obtain fast and accurate indication of the PI performance, photo-DSC of the different kinds of PIs were recorded. Various important polymerization parameters are accessible. The time to reach the maximum polymerization heat ($t_{max}$,[s]) reveals information about the PI activity. The DBC [%] was calculated from the overall heat evolved and the $R_p$ [mol*$L^{-1}$*$s^{-1}$] was obtained from the height of the exothermic peak(17). The Photo-DSCs were conducted on a modified Shimadzu DSC 50 equipped with a home-made aluminium cylinder as described previously (17). Filtered UV-light (320-500 nm) was applied by a light guide (EXFO Omnicure 2000) with a light intensity of 8 mW/$cm^2$ at the level of the surface of the cured samples. The measurements were carried out in EEEA ($H_0$ = 80.5 kJ/mol) as a simple monofunctional model monomer and—for water soluble compounds—in a mixture of DEBAAP ($H_0$ = 120.6 kJ/mol) and water (5%) using a PI concentration of 0.05 mol*$L^{-1}$. The mass of the samples was $6 \pm 0.2$ mg and the measurements were carried out in an isothermal mode at room temperature under a nitrogen atmosphere.

Photo-DSC investigations of the meta position substituted derivatives **3E** and **3A** showed a very poor initiation activity compared to corresponding para linked compounds **2E** and **2A** (Fig. 2a). Only after extended irradiation time, the ester **3E** showed acceptable DBC. Despite of the possibility of increased reactivity by additional spontaneous decarboxylation reactions, only very poor performance was achieved for **3A** (Table 3). The extremely low reactivity of **3A** might be assigned to some kind of intramolecular interaction of the acid with the carbonyl group of the BP moiety. Therefore, in further investigations the para substitution was preferred.

Next, **4E** and **4A** — that possess an electron-withdrawing acetyl group on the phenyl ring - were investigated. It was expected, that this group is able to stabilize the radical that originates during photochemical excitation (19). Subsequently, a $\beta$-phenylogous cleavage could occur and thus increase the initiation activity. Because of the poor solubility of the acid **4A**, only a 0.005 molar solution of the PI could be used for photo-DSC tests.

**Table 2.** . UV-Vis spectroscopy of PIs ($10^{-5}$ M in acetonitrile)

| *PI* | $\lambda_{max}$ *[nm]* | $\varepsilon_{max}$* $10^{-3}$ *[L*$cm^{-1}$ *$mol^{-1}$]* |
|---|---|---|
| **5E** | 254.5 | 615 |
| **5A** | 254.5 | 177 |
| **6** | 255.0 | 758 |
| **3E** | 250.5 | 312 |
| **3A** | 250.5 | 319 |
| **4E** | 252.0 | 327 |
| **4A** | 252.5 | 396 |

**Table 3.** Photo-DSC data of EEEA with PIs **2E**, **2A**, **3E**, **3A**, **4E**, **5A**, **5E, 6** (0.05 M) and **4A** (0.005 M)

| *PI* | $t_{max}$ *[s]* | *DBC [%]* | $R_P$* $10^3$*[mol* $L^{-1}$ * $s^{-1}$]* |
|---|---|---|---|
| **2E** | 28 | 94 | 97 |
| **2A** | 18 | 95 | 139 |
| **3E** | 17 | 62 | 37 |
| **3A** | 13 | 18 | 17 |
| **4E** | 34 | 76 | 22 |
| **4A*** | 25 | 67 | 30 |
| **5E** | 25 | 75 | 25 |
| **5A** | 26 | 78 | 34 |
| **6** | 32 | 90 | 65 |

0.005 M PI solution.

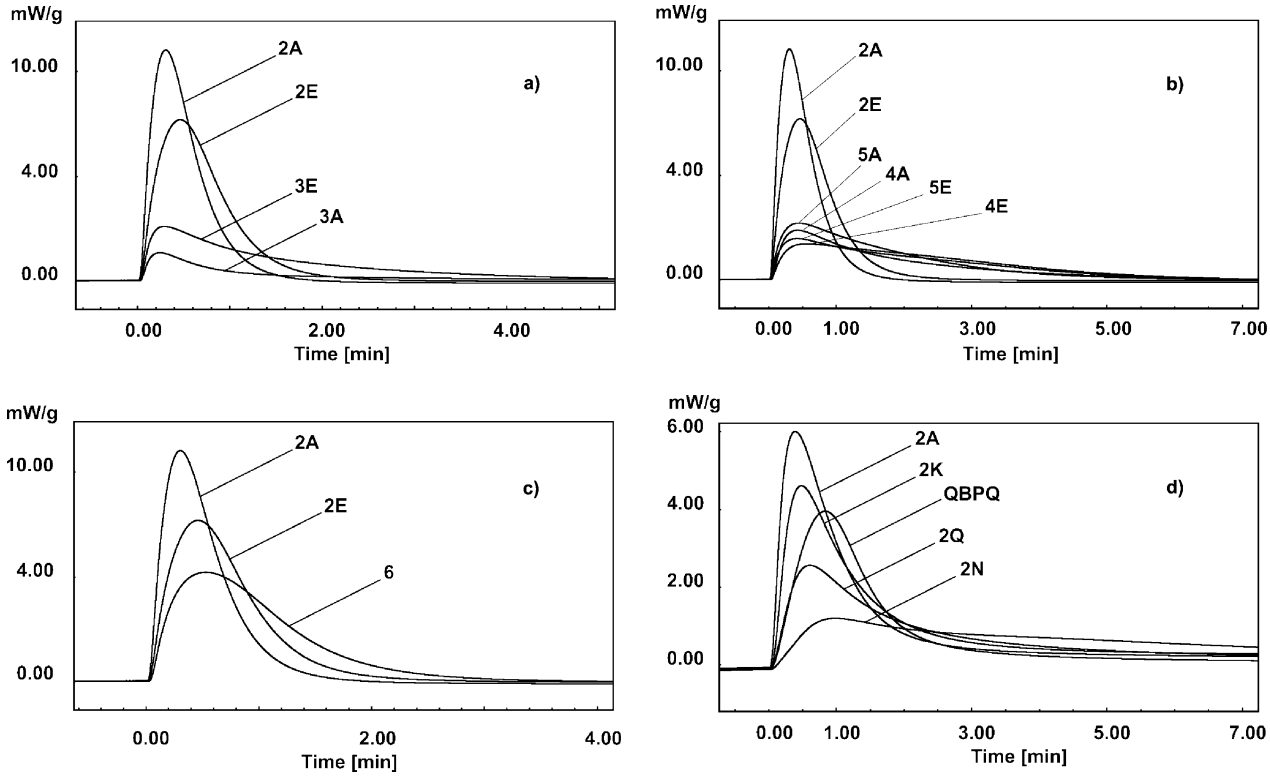



**Fig. 2.** Photo-DSC of EEEA with a) 0.05 M PIs **2E**, **2A**, **3E** and **3A,** b) 0.05 M PIs **2E**, **2A**, **4E**, **5E**, **5A** and 0.005 M PI **4A,** c) 0.05 M PIs **2E**, **2A**, **6** and, d) of DEBAAP with 5 wt% water with 0.05 M PIs **2A**, **2K**, **2N**, **2Q** and **QBPQ**



Although a distinct advantage in the initiation activity compared to the unsubstituted compounds has been described for aceto-substituted N-phenyl glycine (18, 20), an improvement in the photo initiating activity of **4E** and **4A** were not observed. On the contrary, in photo-DSC measurements these PIs performed significantly poorer ($t_{max}$ and $R_P$) than the reference compounds **2E** and **2A** (Fig. 2b, Table 3). Slightly better results of $t_{max}$ and $R_P$ were given when the acid form of the initiator was used. An exact comparison of PIs **4A** and **4E** is not possible due to the poor solubility of the acid and the resulting lower initiator concentration. Despite the tenth part of concentration of **4A,** the $R_P$ and DBC are in the same order of magnitude as for **4E** and the $t_{max}$ is significantly shorter. These results can be related to the decarboxylation ability of the acid functionality. To investigate the influence of a radical or radical cation stabilizing effect of the aromatic moiety itself, PIs **5E** and **5A** without an aromatic ring were also considered. Generally, very similar behavior as for **4A** and **4E** was observed with these PIs. Thus, an unsubstituted phenyl glycine derivative proved to act as the most suitable moiety and was therefore, used in further modifications.

To demonstrate the effect that spontaneous decarboxylation of the coinitiator and therefore prevention of BET has a significant influence on the photoinitiation ability, the reactivity of acid **2A** was compared with the corresponding ethyl ester compound **2E** and **6** (Fig. 2c). The latter PI is a related tertiary phenyl amine that rather has a methyl group than the acetic acid residue.

Although the DBCs for all of these PIs were in the same order of magnitude, the decarboxylation effect was clearly visible in the 1.5 fold $R_P$ of **2A** compared to $R_P$ of **2E** (Table 3). It was quite surprising that in spite of a steric advantage of the methyl group of **6** over the acetic ethyl ester group of **2E**, significantly lower reactivity was observed. The ester group in **2E** seems to be able to activate the hydrogen transfer step. Therefore, with the base structure oft PI **2A,** the optimum performance is given.

As in a **BP**/(phenylthio)acetic acid – PI system,, the transformation of the coinitiator to its tetrabutyl ammonium salt dramatically increased the sensitivity of the system (21), the quaternary tetra butyl ammonium salt **2Q**, the sodium salt **2N** and the potassium salt **2K** of **2A** were investigated in an aqueous monomer formulation (DEBAAP, Fig. 2d). **2A** was used as a reference although a concentration of 0.05 mol*$L^{-1}$ is the upper limit of solubility. Furthermore, the commercially available and industrially used water soluble initiator Quantacure BPQ (**QBPQ**) with an equimolar amount of triethanolamine as coinitiator was used as a reference system.

The photo-DSC of the excellently water soluble **2K** showed only slightly lower activity (higher $t_{max}$) than the highly reactive, but hardly soluble PI **2A**. DBC and $R_P$

**Table 4.** Photo-DSC data of DEBAAP with 5 wt% water with 0.05 M PIs **2A 2K**, **2N, 2Q** and **QBPQ**

| *PI* | $t_{max}$ *[s]* | *DBC [%]* | $R_P * 10^3 [mol * L^{-1} * s^{-1}]$ |
|---|---|---|---|
| **2A** | 23 | 81 | 35.6 |
| **2N** | 59 | 65 | 6.6 |
| **2K** | 29 | 73 | 27.3 |
| **2Q** | 36 | 64 | 15.3 |
| **QBPQ** | 50 | 71 | 23.6 |

were in a similar order of magnitude (Table 4). Compared to the already known initiator **QBPQ**, **2K** showed a similar DBC and a significant improvement in $R_p$ and $t_{max}$. By contrast, the quaternary ammonium salt and the sodium salt showed lower $R_P$. According to prior investigations (12), an explicit relationship between the type of the acid counterion and its coinitiation ability could not be found.

Thus, by **2K** an efficient and excellently water-soluble PI was found which can also be applied in higher concentrations than demonstrated within these studies.

## 4. Conclusions

In the present paper, several new covalently bound Type II PIs based on a **BP** chromophore and a glycine related coinitiator are presented. By variation of the substituent position on the **BP** moiety, the most suitable linking position to the coinitiator was found to be the para-position of **BP**. By modification of the aromatic ring on phenyl glycine, it was shown that neither an electron withdrawing aceto group on the phenyl ring nor a complete lack of this aromatic ring is able to enhance the initiator activity. The 1.5-fold increase of $R_P$ between the ester **2E** and the acid **2A** can be ascribed to the decarboxylation ability of the glycine unit. In addition, it was shown that a sterically hindered methylene group, in the glycine ester **2E** gave an even better initiation performance than the plain methyl group of **6**. For aqueous monomer formulations, several salts of the phenylglycine based PI **2A** were tested, whereas no distinct accordance of the counter ion's properties to the initiation ability could be assigned. The potassium derivative **2K** provided a very good initiation performance and is therefore an excellently water soluble Type II PI based on BP and phenyl glycine. From the viewpoint of photoreactivit, the backbone of **2E** is essential and modifications on the aromatic phenylamino moiety lead to a significant loss of photoreactivity. Mechanistic investigations on the potential ß-phenylogous cleavage are currently carried out.



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