

Substituent Effects on Photoinitiation Ability of Monoaminoanthraquinone-based Photoinitiating Systems for Free Radical Photopolymerization under LEDs

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Abstract:

Three monoamino-substituted anthraquinone derivatives (AAQs), *i.e.* 1-aminoanthraquinone (AAQ), 1-(methyldamino)anthraquinone (MAAQ) and 1-(benzamido)anthraquinone (BAAQ), incorporated with various additives [*e.g.* triethanolamine (TEAOH) and phenacyl bromide (PhC(=O)CH₂Br)] have been investigated for their roles as photoinitiating systems of free radical photopolymerization of (meth)acrylate monomers upon the exposure to UV to green LEDs. The AAQs-based photoinitiating systems, AAQ/TEAOH/PhC(=O)CH₂Br and BAAQ/TEAOH/PhC(=O)CH₂Br photoinitiators exhibited the highest efficiency for the free radical photopolymerization of DPGDA under the irradiation of blue LED and UV LED respectively, which is consistent with the extent of overlap between their absorption spectra and the emission spectra of the LEDs. AAQ/TEAOH/PhC(=O)CH₂Br photoinitiator can also initiate the free radical photopolymerization of different (meth)acrylate monomers, with an efficiency dependent on the chemical structures of these monomers.

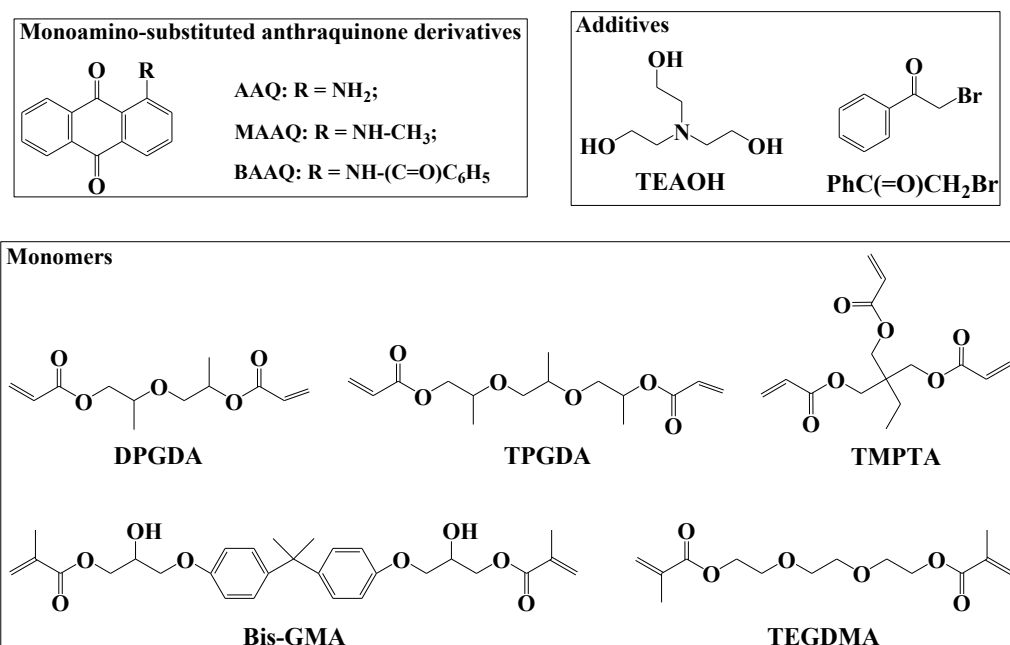
Keywords: aminoanthraquinone derivatives, photoinitiator, photoinitiating system, free radical photopolymerization, LED

Photoinitiators play a significant role in photopolymerization processes as they can determine the polymerization efficiency under irradiation of certain wavelengths of light.^[1] Traditional photopolymerization reactions are normally carried out under UV light (from mercury lamps) for the production of various materials such as coatings, inks, varnishes, adhesives, and microelectronics in industry.^[2] Recently, UV or visible light delivered from light-emitting diodes (LEDs)^[3] have attracted increasing attention for use in photopolymerization^[4] as a greener and milder alternative to traditional methods.^[1d,5] Significant effort has been devoted to designing and synthesizing novel high-performance photoinitiators operating using UV or red light delivered from LEDs.^[6] However, rather than design new compounds, it is industrially attractive to determine if existing commercial compounds (*e.g.* dyes) might be equally suitable.

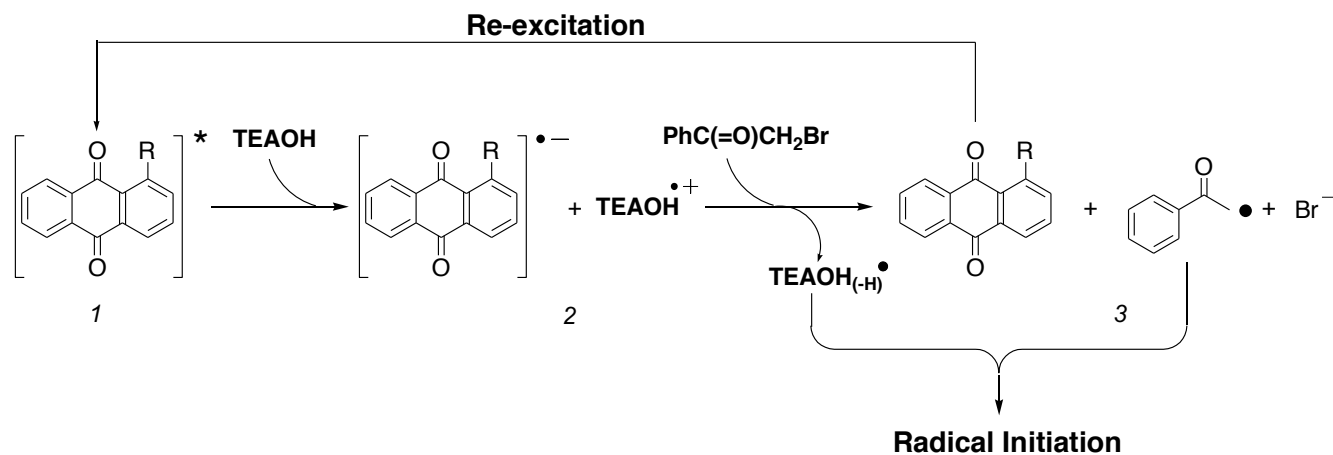
Amino-substituted anthraquinones (AQs) have widespread applications in biology, pharmaceutical chemistry, and the dye industry,^[7] and exhibit a range of photophysical properties that make them promising targets as photoinitiators.^[8] Recently, several 9,10-anthraquinone derivatives (AQs)^[9] including multihydroxyanthraquinones^[10] and disubstituted aminoanthraquinones^[11] have been reported as excellent photoinitiators of polymerization. In each case their behaviour and suitability for different monomers and different colours of light depended heavily on their substitution pattern. With this in mind, and with a view to expanding the repertoire of visible-light photopolymerization, in the present work we investigate the photoinitiation mechanism and ability of monoamino-substituted anthraquinone derivatives, *i.e.* 1-aminoanthraquinone (AAQ), 1-(methylamino)anthraquinone (MAAQ), and 1-(benzamido)anthraquinone (BAAQ). These compounds were recently investigated as photoinitiators for the cationic polymerization of epoxide and divinyl ether monomers under UV, blue

or green LEDs.^[12] In present work, their suitability for free radical photopolymerization of various (meth)acrylate monomers is investigated.

Free radicals are expected to be generated from the photoinitiating systems consisting of AAQs and typical type II additives/coinitiators [*e.g.* triethanolamine (TEAOH) and phenacyl bromide (PhC(=O)CH₂Br)] (Scheme 1) under light irradiation by analogy with the general behavior of photoinitiating systems described in previous reports (Scheme 2).^[13] Upon excitation the excited AQ undergoes an electron transfer reaction with the TEAOH, which becomes a TEAOH-based free radical (with the loss of one hydrogen) capable of initiating polymerization. The PhC(=O)CH₂Br takes the electron back from the AQ radical anion to re-generate the AQ initiator, with the PhC(=O)CH₂Br anion immediately undergoing reductive cleavage to Br⁻ and a second initiating radical. Similar to that which has been reported previously,^[11a] free energy calculations have been performed to demonstrate the overall thermodynamic favourability for electron transfer upon population of the first excited state (Figure 1). These processes exhibit similar thermodynamic favourabilities to those that have been studied previously and have been shown both theoretically and experimentally to undergo fast electron transfer.



Scheme 1. Chemical structures of the studied monoamino-substituted anthraquinone derivatives (AAQ, MAAQ and BAAQ), additives (TEAOH and PhC(=O)CH₂Br) and monomers (DPGDA, TPGDA, TMPTA, Bis-GMA and TEGDMA).



Scheme 2. Initiation Mechanism.

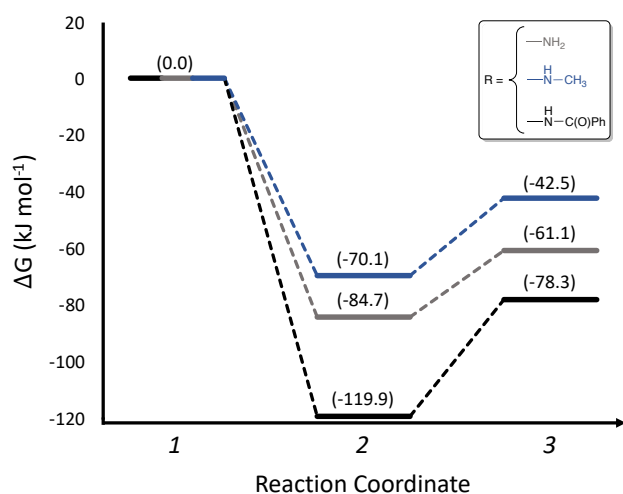


Figure 1. Free energy surface for electron transfer reactions, relative to the anthraquinone's first excited state.

The interaction between the singlet states of AAQs and additives/coinitiators was investigated using the fluorescence quenching approach. The fluorescence emissions of AAQ, MAAQ and BAAQ (associated with their excited singlet states) have been reported previously.^[12] As shown in Figure 2, the

fluorescence of BAAQ was quenched with the addition of TEAOH [Figure 2 (a)], and the interaction rate constant of $^1\text{BAAQ/TEAOH}$ (*i.e.* $k_q \sim 2.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) was determined from the Stern-Volmer treatment [Figure 2 (b); fluorescence lifetime of BAAQ $\tau_0 \sim 2.6 \text{ ns}$]. Similarly, $k_q \sim 2.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ and $\sim 2.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ was obtained for $^1\text{AAQ/TEAOH}$ and $^1\text{MAAQ/TEAOH}$ respectively, which indicated the process was diffusion-controlled. However, no fluorescence quenching was observed for $^1\text{AAQs/PhC(=O)CH}_2\text{Br}$ indicating no reaction between them, *i.e.* AAQs preferentially interacted with TEAOH.

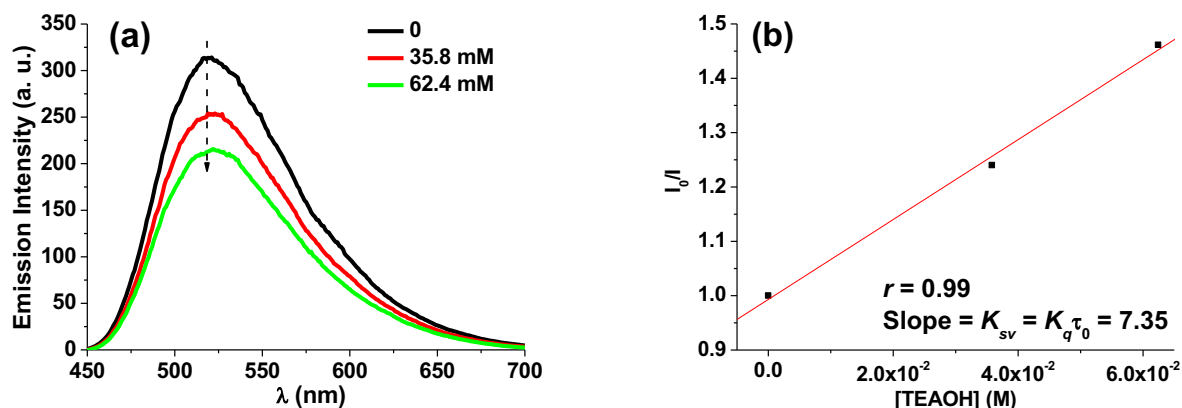


Figure 2. (a) Fluorescence spectra of BAAQ as a function of [TEAOH] in acetonitrile and (b) the relevant Stern-Volmer plot.

The interaction of AAQs with their additives under blue LED irradiation can also be qualitatively studied using steady state photolysis.^[1c] As shown in Figure 3, the UV-vis absorption of AAQ/TEAOH and BAAQ/TEAOH declined with increasing irradiation time due to the photochemical reactions, while no decrease of UV-vis absorption of MAAQ/TEAOH was observed implying an inefficiency for this system. In addition, there was no obvious change for the light absorption of AAQs/PhC(=O)CH₂Br systems during steady state photolysis (Figure S1 in the supporting information SI), which is in agreement with the fluorescence quenching experiments.

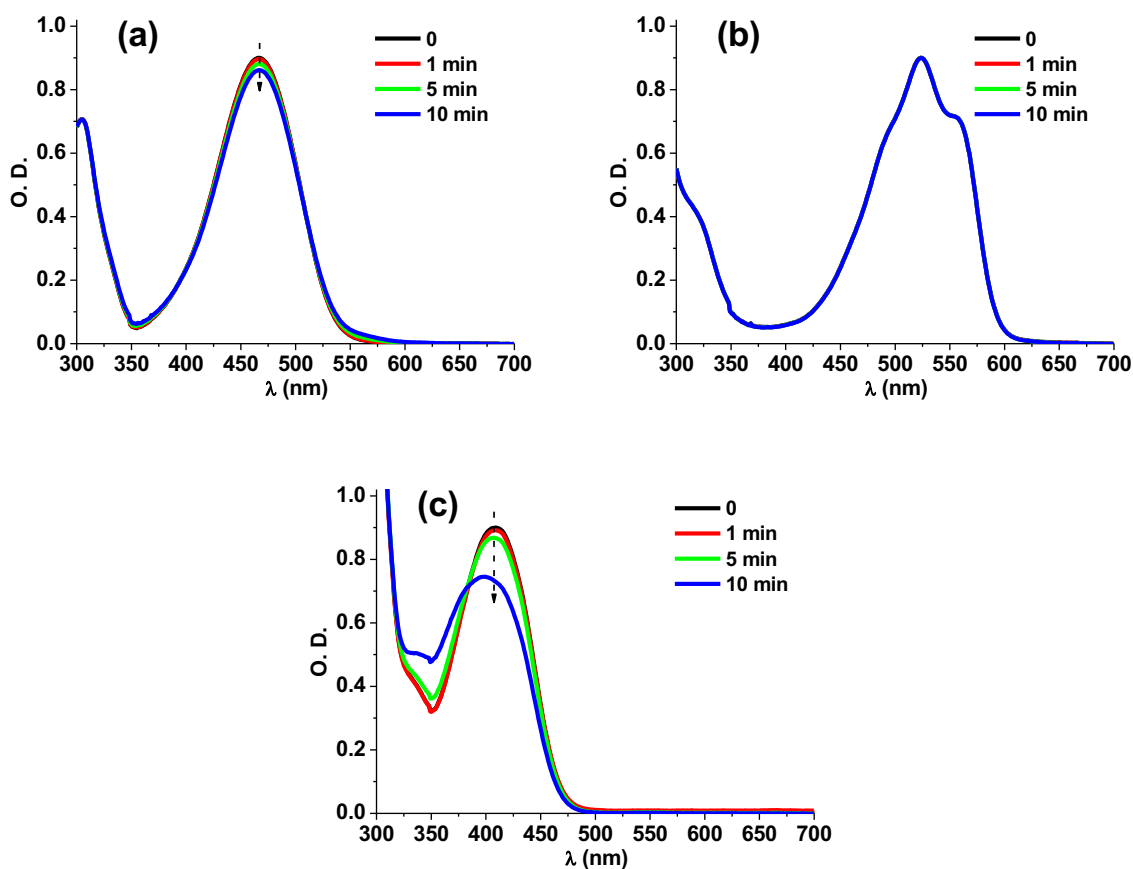


Figure 3. Steady state photolysis of (a) AAQ/TEAOH, (b) MAAQ/TEAOH and (c) BAAQ/TEAOH in acetonitrile ($[\text{TEAOH}] = 60 \text{ mM}$); UV-vis spectra recorded at different irradiation time; Blue LED@455 nm irradiation (60 mW cm^{-2}).

The generated radicals from the interaction of the AAQs and additives under light irradiation can be identified using the Electron Paramagnetic Resonance (EPR) spin trapping technique. As illustrated in Figure 4, the hyperfine splitting constants (HFS) for both the nitrogen (a_N) and the hydrogen (a_H) of two PBN/radical adducts ($a_N = 14.3 \text{ G}$ and $a_H = 2.4 \text{ G}$; $a_N = 14.7 \text{ G}$ and $a_H = 4.6 \text{ G}$) were measured in the AAQ/EDB/PhC(=O)CH₂Br system, which can be assigned to PBN/aminoalkyl radical adducts ($a_N = 14.3 \text{ G}$ and $a_H = 2.4 \text{ G}$)^[14] and PBN/phenacyl radical adducts ($a_N = 14.7 \text{ G}$ and $a_H = 4.6 \text{ G}$)^[15]. It confirmed further the occurrence of reactions in Scheme 2 for the generation of the two types of radicals.

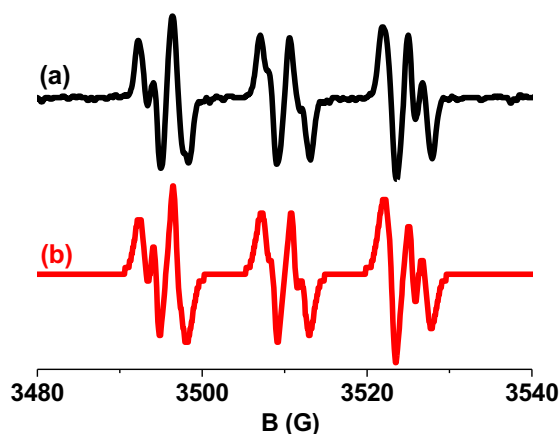


Figure 4. EPR spectrum of the radicals generated in AAQ/EDB/PhC(=O)CH₂Br combination (ethyl dimethylaminobenzoate EDB instead of TEAOH was used here to avoid a high polarity of the sample preventing an EPR analysis) upon the blue LED exposure and trapped by PBN in *tert*-butylbenzene: (a) experimental and (b) simulated spectra.

Free radicals produced from the AAQ-based photoinitiating systems are expected to induce the free radical photopolymerization of (meth)acrylates. As presented in the Figure S2 and Table S1 in the SI, AAQ/TEAOH photoinitiator can initiate the polymerization of TMPTA under the irradiation of blue or green LED and lead to the double bond conversion < 40%. The increase of the amount of TEAOH (from 1% to 2%) in the photoinitiators slightly enhanced the conversion. Interestingly, AAQ/TEAOH photoinitiator can also initiate the polymerization of TPGDA under the irradiation of blue or green LED with the double bond conversion ~50% after 300 s of photopolymerization (Figure S3 in the SI). Even though the well-known camphorquinone (CQ)-based photoinitiating system CQ/TEAOH exhibited higher efficiency (~80% of double bond conversion for TPGDA) than that of AAQ/TEAOH under blue LED irradiation, AAQ/TEAOH can work upon the exposure to green LED while CQ/TEAOH is not efficient. Markedly, the addition of PhC(=O)CH₂Br can dramatically promote the photopolymerization efficiency (51% and 46% of double bond conversions can be achieved under the blue and green LED respectively after 300 s of polymerization) of the AAQ-based photoinitiators, and there was no further enhancement when the PhC(=O)CH₂Br reached to 2%.

The photoinitiation ability of AAQ/TEAOH/PhC(=O)CH₂Br photoinitiator to initiate different monomers was investigated and illustrated in Figure 5. It indicated that AAQ/TEAOH/PhC(=O)CH₂Br was quite efficient for the polymerization of DPGDA with the final double-bond conversion of 94%. The higher polymerization efficiency of DPGDA compared to that of TPGDA (72% of double-bond conversion) can be ascribed to the higher double-bond concentration of DPGDA monomer. The degree of functionality of monomers significantly influenced the polymerization rate and final conversion. Specifically, the higher crosslink-density of the tri-functional monomer TMPTA (51% of double-bond conversion) during the polymerization process can set a limit to the extent of double-bond conversion compared to the di-functional monomers DPGDA and TPGDA. Compared to acrylates with the same functionality, Bis-GMA/TEGDMA blend (di-functional methacrylate) exhibited the lower polymerization rate and double-bond conversion when using the same AAQ/TEAOH/PhC(=O)CH₂Br photoinitiator due to the lower reactivity of methacrylates.

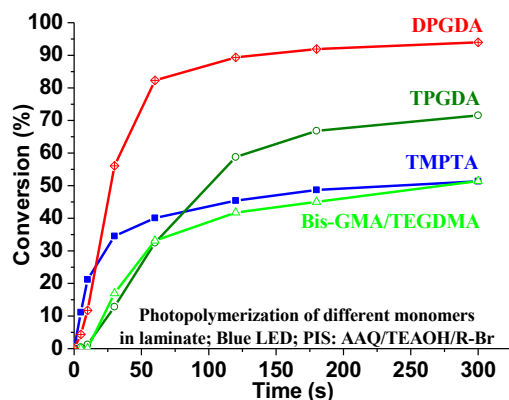


Figure 5. Photopolymerization profiles of different monomers in laminate in the presence of AAQ/TEAOH/PhC(=O)CH₂Br (abbreviated as R-Br in the figure) (0.5%/2%/2%, wt) photoinitiator upon exposure to Blue LED@455 nm (60 mW cm⁻²).

The chemical structures of AAQs also significantly affect their photoinitiation efficiency in free radical polymerization. As presented in Figure 6 (a), AAQ- and BAAQ-based photoinitiators can lead to the polymerization of DPGDA with the final double-bond conversions of 94% and 74% respectively

under blue LED irradiation. AAQ/TEAOH/PhC(=O)CH₂Br photoinitiator exhibited the highest efficiency for the polymerization of DPGDA, while MAAQ/TEAOH/PhC(=O)CH₂Br was inefficient. It implies that the overlap between the light absorption of AAQs and the emission wavelength of the irradiation source^[16] played an important role in the photopolymerization process. In addition, the interaction reactivity of AAQs/additives also affected their efficiency, *i.e.* the inefficiency of MAAQ-based photoinitiator was in agreement with the result of the steady state photolysis [Figure 3 (b)]. Moreover, Figure 1 clearly shows the electron transfer processes to be thermodynamically favourable from the excited states; however, the kinetics is difficult to calculate accurately. Nonetheless, kinetics is expected to follow thermodynamics and the greater efficiency of AAQ for initiation, compared to MAAQ and BAAQ, is consistent with it having the lowest change in free energy from steps 2 to 3 (+23.6 kJ mol⁻¹ compared to +27.6 and +41.7 kJ mol⁻¹, respectively). In addition, AAQs can be regenerated as shown in Scheme 2, which is a photoredox catalysis process. Interestingly, AAQ/TEAOH/PhC(=O)CH₂Br photoinitiator can also work under the irradiation of UV (double-bond conversion of 90%) or Green (double-bond conversion of 79%) LED [Figure 6 (b)], and the relevant efficiency was associated with the extent of overlap between the AAQ absorption spectrum and the emission spectra of the LEDs.^[16] Similarly, thanks to the much better overlap of BAAQ absorption spectrum with the emission spectrum of UV LED compared to that of blue LED, BAAQ/TEAOH/PhC(=O)CH₂Br can more efficiently initiate the free radical polymerization of DPGDA and TMPTA under the irradiation of UV LED (Figure S4 in the SI). In addition, no significant photobleaching was observed during photopolymerization processes, which is in agreement with the results of the steady state photolysis (Figure 3 and Figure S1 in the SI).

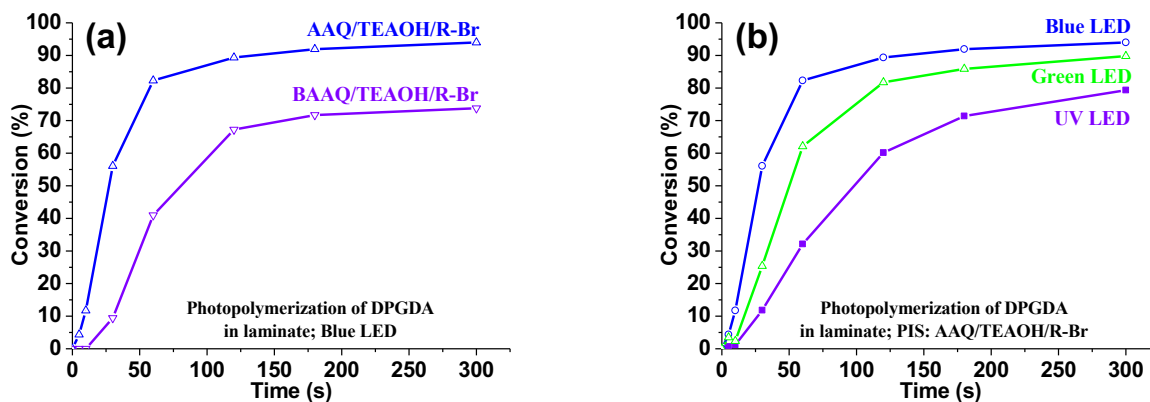


Figure 6. Photopolymerization profiles of DPGDA in laminate in the presence of (a) different AAQs-based photoinitiators upon exposure to Blue LED@455 nm and (b) AAQ/TEAOH/PhC(=O)CH₂Br (abbreviated as R-Br in the figures) upon exposure to UV LED@392 nm, Blue LED@455 nm and Green LED@518 nm. (AAQs: 0.5 wt%; TEAOH or PhC(=O)CH₂Br: 2 wt%; light intensity of LEDs: 60 mW cm⁻²)

In conclusion, the variation in the amino groups of the monoaminoanthraquinone derivatives can strongly affect their light absorption properties and reactivities with additives (*e.g.* tertiary amines). Free radicals can be generated from the interaction between AAQs and additives under the light irradiation from LEDs. Among all the investigated AAQs-based photoinitiators, AAQ/TEAOH/PhC(=O)CH₂Br and BAAQ/TEAOH/PhC(=O)CH₂Br photoinitiators exhibited the highest efficiency for the free radical photopolymerization of DPGDA under the irradiation of blue LED and UV LED respectively, which is in agreement with the relevant extent of overlap between their absorption spectra and the emission spectra of the LEDs. AAQ/TEAOH/PhC(=O)CH₂Br photoinitiator can also initiate the free radical photopolymerization of different (meth)acrylate monomers and the relevant photoinitiation ability was dependent on the chemical structures of these monomers.

ASSOCIATED CONTENT

Supporting Information is available from the Wiley Online Library or from the author.

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Notes

The authors declare no competing financial interest.

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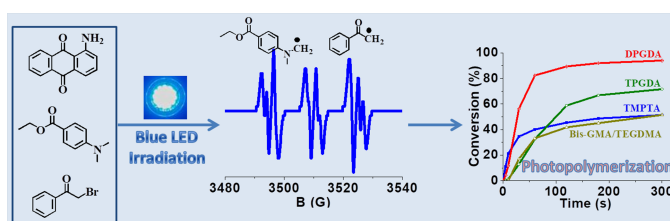
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Substituent Effects on Photoinitiation Ability of Monoaminoanthraquinone-based Photoinitiating Systems for Free Radical Photopolymerization under LEDs



The variation in the amino groups of the monoaminoanthraquinone derivatives can strongly affect their light absorption properties and reactivities with additives (*e.g.* tertiary amines) to generate free radicals. Among all the investigated monoaminoanthraquinone-based photoinitiating systems, 1-aminoanthraquinone-based one exhibited the highest efficiency for the free radical photopolymerization under the irradiation of blue LED and green LED.