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# Anthracene electron-transfer photosensitizers for onium salt induced cationic photopolymerizations

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## Abstract

This article describes the synthesis of several derivatives of anthracene (AN) and their evaluation as electron-transfer photosensitizers for onium salt induced cationic photopolymerizations. The synthetic methods that were employed involved straightforward and high yield routes to these derivatives. Using Fourier transform real-time infrared spectroscopy (FT-RTIR), the photoinduced polymerizations of several model epoxide and vinyl ether monomers were examined in the presence and absence of the anthracene photosensitizers. It was observed that anthracene derivatives bearing electron-donating substituents markedly accelerated the rates of all the UV irradiation induced photopolymerizations in which diaryliodonium, triarylsulfonium and dialkylphenacylsulfonium salt photoinitiators were used. In each case, the greatest acceleration of the rate of the polymerizations occurred when 9,10-dialkoxyanthracenes were employed as photosensitizers.

*Keywords:* Photosensitization; Anthracene derivatives; Photoinitiated cationic polymerization; Photoinitiators

## 1. Introduction

Over the past decade, onium salt photoinitiated cationic polymerizations have become established as both processes of commercial importance as well as reactions of academic interest. While these polymerizations are useful, it has been pointed out that the rates of the photoinitiated cationic polymerizations of commercially available epoxides are lower than those of the corresponding photoinduced radical polymerizations of acrylate monomers [1]. It has also been observed that the ring-opening polymerizations of oxetane monomers are also comparatively slow and take place at rates similar to epoxides [2]. To overcome this drawback, it has become a common practice to employ photosensitizers in combination with onium salt photoinitiators to enhance the reactivity of these cationic systems [3]. Most onium salts possess absorption bands that are confined to the short wavelength region of the UV spectrum. For this reason, much of the energy emitted by broadband light sources such as commonly used mercury arc lamps is wasted. The use of long wavelength absorbing photosensitizers permits the capture of a higher fraction of the available emitted light from these sources. This contributes to an overall more efficient photolysis of the photoinitiator and consequently, to the generation of a larger number of initiating species than when no photosensitizer is present. The end result is that there is an apparent acceleration of the rate of polymerization of the monomer in the presence of a photosensitizer as compared to when it is absent. The accelerating effect of photosensitizers offers the possibility of several trade-offs, such as increasing productivity, or alternatively, lowered photoinitiator concentrations with resultant lower systems costs. In addition, monochromatic light or narrow band sources such as lasers and light emitting diodes are increasingly being used in photoimaging and reprographic technologies. It is important to be able to "tune" the wavelength of sensitivity of onium salt photoinitiators to these emission sources. Lastly, the use of photosensitizers to enable the employment of solar energy to carry out photopolymerizations is potentially of considerable future importance for the fabrication of a wide assortment of practical items as for example, building panels, roofs, water delivery and sewerage systems in underdeveloped areas of the world [4].

There are several mechanisms by which the photosensitization of onium salts is known to take place, however, electron-transfer photosensitization is the most efficient and generally applicable process for this class of photoinitiators [5,6]. Shown in Scheme 1 is a generalized mechanism that we have proposed for the electron-transfer photosensitization of diaryliodonium salts.

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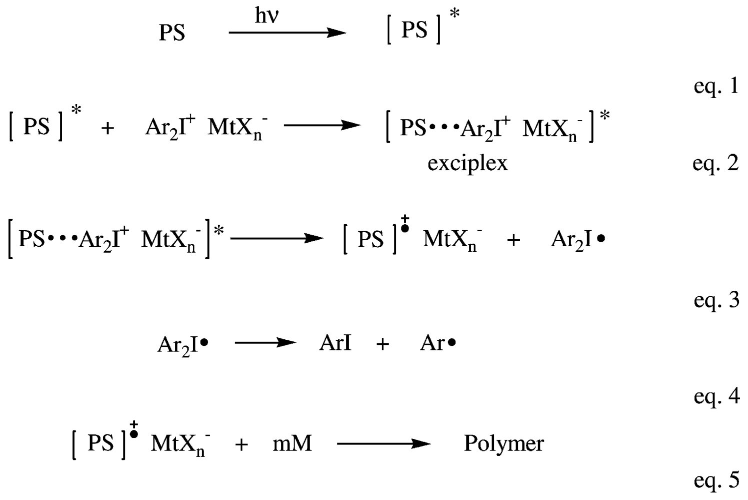


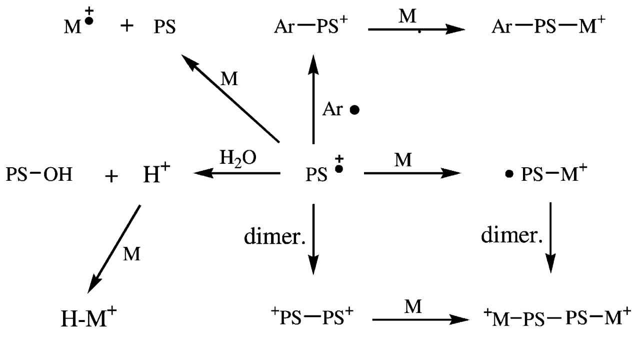
Scheme 1.

In the above scheme, $MtX_n^-$ represents a weakly nucleophilic counterion such as $BF_4^-$, $PF_6^-$, $SbF_6^-$, $(C_6F_5)_4B^-$, etc. Analogous mechanisms can be written for the photosensitization of triarylsulfonium and dialkylphenacylsulfonium salt photoinitiators. Electron-transfer photosensitization relies first, on the absorption of light by the photosensitizer, PS, to give the corresponding excited species [PS]* (Eq. (1)). An excited state complex (exciplex) is often formed as an intermediate between the onium salt and the excited photosensitizer (Eq. (2)). Rodrigues and Neumann [7,8] have alternatively suggested the possibility that electron-transfer can occur by the photoinduced excitation of a ground state complex formed between the onium salt and the photosensitizer. In either case, the onium salt is reduced by a formal one electron-transfer between the two reaction partners (Eq. (3)). The rapid decomposition of the resulting unstable diaryliodine free radical (Eq. (4)) retards back electron-transfer and renders the overall process irreversible. Due to their lower reduction potentials, diaryliodonium salts are more easily photosensitized by an electron-transfer process than the corresponding triarylsulfonium or dialkylphenacylsulfonium salts [9]. Lastly (Eq. (5)), the photosensitizer cation radical, $PS^{\bullet+}$, induces the cationic polymerization of the monomer.

It should be noted that in the usual context, the term "photosensitizer" as applied to electron-transfer photosensitization is a misnomer. "True" photosensitizers serve the simple function of transferring energy to a substrate during a photoreaction and are recovered intact at the end of the reaction. As shown in Scheme 1, electron-transfer photosensitizers undergo a photoinduced redox reaction in which the corresponding cation radical, $PS^{\bullet+}$, is formed. This latter species reacts further via the various mechanisms depicted in Scheme 2 that result in the consumption of the photosensitizer and induce polymerization of a monomer.

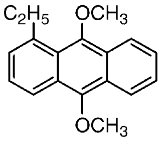
Previously, we have reported that a wide variety of electron-rich polynuclear aromatic compounds such as anthracene (AN), pyrene and perylene are efficient electron-transfer photosensitizers for diaryliodonium and triarylsulfonium salt cationic photoinitiators [10–12]. Recently, Toba et al. [13] and Scranton [14] have studied the use of these same photosensitizers for the photolysis of onium salts. However, such polynuclear aromatic compounds and their simple substituted derivatives suffer from several serious drawbacks that limit their utility as photosensitizers in most practical applications. These compounds generally possess poor solubility in monomers of interest for cationic photopolymerizations. In addition, they have high vapor pressures at room and elevated temperatures and are readily lost from liquid monomer films by evaporation or sublimation. Moreover, these compounds are generally regarded as toxic.

Early in the development of the field of photoinitiated cationic polymerizations, anthracene, was identified and employed as an efficient photosensitizer for both triarylsulfonium and diaryliodoniium salt cationic photoinitiators. Subsequently, dialkylphenacylsulfoniium salts were developed as a new series of cationic photoinitiators and anthracene was again investigated and was found to also function as an efficient electron-transfer photosensitizer for these latter photoinitiators [15]. While anthracene displays very good electron-transfer photosensitizing characteristics for all three types of onium salt photoinitiators, it is objectionable



Scheme 2.

for practical uses due to the same considerations as enumerated above.[1] Higher molecular weight derivatives of anthracene often display reduced volatility as well as lower toxicity and, depending on the character of the substituents, can possess good photosensitizing ability for onium salt cationic photoinitiators. For example, as early as 1975, Smith [16] reported that 2-ethyl-9,10-dimethoxyanthracene (EDMA) is an excellent photosensitizer for diaryliodonium and triarylsulfonium salts. More recently, Priou [17] reported that EDMA is a useful photosensitizer for the photopolymerization of epoxy-modified silicones in the presence of diaryliodonium salt photoitiators. Sitzmann et al. [18] described the use of this same photosensitizer for use in stereolithographic applications that employ onium salt induced cationic polymerization. At the present time, EDMA remains relatively expensive and available only in small quantities from laboratory supply houses.



**EDMA**

Other studies by DeVoe et al. [19,20] showed that 9,10-diethoxyanthracene is a photosensitizer for diaryliodonium salts. However, these workers did not investigate the use of this photosensitizer in cationic photopolymerizations. A survey of the literature indicated that a variety of anthracene derivatives could be readily prepared in high yields using straightforward, cost effective methodologies. Accordingly, we have decided to evaluate the photosensitizing activities of several anthracene derivatives and compare the results to develop structure property relationships.

## 2. Experimental details

### 2.1. Materials

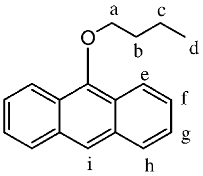
All starting materials, monomers, anthracene photosensitizers and reagents were purchased from the Aldrich (Milwaukee, WI) and used without purification unless otherwise noted. Samples of 9-*n*-butoxyanthracene, 9,10-di-*n*-propoxyanthracene (DPA) and 9,10-di-*n*-butoxyanthracene (DBA) were kindly provided as gifts by the Kawasaki Kasei Chemical Co. (Kawasaki, Japan). Cyclohexene oxide (CHO) was stirred over and then distilled from calcium hydride prior to use. (3-Ethyl-3-oxetanylmethyl)phenyl ether (POX) and bis(3-ethyl-3-oxetanylmethyl)ether (DOX) were kindly provided by the Toagosei Chemical Co. (Nagoya, Japan). 3,4-Epoxycyclohexylmethyl 3′,4′-epoxycyclohexane carboxylate (ERL-4221E) was purchased from the Union Carbide Corp. (Bound Brook, NJ). The photoinitiators, (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC10) [21] and (4-*n*-decyloxyphenyl)diphenylsulfonium hexafluoroantimonate (SOC10) [22] *S*-dodecyl-*S*-methyl-*S*-phenacylsulfonium hexafluoroantimonate (DPS-$C_1C_{12}$) [23] were prepared as described previously. Melting points were recorded on a Thomas Hoover melting point apparatus and are uncorrected.

### 2.2. Absorption and NMR spectra

UV absorption spectra were measured in methanol using a Perkin-Elmer Lambda 2 UV-Vis Spectrometer. Melting points were taken on a Thomas Hoover capillary melting point apparatus and are uncorrected. $^1H$ NMR spectra were obtained using a Varian XL 500 MHz spectrometer at room temperature in $CDCl_3$. Elemental analyses were performed by Quantitative Microanalysis, Norcross, GA.

### 2.3. Synthesis of 9-n-butoxyanthracene (MBA)

There were placed in a 250 ml round bottom flask equipped with a magnetic stirrer and reflux condenser 19.4 g (0.1 mol) anthrone (AR), 20.6 g (0.15 mol) *n*-bromobutane, 2.0 g tetra-*n*-butylammonium bromide (TBAB), 11.2 g (0.2 mol) potassium hydroxide, 10 ml water and 50 ml toluene. The reaction mixture was heated to reflux and maintained at that temperature for 5 h. At the beginning, the color of the reaction mixture was deep red. As the reaction proceeded, the color lightened until a light orange color was obtained. After cooling, the reaction mixture was transferred to a separatory funnel and the aqueous layer separated and discarded. The solvent was removed from organic layer using a rotary evaporator leaving an orange partially crystalline solid. Recrystallization twice from isopropanol gave 9-*n*-butoxyanthracene as a pale yellow crystalline compound with a melting point of 84–85 °C. The yield was 50%.



$^1H$ NMR 500 MHz ($CDCl_3$) $\delta$ (ppm) 4.24 ($H_a$, t, 2H); 2.08 ($H_b$, m, 2H); 1.76 ($H_c$, m, 2H); 1.12 ($H_d$, t, 3H); 8.33 ($H_e$, d, 2H); 7.49 ($H_{f,g}$, m, 4H); 8.02 ($H_h$, d, 2H); 8.24 ($H_i$, d, 1H).

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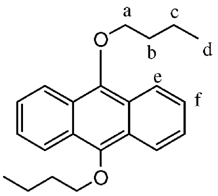
[1] A comprehensive summary toxicology report with extensive referencing is available at the US Environmental Protection Agency website (http://risk.lsd.ornl.gov/tox/profiles/anthracene.shtml). While the chronic oral toxicity of anthracene is very low (17 g/kg in mice), it is an eye, skin and inhalation irritant. Pure anthracene appears to have either a very low or non-existent carcinogenicity. However, it is a photosensitizer and both the toxicity and carcinogenicity are enhanced in the presence of UV light.

### *2.4. Synthesis of 9,10-di-n-butoxyanthracene (DBA)*

There were placed in a three neck round bottom flask equipped with a magnetic stirrer, reflux condenser, addition funnel and nitrogen inlet 2.0 g (9.6 mmol) of anthraquinone, 2.0 g (11.5 mmol) of sodium dithionite, 3.0 g sodium hydroxide, 25 ml of acetone and 30 ml of water. The mixture was heated to reflux under nitrogen for 2.5 h during which time the anthraquinone dissolved and a deep red solution was formed. The reaction mixture was cooled to room temperature and 10 ml (92 mmol) of *n*-bromobutane was added and the reaction mixture stirred for 2 days. During that time, the red color gradually faded and a pale yellow solution was formed. After extracting the organic phase with hexane, washing with an aqueous dilute solution of sodium dithionite, the solution was dried over anhydrous magnesium sulfate. Using a rotary evaporator, the solvents were removed and the solid crude product recrystallized from acetone. There were obtained 0.7 g (21% yield) of 9,10-di-*n*-butoxyanthracene as a pale yellow crystalline solid having a mp of 110–112 °C ([24] mp 116 °C).



$^1$H NMR 500 MHz ($CDCl_3$) $\delta$ (ppm) 4.18 ($H_a$, t, 4H); 2.05 ($H_b$, m, 4H); 1.72 ($H_c$, m, 4H); 1.08 ($H_d$, t, 6H); 8.31 ($H_e$, d, 4H); 7.48 ($H_f$, m, 4H).

### *2.5. Kinetic studies of photosensitized cationic polymerizations*

The photosensitized cationic polymerizations of the epoxides, oxetanes and 2-chloroethyl vinyl ether (CEVE) studied in this work were monitored using Fourier transform real-time infrared spectroscopy (FT-RTIR). The apparatus and techniques used in these experiments have been described in previous publications from this laboratory [25,26]. Unless otherwise noted, all photopolymerizations were conducted under ambient air conditions using broadband UV irradiation at various intensities. In each case, a control kinetic study was conducted in which the photosensitizer was omitted. Each photosensitization study consisted of data from three to five kinetic runs that were averaged to give the final conversion versus time curve.

The kinetic parameter, $R_p/[M_o]$, for selected kinetic runs was determined from the initial slopes of the irradiation time-conversion curves according to Eq. (6).

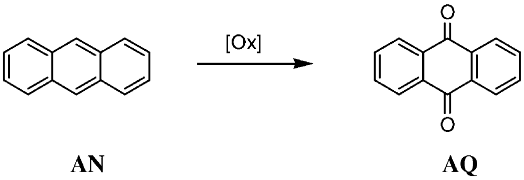
$$\frac{R_p}{[M_o]} = \frac{[\text{conversion}]_{t_2} - [\text{conversion}]_{t_1}}{[t_2 - t_1]} \tag{6}$$

where $R_p$ and $[M_o]$ are, respectively, the rate of polymerization and the initial monomer concentration and the conversions are as determined from the curves at irradiation times $t_1$ and $t_2$.

## 3. Results and discussion

### *3.1. Synthesis of anthracene photosensitizers*

Among the most facile reactions that anthracene undergoes is oxidation. When AN is treated with various oxidants such as nitric acid, chromic acid, or sodium chlorate, 9,10-anthraquinone (AQ) (Eq. (7)) is obtained in high yield [27]. 9,10-Anthraquinone is readily available, inexpensive intermediate that is widely employed for the industrial production of dyes, pharmaceuticals and photochemicals.

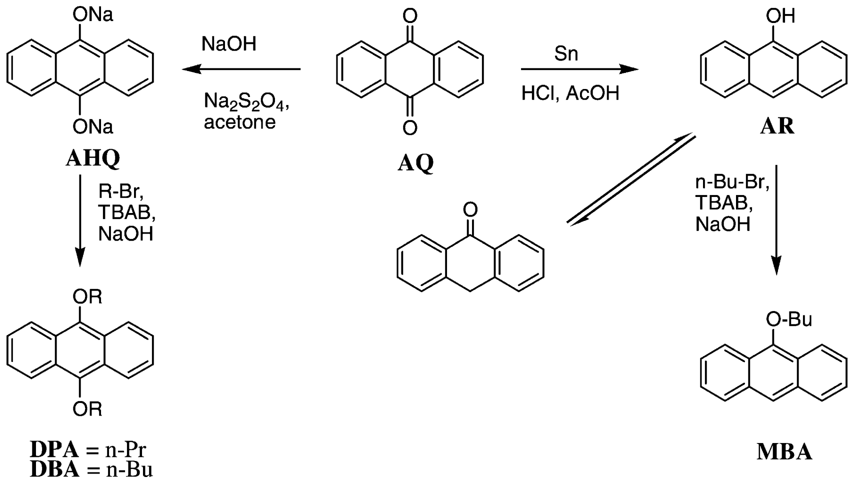


(7)

AN has an especially rich chemistry and a wide variety of derivatives can be prepared using this compound as a starting substrate. As noted in Scheme 1, photosensitizers function as an electron donors in the electron-transfer photosensitization of onium salts. Consequently, we considered only those anthracene derivatives bearing electron-donating substituents that would tend to enhance this property. Shown in Scheme 3 is a summary of the synthetic routes employed in this study for the preparation of anthracene photosensitizers using AQ as the starting material.

The treatment of AQ with tin and hydrochloric acid in glacial acetic acid gives anthrone [28]. AR is in equilibrium (89%:11%) with its tautomer, anthranol, and consequently exhibits both the chemical and spectroscopic properties of a phenol and an aromatic ketone. Under basic conditions and in the presence of tetra-*n*-butylammonium bromide as a catalyst, anthrone can be readily alkylated with primary alkyl halide such as *n*-butyl bromide to give MBA. In the presence of basic sodium dithionite in acetone, AQ is reduced and converted to the disodium salt, AHQ [24,29]. Double alkylation of AHQ with the appropriate alkyl bromide [30,31] yields 9,10-dialkoxyanthracenes, DPA and DBA. Patents describing the use of other reducing agents in this sequence of reactions have also issued [32,33]. It should also be mentioned that AR, MBA, DBA and DPA are now commercially available in pilot quantities supplied by Kawasaki Kasei Chemical Co. [34]. A survey of the patent literature revealed that the commercial route [35] to DBA and DPA as depicted in Scheme 4 is somewhat different than that employed in this work.

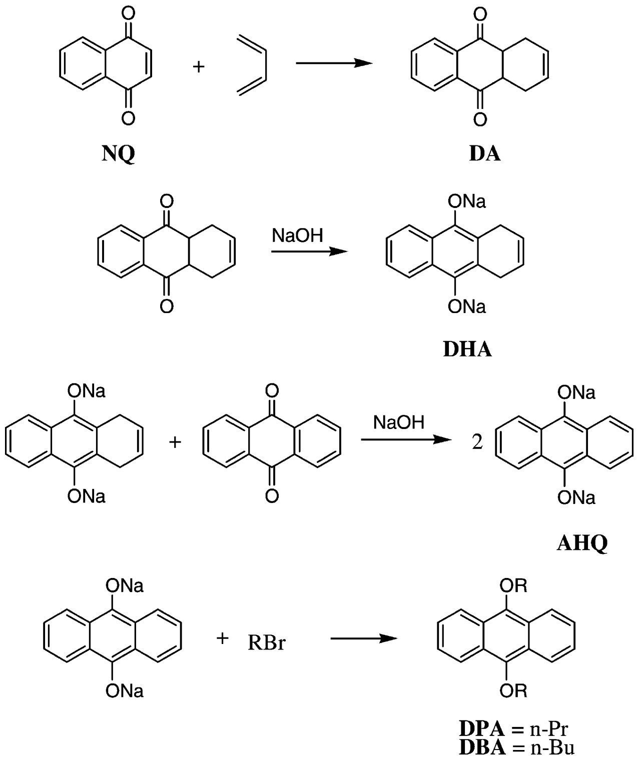
1,4-Naphthoquinone (NQ), is first condensed with butadiene in a Diels-Alder reaction to give 1,4,4A,9A-tetrahydroanthraquinone (DA). Treatment of DA with base gives the disodium salt DHA. AQ is reduced with DHA in the



Scheme 3.

presence of base to yield two moles of AHQ, which is doubly alkylated in the presence of the appropriate alkyl bromide to give either DBA or DPA.

The compounds prepared and described in this article were found to be identical in all respects (i.e. melting point, $^1H$ NMR and UV spectra) with samples of the corresponding compounds obtained from commercial sources. Table 1 gives the melting points and UV spectral characteristics of the anthracene derivatives that were prepared and used during the course of this investigation. All the anthracene compounds display prominent blue fluorescence.



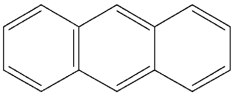
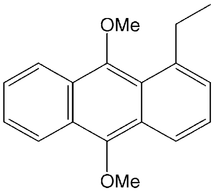
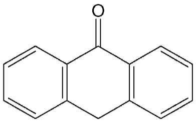
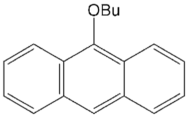
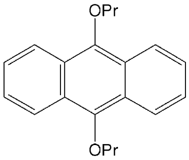
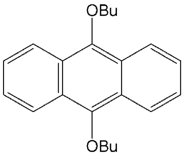
Scheme 4.

Appending hydroxy or alkoxy groups to the anthracene nucleus has three major effects. First, the melting points of those compounds are lowered and their solubilities in various organic monomers are greatly improved as compared to anthracene while their volatility is markedly decreased. At the same time, inclusion of these substitutents produces a substantial bathochromic shift in the UV-Vis absorption spectra of the respective compounds relative to anthracene. This can be seen both in Table 1 and also depicted in the comparative spectra shown in Fig. 1. The inset in this figure shows the absorption bands in the long wavelength region. The toxicology of the derivatives described here has not yet been determined and is beyond the scope of this investigation.

### 3.2. Onium salt photosensitization studies

The cationic polymerization of several monomer systems was used as a highly sensitive probe to detect and assess the photosensitizing efficiencies of anthracene derivatives on the photolysis of various onium salts. To this end, we have employed Fourier transform infrared spectroscopy to monitor the kinetics of the disappearance of the functional groups of the monomers undergoing onium salt photoinitiated cationic polymerization. The activity of each of the anthracene photosensitizers was examined as a function of the structure of the photoinitiator and type of monomer used. Table 2 gives the structures of the photoinitiators and vinyl and heterocyclic monomers employed during the course of this investigation. Three onium salt photoinitiators, (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC10), (4-*n*-decyloxyphenyl)diphenylsulfonium hexafluoroantimonate (SOC10) and DPS-$C_1C_{12}$ were used bearing the $SbF_6^-$ and $PF_6^-$ anions. The five cationically polymerizable monomers employed in these studies are shown together with the IR bands that were monitored during the kinetic studies. In each case, a control kinetic run was included in which the prospective photosensitizer was omitted.

Table 1
Characteristics of anthracene photosensitizers (MeOH, $2 \times 10^{-5}\,mol\,l^{-1}$)

| Notation | Structure | mp (°C) | UV spectra | |
|---|---|---|---|---|
| | | | $\lambda_{max}$ (nm) | $\varepsilon$ |
| AN | Anthracene  | 216–218 | 218 | 15220 |
| | | | 220 | 15190 |
| | | | 251 | 163470 |
| | | | 294 | 930 |
| | | | 309 | 1690 |
| | | | 323 | 3620 |
| | | | 339 | 6700 |
| | | | 356 | 9850 |
| | | | 375 | 9480 |
| EDMA | 2-Ethyl-9,10-dimethoxyanthracene  | 117–119 | 220 | 18240 |
| | | | 253 | 101260 |
| | | | 261 | 154130 |
| | | | 361 | 6450 |
| | | | 380 | 8860 |
| | | | 401 | 7360 |
| AR | 9-Anthrone(9-anthranol)  | 155–158 | 258 | 33990 |
| | | | 269 | 20140 |
| | | | 308 | 4520 |
| | | | 367 | 730 |
| MBA | 9-*n*-Butoxyanthracene  | 78–79 | 218 | 14640 |
| | | | 248 | 98410 |
| | | | 255 | 154540 |
| | | | 334 | 3180 |
| | | | 350 | 5650 |
| | | | 368 | 8580 |
| | | | 388 | 7670 |
| DPA | 9,10-Dipropoxyanthracene  | 93–95 | 217 | 19490 |
| | | | 251 | 99260 |
| | | | 258 | 152900 |
| | | | 362 | 7410 |
| | | | 381 | 11230 |
| | | | 403 | 9590 |
| DBA | 9,10-Dibutoxyanthracene  | 110–112 | 217 | 20020 |
| | | | 252 | 99540 |
| | | | 259 | 153770 |
| | | | 363 | 7660 |
| | | | 381 | 11530 |
| | | | 403 | 9910 |

The photopolymerization studies were conducted at such light intensities so as to slow the polymerizations sufficiently to enable convenient monitoring of the polymerizations. Accordingly, orienting experiments were conducted for each photoinitiator/monomer system prior to carrying out a kinetic study. For example, kinetic studies were conducted using IOC10 in the photopolymerization of cyclohexene oxide at light intensities of 310, 140 and $55\,mJ\,cm^{-2}\,min^{-1}$. It was found that only at the lowest light intensity ($55\,mJ\,cm^{-2}\,min^{-1}$) was the polymerization sufficiently slowed to make discrimination between the various photosensitizers possible. Since broadband (i.e. unfiltered) UV irradiation was used in all cases, the resulting overall observed polymerization rates are a combination of the contributions of both the direct and photosensitized polymerization processes. Comparison with a control curve in which the photosensitizers is omitted gives an estimation of the contribution of photosensitization to the overall rate. The results of the FT-RTIR kinetic studies of the cationic photopolymerizations of the above five monomers in the presence of anthracene and its derivatives are summarized in Table 3. This table lists the kinetic parameters $R_p/[M_o]$ determined from the slopes of the initial portion of the conversion versus time curves. This parameter is directly proportional to the rate of polymerization of a specific monomer. To quantify the rate enhancement in a

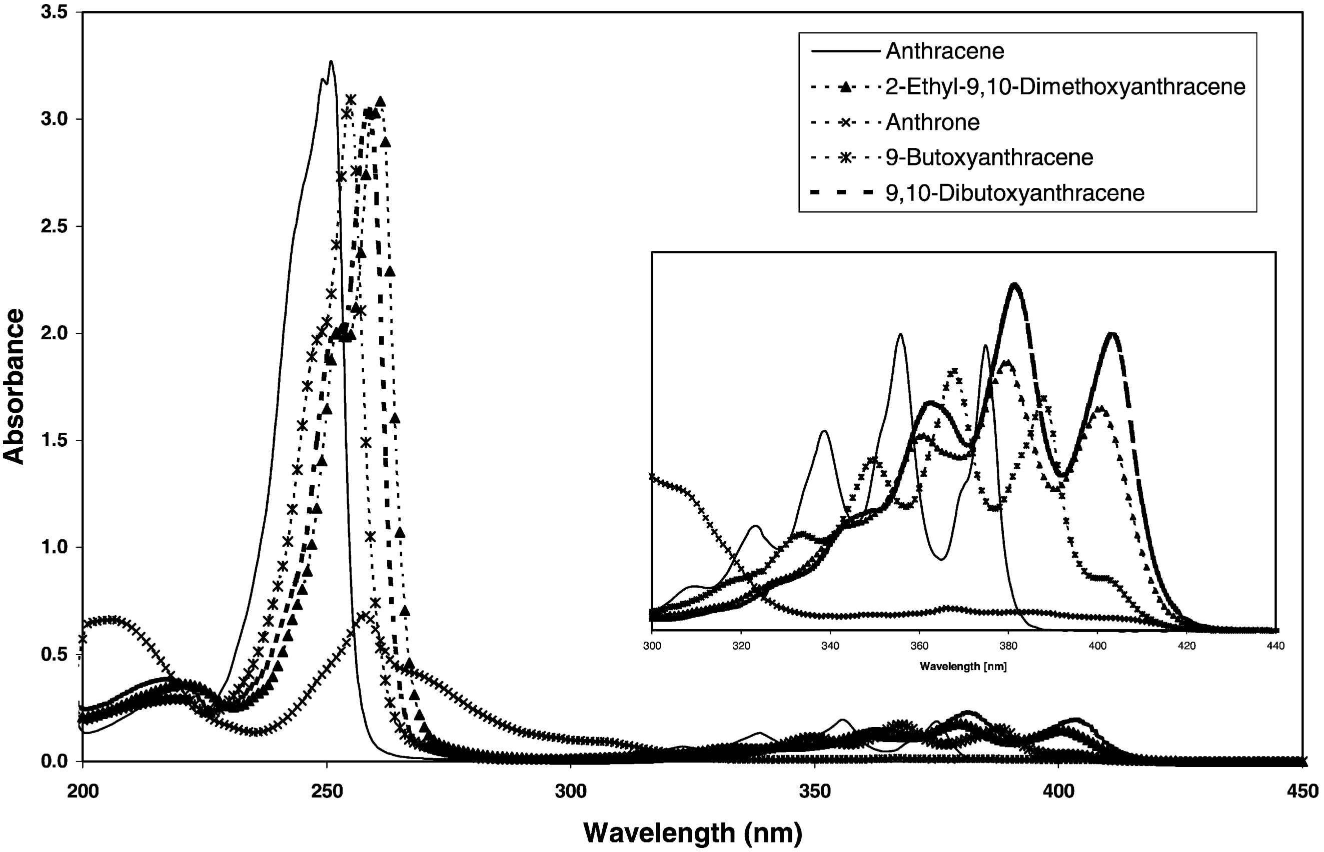


Fig. 1. UV spectra of anthracene photosensitizers in methanol.

Table 2
Structures of photoinitiators and monomers

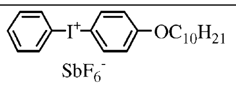
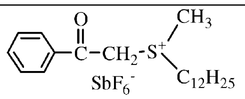
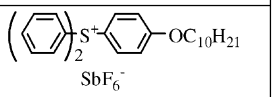
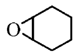
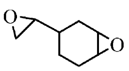
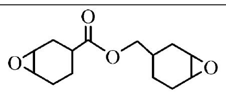
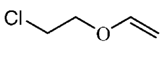
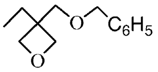
| **Photoinitiators** | | |
|---|---|---|
| <br>**IOC10**<br>(4-n-decyloxyphenyl)phenyliodonium $SbF_6^-$ | <br>**DPS-$C_1C_{12}$ $SbF_6^-$**<br>S-methyl-S-n-dodecyl phenacylsulfonium $SbF_6^-$ | <br>**SOC10**<br>(4-n-decyloxyphenyl)diphenylsulfonium $SbF_6^-$ |
| **Monomers** | | |
| <br>**CHO**<br>cyclohexene oxide<br>781 cm$^{-1}$ | <br>**VCHDO**<br>4-vinylcyclohexene dioxide<br>818 cm$^{-1}$ | <br>**ERL-4221E**<br>3,4-epoxycyclohexylmethyl 3’,4’ –epoxycyclohexanecarboxylate<br>748 cm$^{-1}$ |
| <br>**CEVE**<br>2-chloroethyl vinyl ether<br>1620 cm$^{-1}$ | | <br>**POX**<br>3-ethyl-3-oxetanylmethyl phenyl ether<br>692 cm$^{-1}$ |

Table 3
FT-RTIR kinetic data for anthracene photosensitizers

| Entry | Monomer | Photoinitiator (concentration, mol%) | Photosensitizer (concentration, mol%) | Light intensity ($\mathrm{mJ\,cm^{-2}\,min^{-1}}$) | $R_p/[M_o]$ ($\times 10^2\,\mathrm{s^{-1}}$) | AF |
|---|---|---|---|---|---|---|
| 1 | CHO | IOC10 (0.1) | – | 55 | 4.6[a] | – |
| 2 | | | AN (1.0) | | 14 | 3.0 |
| 3 | | | AR (1.0) | | 5.1 | 1.1 |
| 4 | | | MBA (1.0) | | 17 | 3.7 |
| 5 | | | DBA (1.0) | | 25 | 5.4 |
| 6 | CHO | IOC10 (0.1) | – | 55 | 4.6[a] | – |
| 7 | | | EDMA (1.0) | | 22 | 4.8 |
| 8 | | | DPA (1.0) | | 24 | 5.2 |
| 9 | | | DBA (1.0) | | 27 | 5.9 |
| 10 | CHO | IOC10 (0.1) | – | 95 | 3.7[a] | – |
| 11 | | | AN (1.0) | | 15 | 4.1 |
| 12 | | | AnBr (1.0) | | 6.7 | 1.8 |
| 13 | | | AnCHO (1.0) | | 2.7 | 0.73 |
| 14 | | | AnCOOH (1.0) | | 3.8 | 1.0 |
| 15 | CHO | SOC10 (0.1) | – | 310 | 0.67[a] | – |
| 16 | | | AN (1.0) | | 1.1 | 1.6 |
| 17 | | | AN (1.0) | | 3.6 | 5.4 |
| 18 | | | MBA (1.0) | | 6.7 | 10 |
| 19 | | | DBA (1.0) | | 13 | 19 |
| 20 | VCHDO | DPS-$C_1C_{12}$ $PF_6^-$ (1.0) | – | 440 | 0.58[a] | – |
| 21 | | | MBA (1.0) | | 4.1 | 7.1 |
| 22 | | | DPA (1.0) | | 7.8 | 13 |
| 23 | | | DBA (1.0) | | 8.3 | 14 |
| 24 | VCHDO | DPS-$C_1C_{12}$ $PF_6^-$ (1.0) | – | 360 | 0.61 | – |
| 25 | | | DPA (0.10) | | 2.1 | 3.4 |
| 26 | | | DPA (0.25) | | 3.2 | 5.2 |
| 27 | | | DPA (0.50) | | 4.8 | 7.9 |
| 28 | | | DPA (1.0) | | 7.1 | 12 |
| 29 | | | DPA (1.5) | | 8.2 | 13 |
| 30 | ERL-4221E | DPS-$C_1C_{12}$ $PF_6^-$ (1.0) | – | 1020 | 0.28 | – |
| 31 | | | MBA (1.0) | | 0.93 | 3.3 |
| 32 | | | DBA (1.0) | | 1.0 | 3.6 |
| 33 | | | DPA (1.0) | | 1.1 | 3.9 |
| 34 | POX | DPS-$C_1C_{12}$ $PF_6^-$ (1.0) | – | 1620 | 0.15 | – |
| 35 | | | MBA (1.0) | | 0.35 | 2.3 |
| 36 | | | DBA (1.0) | | 0.37 | 2.5 |
| 37 | | | DPA (1.0) | | 0.42 | 2.8 |
| 38 | CEVE | DPS-$C_1C_{12}$ $SbF_6^-$ (1.0) | – | 275 | 0.96[a] | – |
| 39 | | | MBA | | 17 | 18 |
| 40 | | | DPA | | 34 | 35 |

[a] Value determined after the induction period.

given monomer system due to photosensitization we have defined, as shown in Eq. (8), an acceleration factor (AF), due to photosensitization as the ratio of the kinetic parameters determined in the presence and absence of the added anthracene photosensitizer.

$$\mathrm{AF} = \frac{(R_p/[M_o])_{\text{photosens}}}{(R_p/[M_o])_{\text{alone}}} \tag{8}$$

Fig. 2 shows the results of a FT-RTIR study in which the photopolymerization of cyclohexene oxide was carried out in the presence of AN, AR, MBA and DBA, as photosensitizers with (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate as the photoinitiator. All four anthracene derivatives display photosensitizing activity as evidenced first by the marked reduction in the induction period and by the enhanced rates of polymerization of this monomer in comparison with the control curve (Table 3, entries 1–5). AR (AF = 1.1) displays the poorest activity as a photosensitizer. The main effect of this photosensitizer can be seen as a reduction in the length of the induction period. As noted in Table 3, because there was a substantial induction period, the $R_p/[M_o]$ value for the control curve was taken at the end

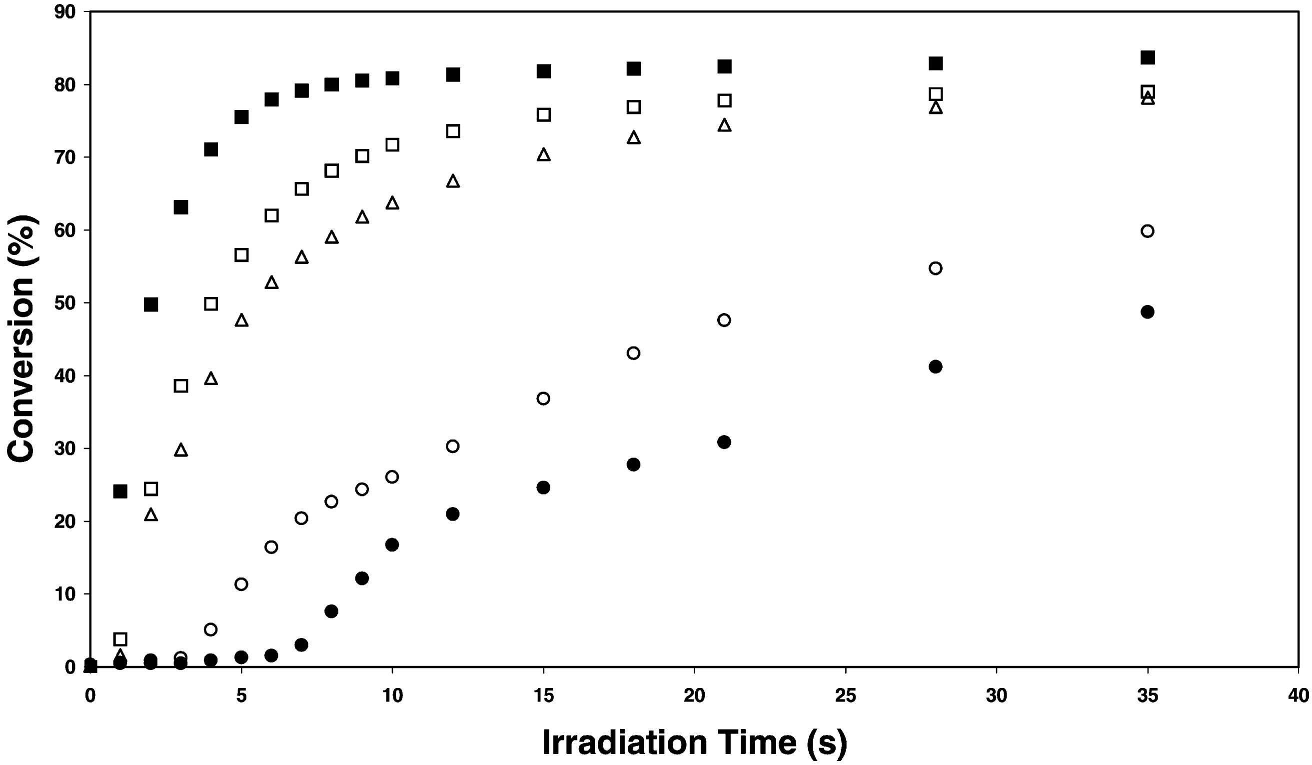


Fig. 2. Comparison of the photopolymerization of CHO in the presence of 1.0 mol% of various anthracene photosensitizers. No photosensitizer (●); anthrone (○); anthracene (△); 9-*n*-butoxyanthracene (□); 9,10-di-*n*-butoxyanthracene (■); 1.0 mol% IOC10; light intensity: 55 mJ $cm^{-2}$ $min^{-1}$.

of the induction period. At the same time, DBA (AF = 5.4) is an excellent photosensitizer while MBA (AF = 3.7) exhibits only a slightly lower response. In Fig. 3 are compared the efficiency of photosensitization of several other photosensitizers for the IOC10 photoinitiated polymerization of CHO. As might be expected, DPA shows similar activity as DBA. Both of these compounds are slightly better as photosensitizers than EDMA (Table 3, entries 6–9).

In Fig. 4 is shown an evaluation of the photosensitizing abilities of three 9-substituted anthracene derivatives bearing electron-withdrawing groups. Included in this figure for comparison are a kinetic curve for anthracene and a control curve in which no photosensitizer is present. All these compounds display lower photosensitization efficiencies (Table 3, entries 10–14) compared to anthracene. 9-Bromoanthracene (AnBr) is nearly as efficient as anthracene while 9-anthraldehyde (AnCHO) and 9-anthracenecarboxylic acid (AnCOOH) are inactive as photosensitizers for the photolysis of IOC10. It may be concluded from this and the previous data that those anthracene compounds that possess substituents that increase the electron density on the anthracene nucleus are the most active for the photosensitization of onium salt photoinitiators.

An analogous study of the photosensitization of the cationic ring-opening polymerization of CHO by anthracene compounds bearing electron-donating substitutents using the triarylsulfonium salt, (4-*n*-decyloxyphenyl)diphenylsulfonium hexafluoroantimonate, as the photoinitiator is depicted in Fig. 5. It is noteworthy, that the anthracene derivatives are also active photosensitizers for this class of sulfonium salt photoinitiators (Table 3, entries 15–19). The same order of efficiency in photosensitization was observed here as with IOC10, i.e. DBA > MBA > AN > AR. However, the enhancements of the rates of polymerization by the anthracene derivatives using SOC10 are even greater than for IOC10. To complete the survey of photosensitization by anthracene derivatives with various photoinitiators, a complimentary study of the photopolymerization of 4-vinylcyclohexene dioxide (VCHDO) using *S*-methyl-*S*-*n*-dodecylphenacylsulfonium hexafluorophosphate (DPS-$C_1C_{12}$ $PF_6^-$) as a photoinitiator was carried out and is shown in Fig. 6 and Table 3, entries 20–23. As with diaryliodonium and triarylsulfonium salts, the three anthracene compounds display excellent photosensitization characteristics for dialkylphenacylsulfonium salts as well. In this study, DBA and DPA are essentially identical (AF = 14 and 13) with respect to their reactivity while MBA (AF = 7.1) displays a slightly lesser efficiency of photosensitization. Within 10 s, the photosensitized polymerizations to proceed to their plateau conversions. In contrast, the polymerization carried out in the absence of a photosensitizer requires more than 160 s to reach the same conversion. These results are particularly of interest for the DPS photoinitiators since they generally have lower

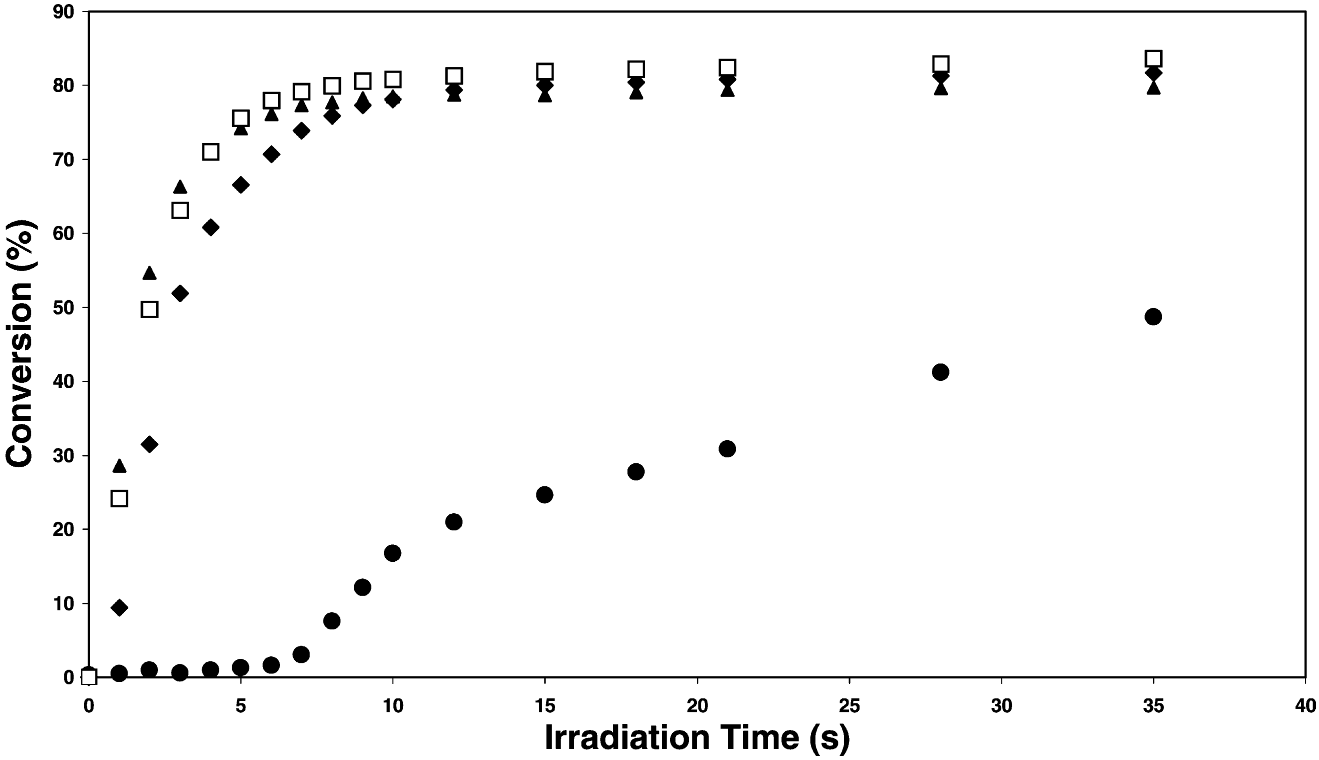


Fig. 3. FT-RTIR study of the effect of the structure of photosensitizers on the photoinitiated polymerization of CHO. No photosensitizer (●); 2-ethyl-9,10-dimethoxyanthracene (◆); 9,10-di-*n*-propoxyanthracene (▲); 9,10-di-*n*-butoxyanthracene (□); 1.0 mol% photosensitizer; 1.0 mol% IOC10; light intensity: 55 mJ cm$^{-2}$ min$^{-1}$.

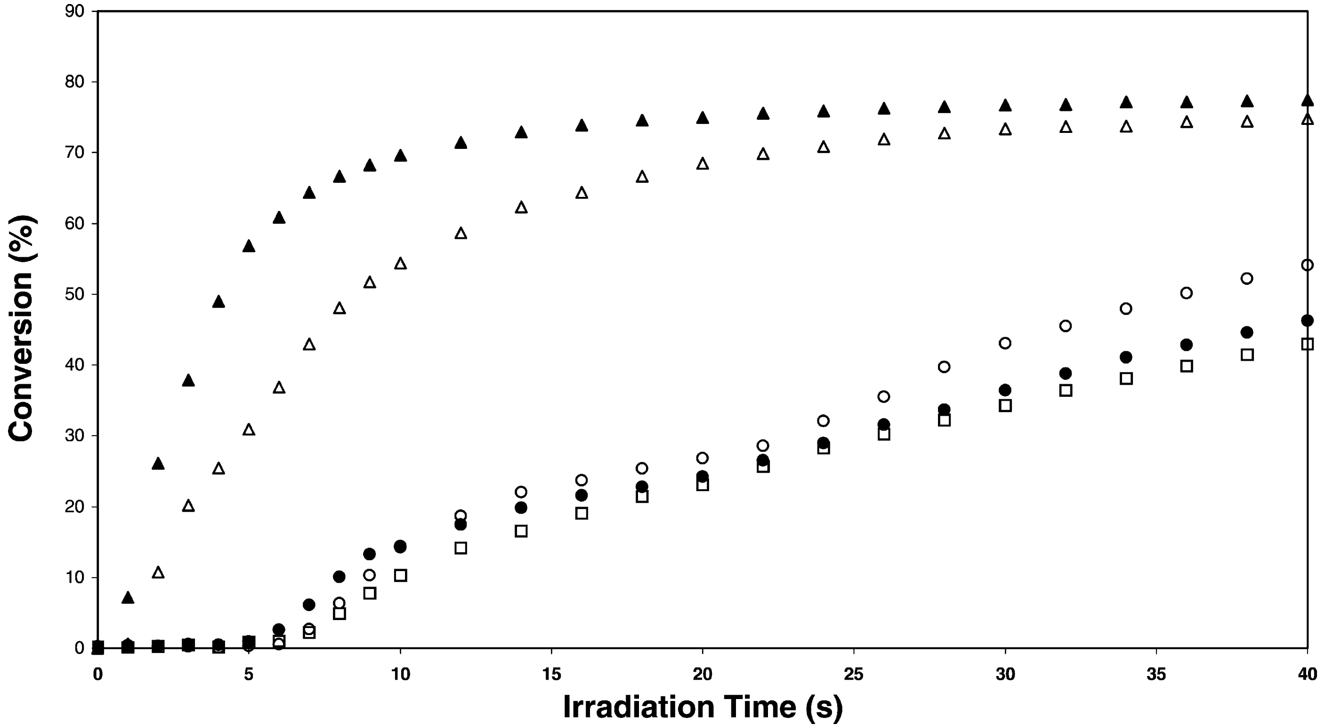


Fig. 4. Evaluation of the photosensitizing ability of anthracene derivatives bearing electron-withdrawing groups. No photosensitizer (●); anthracene (▲); 9-bromoanthracene (△); 9-anthracenecarboxylic acid (○); 9-anthraldehyde (□); 1.0 mol% photosensitizer; 1.0 mol% IOC10; light intensity: 95 mJ cm$^{-2}$ min$^{-1}$.

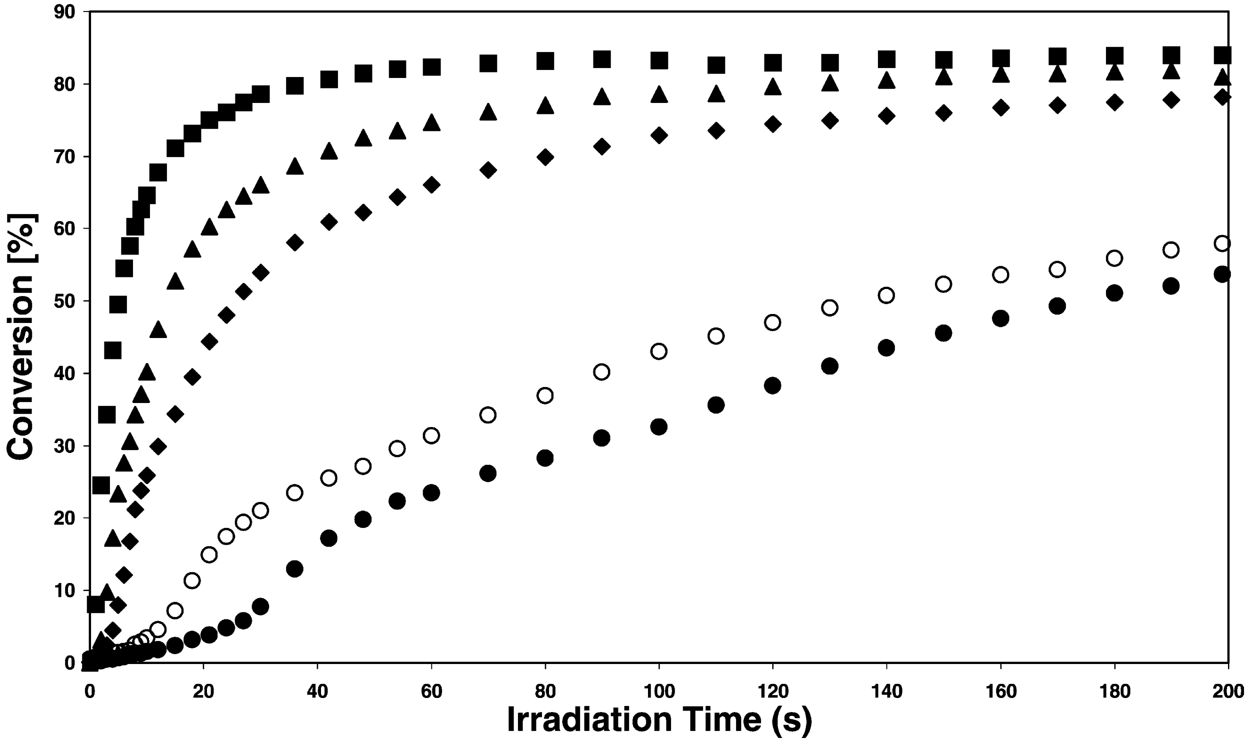


Fig. 5. FT-RTIR study of the effect of the structure of photosensitizers on the photoinitiated polymerization of CHO. No photosensitizer (●); anthrone (○); anthracene (◆); 9-*n*-butoxyanthracene (▲); 9,10-di-*n*-butoxyanthracene (■); 1.0 mol% photosensitizer; 1.0 mol% SOC10; light intensity: 310 mJ cm$^{-2}$ min$^{-1}$.

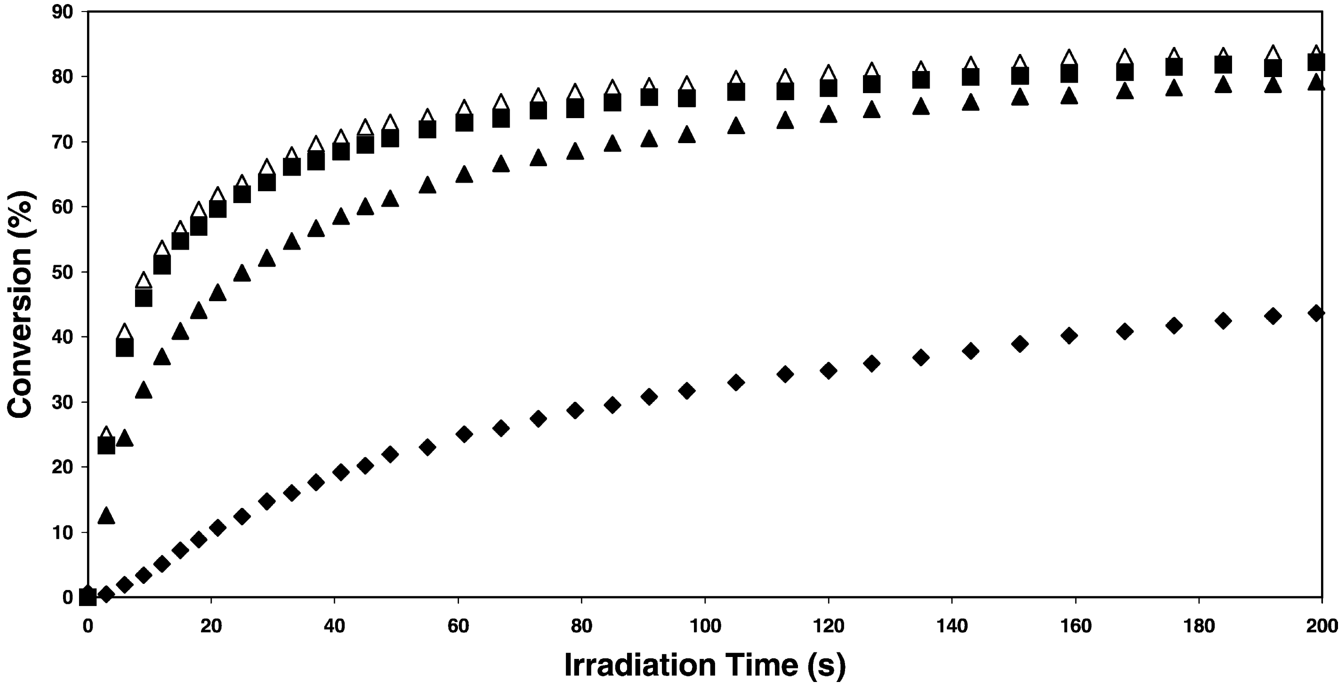


Fig. 6. Comparison of the photopolymerization of VCHDO in the presence of 1.0 mol% of various anthracene photosensitizers. No photosensitizer (◆); MBA (▲); DPA (■); DBA (△); 1.0 mol% DPS-$C_1C_{12}$ $PF_6^-$; light intensity: 440 mJ cm$^{-2}$ min$^{-1}$.

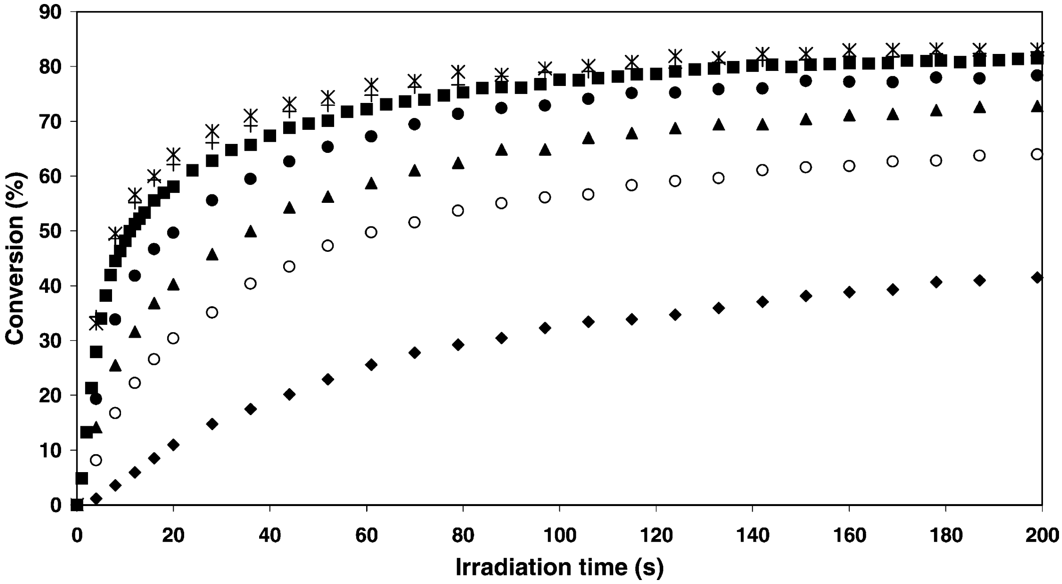


Fig. 7. Study of the effect of DPA concentration on the DPS-$C_1C_{12}$ $PF_6^-$ (1.0 mol%) photoinitiated polymerization of VCHDO. No sensitizer (◆); 0.1 mol% (○); 0.25 mol% (▲); 0.5 mol% (●); 1.0 mol% (■); 1.5 mol% (✱); 2.0 mol% (+); light intensity: 360 mJ $cm^{-2}$ $min^{-1}$.

quantum yields and consequently display lower efficiency than diaryliodonium or triarylsulfonium salt photoinitiators.

A study of the effect of DPA concentration on the DPS-$C_1C_{12}$ $PF_6^-$ (1.0 mol%) photoinitiated polymerization of VCHDO is depicted in Fig. 7 and Table 3, entries 24–29. An increase in the rate of the photosensitized polymerizations with a corresponding increase in the concentration of the photosensitizer can be observed up to a stoichiometric equivalency with the photoinitiator (1.0 mol%, entry 28). Beyond this point, further increase in the concentration of the photosensitizer has little effect on the rate.

The use of anthracene-type photosensitizers in the cationic photopolymerization of other types of monomers is depicted in Figs. 8–10. Fig. 8 and Table 3, entries 30–33 show a comparison of the photopolymerization of the difunctional epoxide monomer, 3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexane carboxylate, in the presence of 1.0 mol% of DBA, MBA and DPA. While clear evidence of photosensitization can be seen in this figure, the performance of the three photosensitizers in ERL-4221E is somewhat less than for either CHO or VCHDO. It should also be noted that the light intensity employed during the polymerization of this monomer was high (1020 mJ $cm^{-2}$ $min^{-1}$) as compared to that used for the other epoxide monomers. In Fig. 9, is shown the effect of photosensitization on the cationic oxetane ring-opening polymerization of (3-ethyl-3-oxetanylmethyl) phenyl ether (POX) with DPS-$C_1C_{12}$ $PF_6^-$ as the photoinitiator. All three photosensitizers, MBA, DBA and DPA display very similar and modest enhancement of the rates of polymerization of this monomer (AF = 2.3, 2.5 and 2.8, respectively). Lastly, the photosensitized polymerization of 2-chloroethyl vinyl ether is depicted in Fig. 10 and Table 3, entries 38–40. In this case, the photoinitiator, DPS-$C_1C_{12}$ $SbF_6^-$, was employed due to its better solubility in this monomer. Very little polymerization of the monomer is observed in the absence of a photosensitizer until a irradiation period of approximately 20 s and then polymerization proceeds slowly. In contrast, the use of MBA or DPA as photosensitizers results in a great reduction in the induction period and very rapid photopolymerization of this monomer.

### 3.3. Interpretation of the results

There are several structural and electronic factors that contribute to the ability of a compound, including those anthracene derivatives described here, to function as an electron-transfer photosensitizer of an onium salt cationic photoinitiator. First, a photosensitizer must possess strongly absorbing bands in the spectral region of interest. Second, the energy, multiplicity and lifetime of the excited state are crucial parameters that determine whether interaction with an onium salt is possible. It is important that the excited state of the photosensitizer be as high an energy and as long lived as possible to afford the greatest probability of encountering and interacting with the onium salt in dilute solution. Typically, electron-transfer photosensitization in polynuclear hydrocarbons takes place by interaction of the excited singlet state of the photosensitizer with the onium salt. Processes that rapidly quench the excited singlet state such as fluorescence or intersystem crossing to the excited triplet compete with and diminish the efficiency of electron-transfer photosensitization. Third, since electron-transfer photosensitization is, in essence, a redox reaction that takes place between the excited photosensitizer and the ground state onium salt, it is necessary to consider the relative redox potentials of these species. The relationship between the two respective redox potentials can

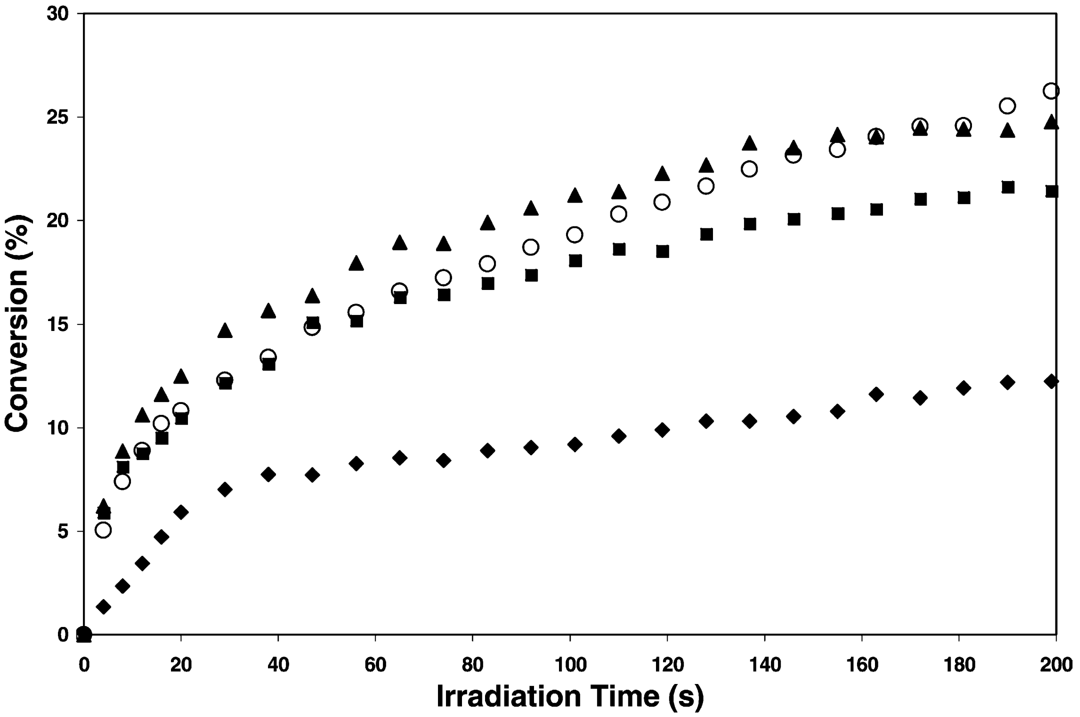


Fig. 8. Comparison of the photopolymerization of ERL-4221E in the presence of 1.0 mol% of anthracene photosensitizers. No photosensitizer (◆); DBA (■); MBA (○); DPA (▲); 1.0 mol% DPS-$C_1C_{12}$ $PF_6^-$; light intensity: 1020 mJ cm$^{-2}$ min$^{-1}$.

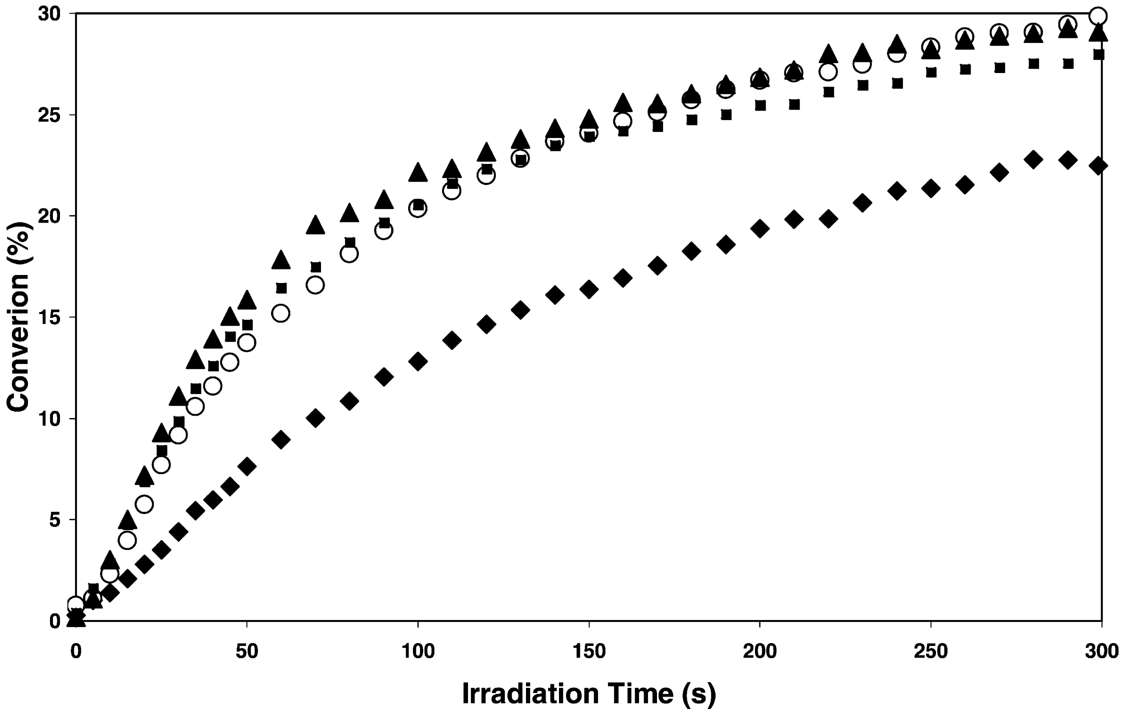


Fig. 9. Comparison of the photopolymerization of POX in the presence of 1.0 mol% of anthracene photosensitizers. No photosensitizer (◆); DBA (■); MBA (○); DPA (▲); 1.0 mol% DPS-$C_1C_{12}$ $PF_6^-$; light intensity: 1620 mJ cm$^{-2}$ min$^{-1}$.

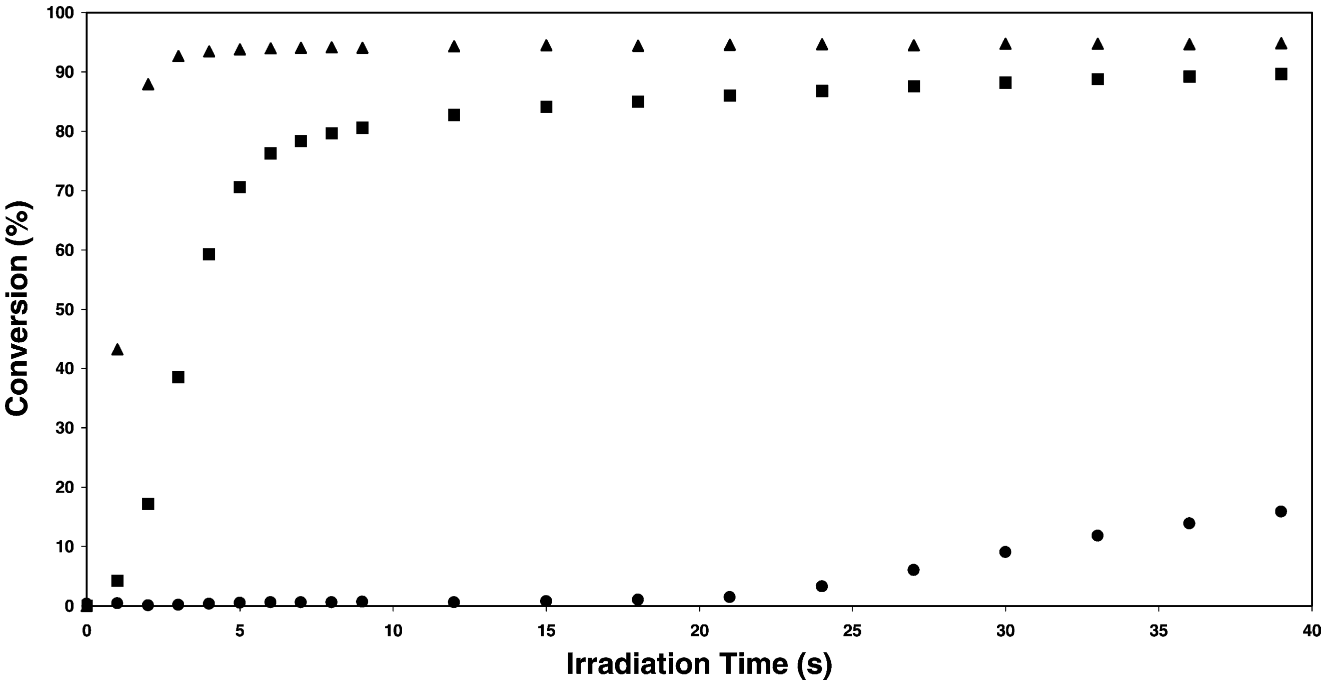


Fig. 10. Photosensitized photopolymerization of CEVE in the presence of 1.0 mol% of anthracene photosensitizers. No photosensitizer (●); MBA (■); DPA (▲); 1.0 mol% DPS-$C_1C_{12}$ $SbF_6^-$; light intensity: 275 mJ $cm^{-2}$ $min^{-1}$.

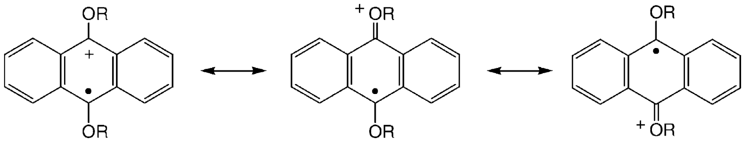
be expressed by the modified Gibbs free energy equation shown below [36].

$$\Delta G = 23.06(E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red}}) \tag{9}$$

Where $E_{1/2}^{\text{ox}}$ is the oxidation potential of the photoexcited anthracene photosensitizer and $E_{1/2}^{\text{red}}$ is the reduction potential of the onium salt photoinitiator. A general criterion that must be met for efficient electron-transfer between the excited photosensitizer and the onium salt to take place is that the value of $\Delta G$ must be of the order of at least $-10$ kcal $mol^{-1}$. Often, back electron-transfer can also take place in competition with electron-transfer in the forward direction, but decreases with increasing magnitude of the value of the free energy. While the factors cited above are widely known from a general perspective, it is not often that they are known for a particular compound or series of compounds since they must be experimentally determined in each case [37].[2] This is the situation for many of the anthracene derivatives described in this article. However, it is possible to qualitatively explain most of the results that have been obtained in this study.

As was discussed previously, the UV absorption spectra (Fig. 1) of the alkoxy-substituted anthracene compounds possess intense, short and long wavelength absorption bands that enable them to effectively capture the complimentary light emission at these same wavelengths from the light source. Long wavelength absorption bands are missing both in anthracene and anthrone. Moreover, in anthrone, the short wavelength absorption band is also much reduced. This can be attributed to the fact that the 9-hydroxyanthracene structure is the minority tautomer in the antranol/anthrone equilibrium. Consequently, anthrone is rather poorly effective as a photosensitizer for onium salt photolysis.

As already noted in Scheme 1, during electron-transfer photosensitization, the anthracene compound undergoes a one electron photooxidation by interaction with the onium salt. For this reason, those anthracene derivatives possessing electron donor substituents that effectively increase the reduction potential and, further, stabilize the cation radical that is formed would be expected to provide the best photosensitization activity. For example, 9,10-dialkoxyanthracenes would be expected to provide stabilization of the cation radical through structures such as those shown below in Eq. (10).



(10)

This is what was observed during the studies described herein. Generally speaking, DBA and DPA bearing two alkoxy substituents are more effective than MBA with one

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[2] Anthracene singlet energy 76.3 kcal $mol^{-1}$ singlet lifetime 4.9–5.3 ns quantum yield for intersystem crossing 0.72 quantum yield for fluorescence 0.27.

*n*-butoxy group. MBA, in turn, is more effective than anthracene as a photosensitizer. Such structures as shown above are also consistent with the work of Sahyun et al. [38]. These investigators have shown that 9,10-diethoxyanthracene cation radical generated by photolysis in the presence of diaryliodonium salts undergoes first, phenylation by reaction of the above 9,10-ethoxyanthracene cation radical with the diaryliodine free radical or the phenyl radical followed by dealkylation to give 9-ethoxy-9-phenyl-10-anthrone.

Lastly, in this article we have demonstrated that anthracene derivatives are capable of photosensitizing the photolysis of three different types of onium salt photoinitiators. Qualitatively, diaryliodonium salts (IOC10) are more easily photosensitized by these compounds than the corresponding triarylsulfonium salts (SOC10) while dialkylphenacylsulfonium salts (DPS-$C_1C_{12}$) are intermediate. These results can be related to difference in the oxidation potentials of these onium salts. IOC10 with a lower reduction potential ($E^{\mathrm{red}}_{1/2} = -0.2\,\mathrm{V}$, $-4.6\,\mathrm{kcal\,mol^{-1}}$) is more easily reduced than SOC10 ($E^{\mathrm{red}}_{1/2} = -1.01$ to $-1.46\,\mathrm{V}$, $-23$ to $-34\,\mathrm{kcal\,mol^{-1}}$) [39]. The reduction potential of dialkylphenacylsulfonium salts has been found to be intermediate ($E^{\mathrm{red}}_{1/2} = -0.7\,\mathrm{V}$, $-16\,\mathrm{kcal\,mol^{-1}}$) between diaryliodonium and triarylsulfonium salts [40]. The reduction potential for excited anthracene is $-40\,\mathrm{kcal\,mol^{-1}}$ [9]. The introduction of electron-donating substitutents would be expected to lower this value somewhat. However, the value of $\Delta G$ for all the onium salts would be negative (ca. $-40\,\mathrm{kcal\,mol^{-1}}$ for diaryliodonium salts; $-11$ to $-22\,\mathrm{kcal\,mol^{-1}}$ for triarylsulfonium salts; $-29\,\mathrm{kcal\,mol^{-1}}$ for DPS salts). These results support the mechanism proposed in Scheme 1.

## 4. Conclusions

During the course of this work, we have demonstrated that anthracene compounds substituted with electron-donating substituents can be prepared using straightforward, simple synthetic methods. These anthracene compounds display good solubility in a wide range of both polar and nonpolar solvents and monomers. FT-RTIR kinetic studies show that they also possess excellent activity as photosensitizers for photoinitiated vinyl ether, oxetane and epoxide ring-opening cationic polymerizations employing a broad spectrum of onium salt photoinitiators including: diaryliodonium, triarylsulfonium and dialkylphenacylsulfonium salts. 9,10-Dialkoxyanthracenes displayed the highest efficiency as photosensitizers for onium salt photoinitiators while anthracenes bearing electron-withdrawing substitutents exhibited poor photosensitizing characteristics.

This work shows that it is possible to rationally design highly effective anthracene electron-transfer photosensitizers for onium salt induced photopolymerizations that also possess other desirable characteristics such as low volatility and good solubility.

## Acknowledgements

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