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Synthesis and Evaluation of S-Aryl-S,S-cycloalkylsulfonium Salts as Cationic Photoinitiators

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A series of well characterized S-aryl-S,S-cycloalkylsulfonium salts was prepared using a simple, straightforward synthetic method. Due to their poor absorption characteristics at UV wavelengths greater than 300 nm, these compounds were found to display sluggish photoinitiation activity when the cationic photopolymerizations of various monomers were attempted in this spectral range. Using 9,10-dialkoxyanthracenes as electron-transfer photosensitizers, the cationic polymerization of several typical vinyl and heterocyclic monomers were carried out. Optical pyrometry and real-time infrared spectroscopy were employed to monitor the course of these photopolymerizations. The thermal stability of the photoinitiators at room temperature in the presence of reactive monomers was excellent. A mechanism for the photolysis of S-aryl-S,S-cycloalkylsulfonium salts and their photoinitiation of cationic polymerization was proposed.

Keywords sulfonium salts, cationic polymerization, photopolymerization, ring-opening polymerization, vinyl polymerization, photosensitization

Introduction

Triarylsulfonium salts bearing anions of poor nucleophilic character were first reported by Crivello and Lam (1) in 1979 to be a novel class of efficient photoinitiators for cationic polymerization. Since that time, the field of photoinitiated cationic polymerization has expanded rapidly (2). Triarylsulfonium salt cationic photoinitiators are currently in widespread and increasing commercial use and are employed in such applications as printing inks, adhesives, can and beverage coatings, as well as in photo- and stereolithography.

Triarylsulfonium salt photoinitiators possess many attractive features that have played a major role in their acceptance in many diverse commercial applications. They are highly photosensitive to UV irradiation and efficiently initiate a wide variety of vinyl and ring-opening cationic photopolymerizations. Formulations containing these photoinitiators with reactive monomers have very long shelf lives in the absence of UV light. Moreover, mixtures of monomers and triarylsulfonium salt photoinitiators can be

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heated to temperatures in excess of 120°C without thermally initiating polymerization. The excellent thermal latency displayed by triarylsulfonium salts is a highly desirable characteristic in all practical applications and allows for both the easy clean up and in the reuse of these photosensitive materials. It is possible to broaden the spectral absorption characteristics of these photoinitiators through modifications in their structure and also through the use of photosensitizers. Commercially available triarylsulfonium salt photoinitiators have very low orders of oral, skin and eye toxicity. Lastly, these photoinitiators are relatively inexpensive which allows their use in low-cost high-volume items such as coatings, printing inks and adhesives.

In contrast to the considerable literature on the use of triarylsulfonium salt photoinitiators, there are only a few reports of the use of other classes of sulfonium salts as cationic photoinitiators. The absence of UV absorbing chromophores in trialkylsulfonium salts precludes their use as photoinitiators. However, there are several reports describing the use of the corresponding S-alkyl-S,S-diarylsulfonium and S-aryl-S,S-dialkylsulfonium salts as photoinitiators for cationic vinyl and ring-opening polymerizations. Pappas et al. (3, 4) treated epoxides with dialkyl sulfides, alkylaryl sulfides and phenyl sulfide in the presence of strong Brønsted acids such as HPF_6 and isolated and characterized the corresponding hydroxy sulfonium salt products. They also demonstrated that such S-alkyl-S,S-diarylsulfonium salts are photoactive and can be used as photoinitiators for the ring-opening polymerization of epoxide monomers. In addition, Endo et al. (5, 6) and Takahashi (7) have described the development of S-alkyl-S,S-diarylsulfonium salts and S-aryl-S,S-dialkylsulfonium salts as photoinitiators for cationic ring-opening polymerizations. Saeva et al. (8, 9) have conducted photolysis studies of S-benzylthianthrenium salts and dialkyl-1-naphthylsulfonium salts. Recent papers (10–13) from this laboratory have reported the use of S,S-dialkyl-S-phenacylsulfonium salts and S,S-dialkyl-S(4-hydroxyphenyl)sulfonium salts as important new classes of cationic photoinitiators.

In this article, we describe a convenient method for the synthesis of S-aryl-S,S-cycloalkylsulfonium salts, their characterization and their use as cationic photoinitiators. Comparative studies of the photosensitivity of these photoinitiators with triarylsulfonium salts were carried out using optical pyrometry and real-time infrared spectroscopy.

Experimental

Materials

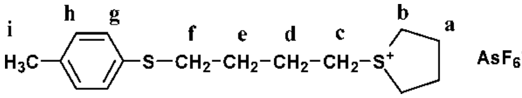
Cyclohexene oxide, 1,2-epoxyhexane and the various cyclic sulfides used in this work were obtained from the Aldrich Chemical Company, Milwaukee, WI. Cyclohexene oxide was dried and distilled prior to use. Limonene oxide was received from the Viking Chemical Company, Blooming Prairie, MN. Triethylene glycol divinyl ether (DVE-3) was a gift of the Specialty Products Division of the GAF Corporation, Wayne, NJ. 3,4-Epoxycyclohexylmethyl 3′,4′-epoxycyclohexanecarboxylate (ERL-4221E) was purchased from the Union Carbide Corporation, Bound Brook, NJ. Unless otherwise noted, all other reagents, monomers and photoinitiators were used as received without further purification. The diaryliodonium salts (14) and tris(4-methylphenyl)sulfonium hexafluoroarsenate (15) used in this investigation were prepared as described in earlier publications.

General Synthesis of S-Aryl-S,S-cycloalkylsulfonium Salts

The following synthesis of S-4-t-butylphenyl-S,S-tetramethylenesulfonium hexafluorophosphate is typical of the general procedure used for S-aryl-S,S-cycloalkylsulfonium salts **1–5** prepared during the course of this investigation.

There were added to a 50 mL round bottom flask fitted with a magnetic stirrer, reflux condenser 8.8 g (0.1 mol) of tetrahydrothiophene, 0.2 g of cupric benzoate and 0.025 mol (13.45 g) of di(4-t-butylphenyl)iodonium hexafluorophosphate. The reaction mixture was heated at reflux (119°C) for 6 h. After cooling, the reaction mixture was transferred to an Erlenmeyer flask and the semisolid product extracted thrice with 20 mL portions of diethyl ether to remove the excess starting materials and 4-t-butyliodobenzene byproduct and then washed with 30 mL of deionized water. Finally, the solid product was recrystallized from isopropyl alcohol to give a colorless crystalline product with a melting point of 178–181°C.

Characterization of Sulfonium Salt 7



^{1}H-NMR spectrum DMSO-d$_6$, δ(ppm) H$_a$, t, 2.96; H$_b$, t, 3.18; H$_c$, m, 3.58; H$_d$, m, 1.70; H$_e$, m, 1.82; H$_f$, m 2.20; H$_g$, A$_2$B$_2$, 7.28; H$_h$, A$_2$B$_2$, 7.14; H$_i$, s, 2.28. Elemental Analysis for $C_{15}H_{23}S_2AsF_6$ Calc: %C = 39.48; %H = 5.08. Found: 39.48; %H = 5.06.

Instrumentation

^{1}H-NMR spectra were obtained using a Varian XL 500 MHz spectrometer at room temperature in DMSO-d$_6$ or $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. UV Spectra were recorded in methanol using a Perkin-Elmer (Stamford, CN) Lambda 2 UV/Vis Spectrometer.

Photolysis of Sulfonium Salt 1

The photolysis of a saturated solution of sulfonium salt **1** in methanol was conducted in a quartz vessel using a Rayonet Photochemical Reactor (New England Ultraviolet Corp) equipped with sixteen 254 nm lamps for 1 h at room temperature. GC/MS experiments were performed on a Shimadzu QP5050 mass-spectrometer interfaced with Shimadzu 17G gas chromatograph. Mass spectra were collected in electron ionization mode (70 eV) in mass range from m/z 40 to m/z 450. The samples were injected onto a Restek RST-5 column (5% diphenyl 95% dimethylsiloxane stationary phase, 0.25 μ particle size, column length-30 m, column ID–0.25 mm) in a split mode at split ratio of 5:1. Helium was used as a carrier gas. The temperature gradient was: starting temperature 50°C, hold for 8 min, from 50°C to 100°C at a rate of 10°/min, from 100° to 250° at a rate of 17°/min, hold at 250° for 12 min.

Kinetic Characterization of Photopolymerizations Using Sulfonium Salts

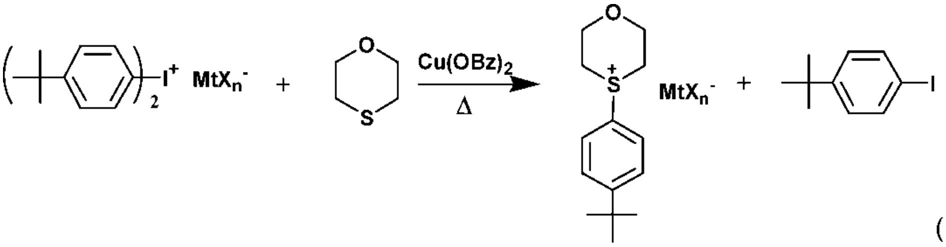
We have previously described the analytical techniques and apparatus used in this laboratory for both real-time infrared spectroscopy (RTIR) (16) and optical pyrometry (OP)

(17, 18). Samples for RTIR and OP kinetic analysis were prepared by sandwiching a liquid monomer containing the designated photoinitiator between two thin (10 μm) films of oriented and corona treated poly(propylene) film using an open polyester mesh as a spacer. The samples were mounted in plastic 2 cm × 2 cm slide frames and then inserted into the sample holder for analysis. The average thickness of the samples was 0.49 mm. Several kinetic runs were performed for each polymerizable system. All kinetic studies were conducted at ambient laboratory temperature (25–28°C) unless otherwise noted.

Results and Discussion

Synthesis of S-Aryl-S,S-cycloalkylsulfonium Salts

A number of synthetic methods for the preparation of S-aryl-S,S-dialkylsulfonium and S-alkyl-S,S-diarylsulfonium salts have been described in the literature (3–13). However, most of these methods provide the desired compounds in low yields by routes that require the use of silver salts of superacids such as $AgPF_6$. Work in this laboratory has discovered a novel route to these compounds that involves treating the appropriate sulfide with a diaryliodonium salt in the presence of a copper (II) compound as a catalyst. An example of the general method employed for the preparation of these compounds depicted in equation (1). In all cases, we have used cyclic sulfides since the resulting S-aryl-S,S-cycloalkylsulfonium salts are stable, well characterized and easily purified crystalline products. Direct, facile arylation of the cyclic sulfide takes place under catalysis by copper compounds to generate the corresponding sulfonium salt bearing the anion of the starting diaryliodonium salt. Here, as in previous cases of onium salt cationic photoinitiators, MtX_n^- represents an anion of low nucleophilic character as for example: PF_6^- or AsF_6^-.

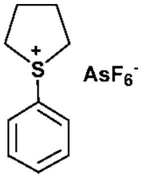
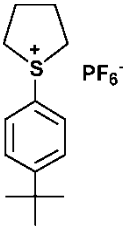
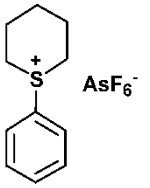
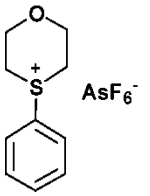
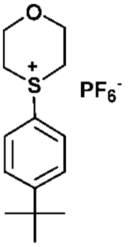


(1)

The sulfonium salts were isolated from the reaction mixture and readily purified by recrystallization to give colorless crystalline compounds soluble in a variety of common solvents but insoluble in water. Table 1 shows the structures of the S-aryl-S,S-cycloalkylsulfonium salts prepared during the course of this work along with their melting points, UV absorption characteristics and the results of their elemental analyses. Yields of these compounds ranged from ~20 % (1) to 80% (5). The sulfonium salts were further characterized by ^{1}H-NMR and the spectra of sulfonium salt **3** is shown in Figure 1. A typical UV spectrum for sulfonium salt **1** is presented in Figure 2.

The above described arylation reaction can be applied to synthesis of many different types of S-aryl-S,S-cycloalkylsulfonium salts. However, some limitations have been observed. For example attempts to prepare **6** by the direct arylation of tetrahydrothiophene

Table 1
Structure and characteristics of S-aryl-S,S-cycloalkylsulfonium salts

Notation	Structure	M.P. (°C)	Elemental analysis Theo.	Elemental analysis Fnd.	UV λ_{max} (ε)
1		148–159	%C = 33.91 %H = 3.70	%C = 34.00 %H = 3.77	224 (8820)
2		178–181	%C = 45.90 %H = 5.78	%C = 45.94 %H = 5.73	233 (14000)
3		157–159	%C = 35.88 %H = 4.11	%C = 35.89 %H = 4.16	222 (11100)
4		155–156	%C = 32.44 %H = 3.54 %H = 8.66	%C = 32.30 %H = 3.72 %S = 8.74	225 (53100) 265 (7900)
5		195–196	%C = 43.98 %H = 5.54	%C = 44.43 %H = 5.62	240 (109007)

with di(4-methylphenyl)iodonium hexafluoroarsenate in the presence of a large excess of the cyclic sulfide did not result in the desired product. Instead, the product **7** was obtained. The formation of **7** can be rationalized, as depicted in Equation (2), as resulting from the further nucleophilic attack of tetrahydrothiophene on **6** with consequent ring-opening of

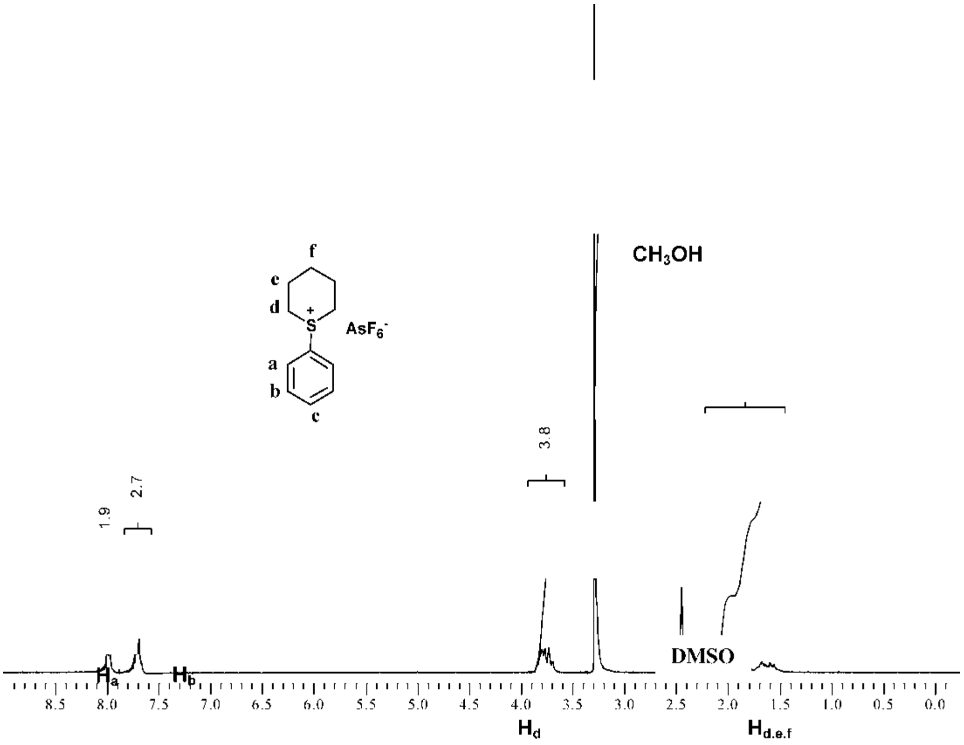


Figure 1. 500 MHz ^{1}H-NMR spectrum of S-phenyl-S,S-pentamethylenesulfonium hexafluroarsenate (**3**) in DMSO-d$_6$.

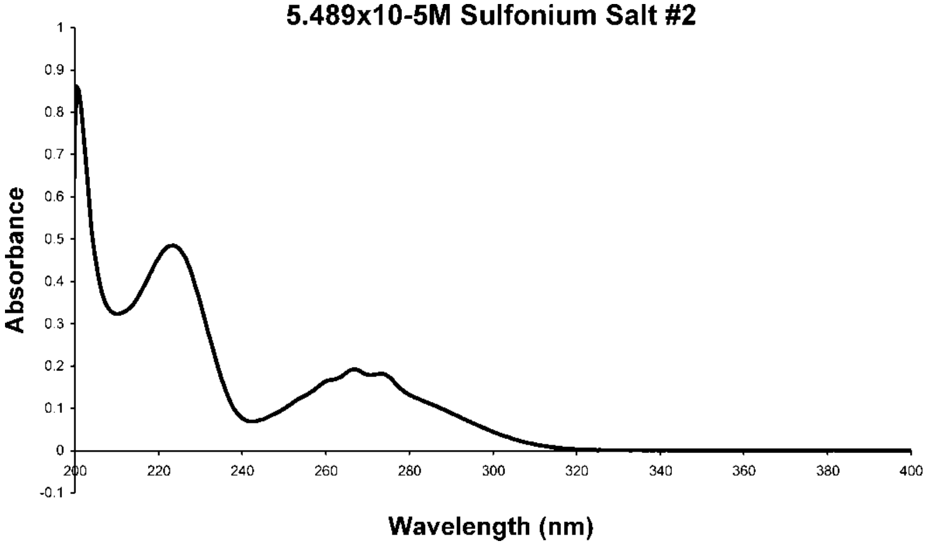
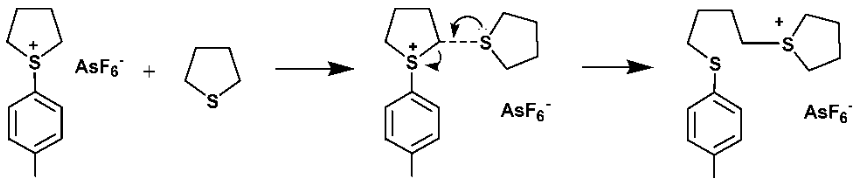


Figure 2. UV spectrum of S-phenyl-S,S-tetramethylenesulfonium hexafluoroarsenate (**1**) in methanol.

the cyclic sulfonium salt. This type of ring-opening reaction of cyclic sulfonium salts is well known and has been employed for the preparation of linear sulfur-containing polymers (19).



(2)

6 **7**

Both the ^{1}H-NMR spectrum and the elemental analysis (reported in the Experimental) confirm the formation of **7**. It is interesting to note that analogous sulfonium salt compounds such as **1** and **4** bearing the cyclic five-membered ring were successfully prepared. In those cases, this side reaction was minimized by reducing the amount of excess cyclic sulfide and by shortening the reaction time. Compounds such as **3**, **4** and **5** bearing strain-free six membered rings were prepared without complications. Attempts to extend this method to the preparation of S-alkyl-S,S-diarylsulfonium salts gave mixtures of sulfonium salt products probably due to transalkylation side reactions.

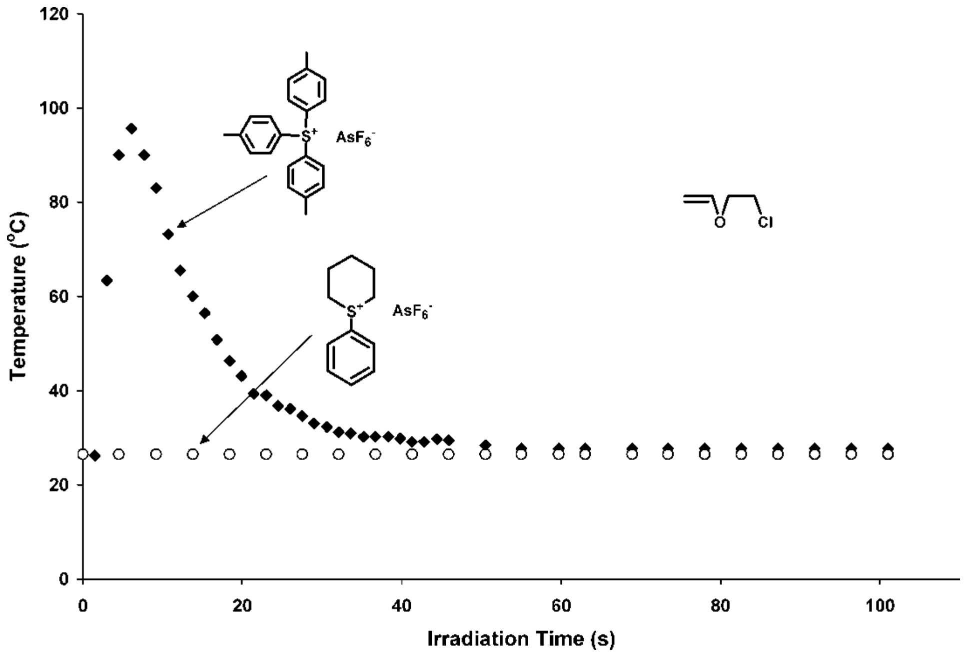


Figure 3. Comparison of the photopolymerization of 2-chloroethyl vinyl ether carried out using 1 mol% of tris(4-methylphenyl)sulfonium hexafluoroarsenate and with S-phenyl-S,S-pentamethylenesulfonium hexafluoroarsenate (**3**) (light intensity 2690 mJ/cm^2 min).

Photoinitiated Cationic Polymerization

To monitor the kinetics of the cationic photopolymerizations reported in this article, extensive use was made in this investigation of two complimentary analytical techniques, real-time infrared spectroscopy (RTIR) and optical pyrometry (OP). Detailed descriptions of these two techniques are given in the Experimental portion of this communication. RTIR has been widely used to follow the course of both free-radical and cationic photopolymerizations and is based on the IR monitoring of the increase or decrease of specific absorption bands due to the disappearance of starting materials or formation of products as a photopolymerization progresses. OP has also been shown to be a highly useful method for monitoring the kinetics of various types of photopolymerization reactions. Employing this method, thin, homogeneous, liquid samples of mixtures of the epoxide monomer and a photoinitiator were sandwiched between two layers of 10 μm oriented and corona treated polypropylene films and irradiated with UV light through a liquid optic cable that transmits wavelengths greater than 300 nm to initiate polymerization. Simultaneously, the temperature of the sample was remotely monitored through the use of an infrared camera (optical pyrometer). Various light intensities were used in the studies depending upon the specific monomer-photoinitiator-photosensitizer system employed. The rate of the increase in the temperature for a given photopolymerization reaction is directly proportional to the rate of consumption of the monomer.

A comparison of the photopolymerization of 2-chloroethyl vinyl ether using S-phenyl-S,S-pentamethylenesulfonium hexafluoroarsenate (**3**) with tris(4-methylphenyl)sulfonium hexafluoroarsenate is shown in Figure 3. Under identical conditions of UV irradiation, the

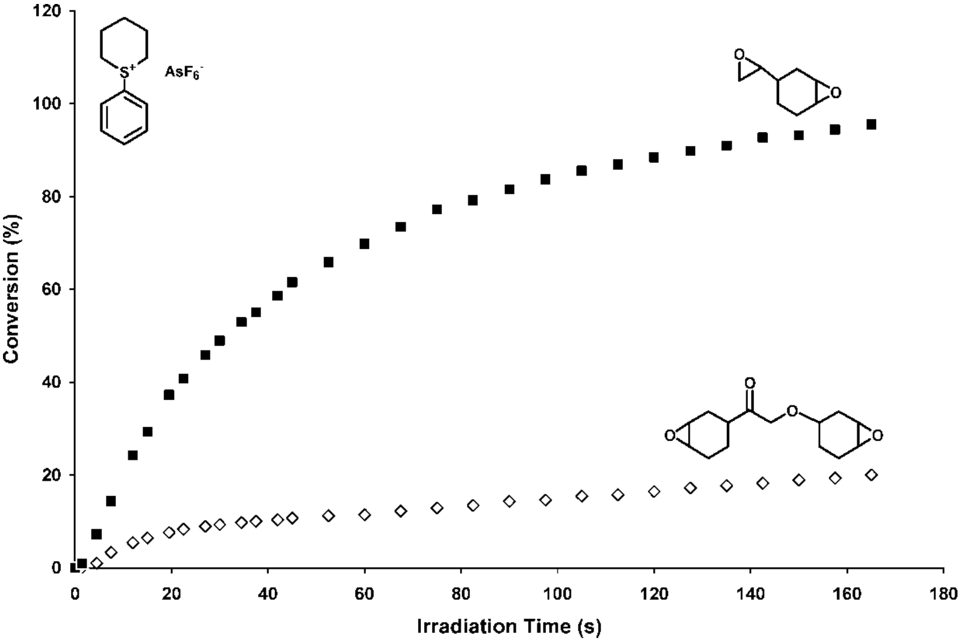


Figure 4. RTIR study of the photopolymerization of 4-vinylcyclohexene dioxide and 3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexanecarboxylate (ERL-4221E) carried out in the presence of 1.0 mol% S-phenyl-S,S-pentamethylenesulfonium hexafluoroarsenate (light intensity 6700 mJ/cm^2 min).

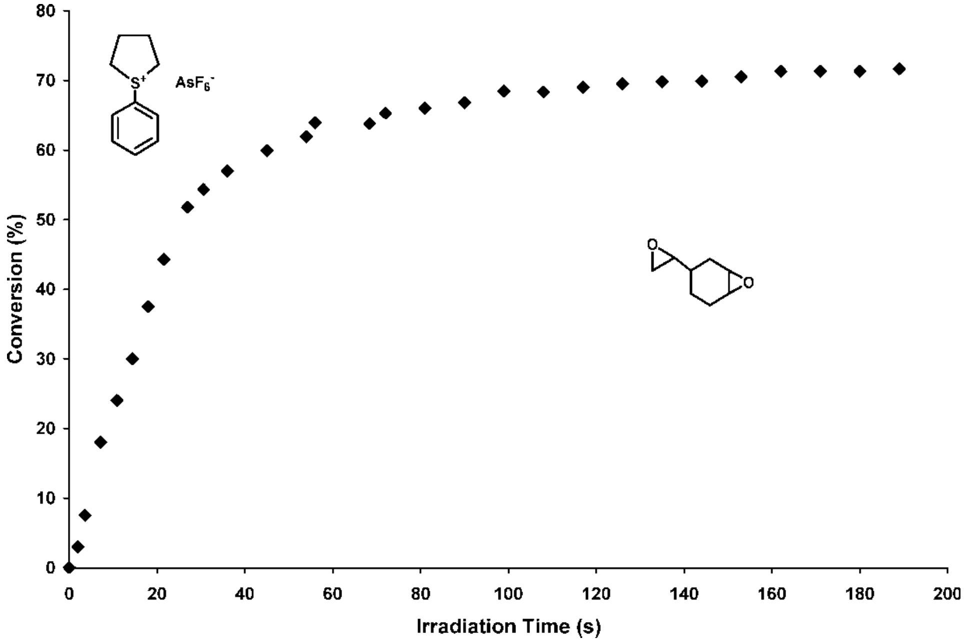


Figure 5. RTIR study of the photopolymerization of 4-vinylcyclohexene dioxide carried out in the presence of 1.0 mol% S-phenyl-S,S-tetramethylenesulfonium hexafluoroarsenate (light intensity 6700 mJ/cm^2 min).

photoinduced polymerization of this monomer proceeds smoothly and rapidly in the presence of the triarylsulfonium salt whereas with corresponding sulfonium salt **3** no detectable polymerization was noted. Figure 4 shows the RTIR results of a study of the photopolymerizations of two biscycloaliphatic epoxide monomers carried out in the presence of S-phenyl-S,S-pentamethylenesulfonium hexafluoroarsenate at a high UV irradiation intensity. The polymerizations of these two monomers proceed rather slowly. Similar results are depicted in Figure 5 for the polymerization of 4-vinylcyclohexene dioxide using S-phenyl-S,S-tetramethylenesulfonium hexafluoroarsenate. Figure 6 gives the results of an OP study of the photopolymerization of 2-chloroethyl vinyl ether using two different sulfonium salts as photoinitiators. Photopolymerization of this very reactive monomer was quite sluggish even at a light intensity of 4320 mJ/cm^2 min. At 687 mJ/cm^2 min no polymerization was observed to take place over the course of 350 seconds of irradiation. All of the above results suggest a poor photoresponse of the S-aryl-S,S-cylcoalkylsulfonium salt photoinitiators. As may be noted in Table 1, all these photoinitiators display rather low UV absorption characteristics at wavelengths above 300 nm that were used in these experiments. Therefore, for effective cationic photopolymerizations at these wavelengths, high intensities and/or long irradiation times are required. In contrast, direct exposure of the above reaction mixtures to direct UV irradiation using a medium pressure mercury arc lamp that includes a broad distribution of wavelengths from 250–400 nm, resulted in rapid polymerization in all cases.

Previously, we have reported that the photolyses of triarylsulfonium and dialkylphenacylsulfonium salts can be photosensitized (20). Particularly effective as electron-transfer photosensitizers were 9,10-dialkoxyanthracenes. Accordingly, the use of these latter compounds as photosensitizers for dialkylarylsulfonium salts was explored.

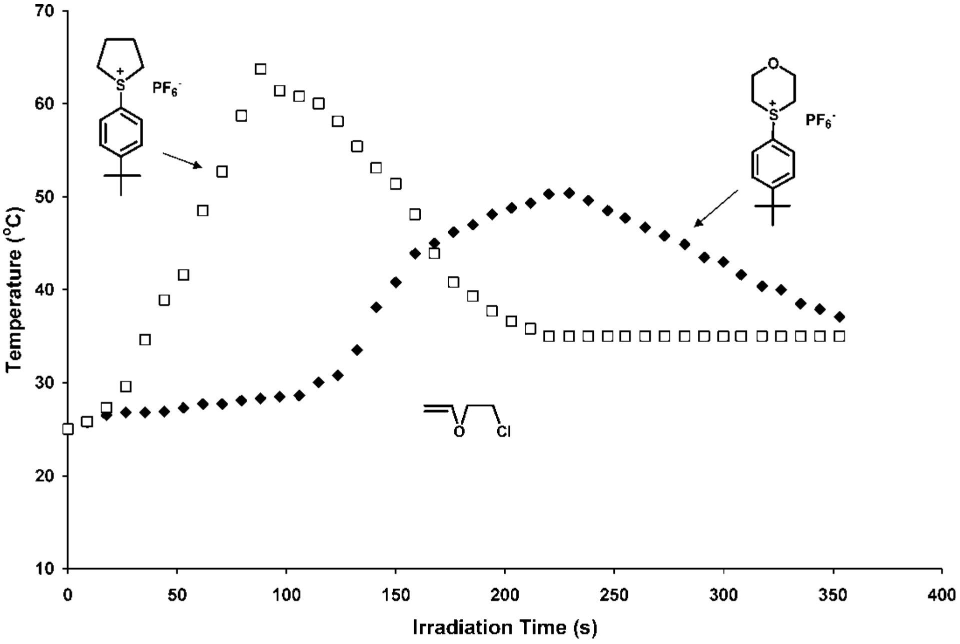


Figure 6. OP monitored photopolymerization of 2-chloroethyl vinyl ether conducted using 1.0 mol% of the indicated sulfonium salt photoinitiators (light intensity 4316 mJ/cm^2 min).

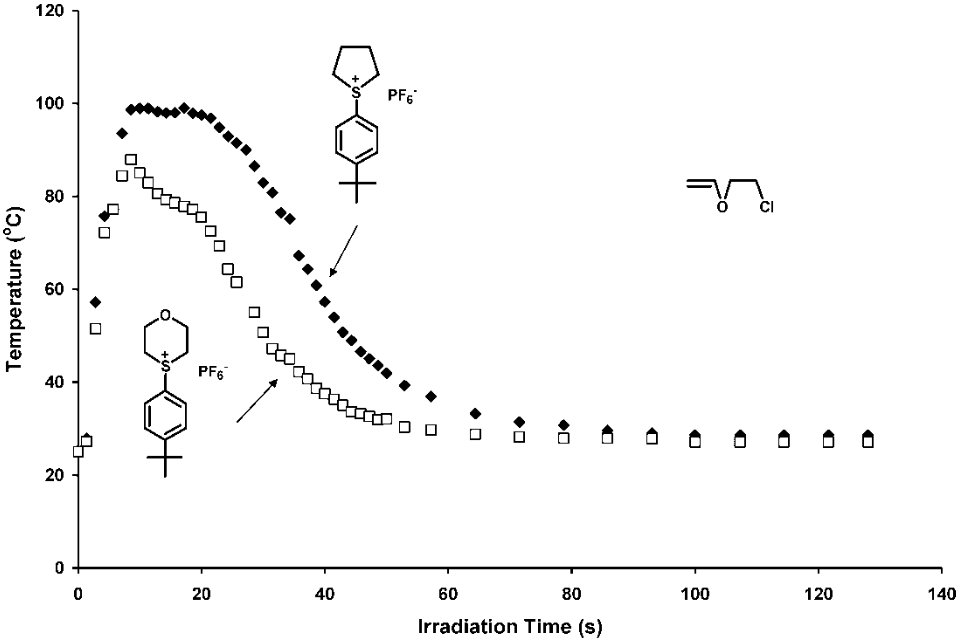


Figure 7. Photosensitized polymerization of 2-chloroethyl vinyl ether using 0.5 mol% 9,10-di-n-propoxyanthracene and 1.0 mol% sulfonium salt photoinitiators (light intensity 687 mJ/cm^2 min).

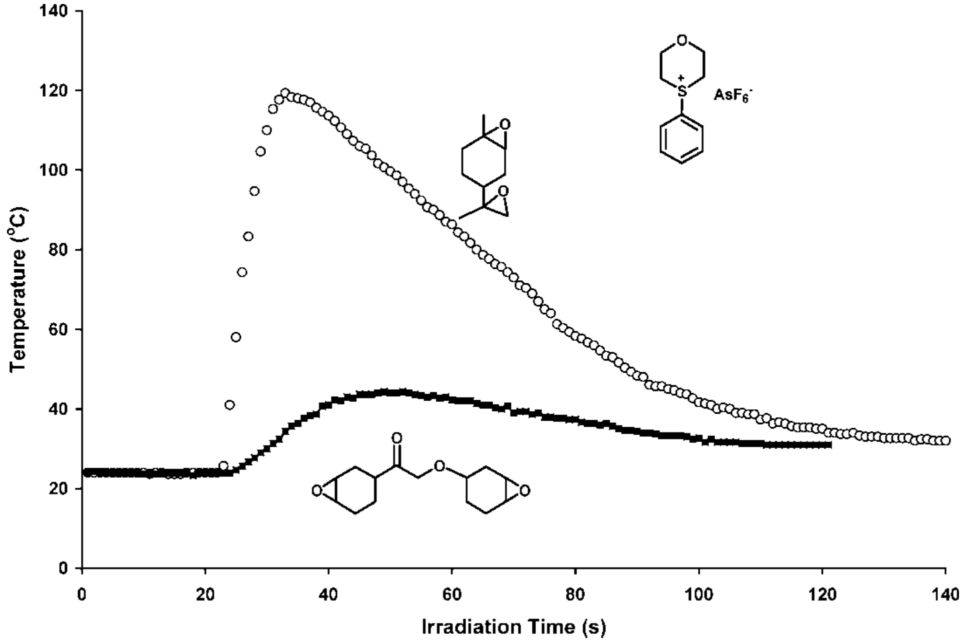


Figure 8. Photosensitized polymerization of limonene dioxide (light intensity 1043 mJ/cm^2 min) 3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexane-carboxylate (ERL-4221E) (light intensity 772 mJ/cm^2 min) carried out in the presence of 1.0 mol% photoinitiator with 0.5 mol% 9,10-di-n-butoxyanthracene as a photosensitizer.

Figure 7 gives the results of the 9,10-di-n-propoxyanthracene photosensitized polymerization of 2-chloroethyl vinyl ether carried out at a light intensity of 687 mJ/cm^2 min using the same two sulfonium salts as employed in Figure 6. As may be noted, the polymerization takes place vigorously at a relatively low light intensity and with almost no induction period. OP studies of the photosensitized polymerizations of limonene dioxide and 3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexane carboxylate (ERL-4221E) by 9,10-di-n-butoxyanthracene in the presence of photoinitiator **4** are depicted in Figure 8. Both these cationic epoxide ring-opening polymerizations take place rapidly after a brief induction period. As expected, limonene dioxide is the more reactive of the two monomers with the maximum temperature of the thin film sample spontaneously reaching 119°C during the photopolymerization. The photopolymerization of triethyleneglycol divinyl ether (DVE-3) using photoinitiator **4** is shown in Figure 9. This photopolymerization also occurs rapidly after an induction period to give a crosslinked polymer.

It should be mentioned that the room temperature stability of solutions of the S-aryl-S,S-cycloalkylsulfonium salts in various vinyl ether and epoxide monomers at room temperature was excellent. When stored in the dark, no polymerization was noted even after 1 week storage.

Mechanism for the Photolysis of S-Aryl-S,S-cycloalkylsulfonium Salts

A mechanism for the photolysis of S-aryl-S,S-cycloalkylsulfonium salts has not been reported in the literature. Accordingly, a basic study of the photolysis of sulfonium salt **1** was carried out in methanol and the products determined by means of GC-mass

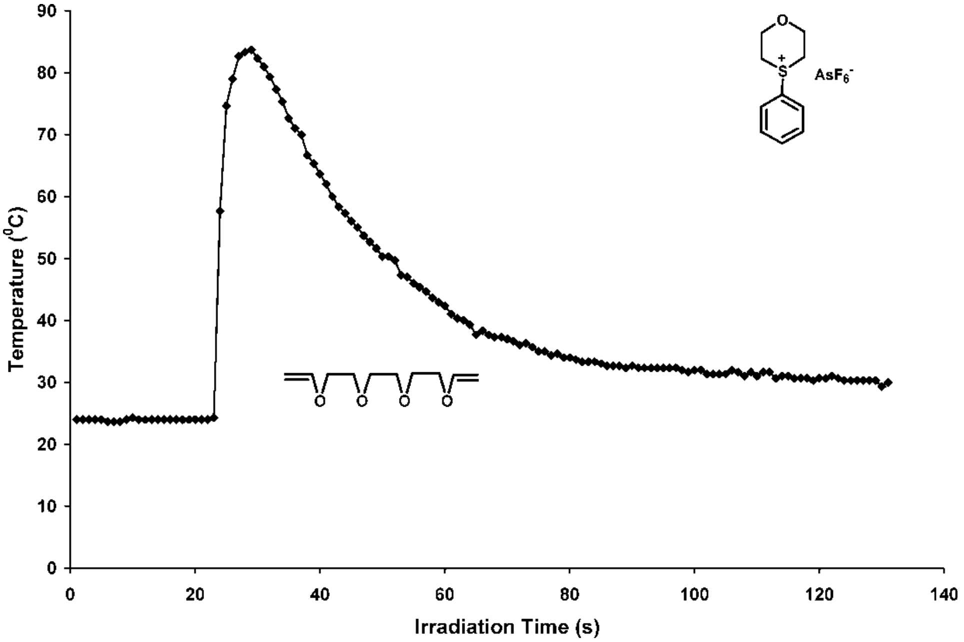
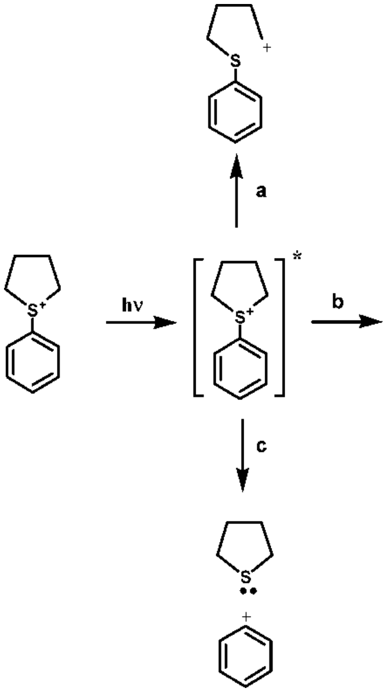


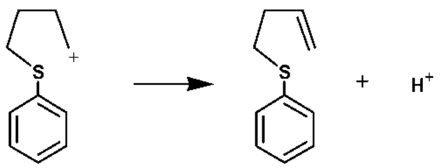
Figure 9. Photosensitized polymerization of triethyleneglycol divinyl ether (DVE-3) carried out in the presence of 1.0 mol% photoinitiator with 0.5 mol% 9,10-di-n-butoxyanthracene as a photosensitizer (light intensity 916 mJ/cm^2 min).



Scheme 1. Mechanism of the photolysis of S-aryl-S,S-cycloalkylsulfonium salts.

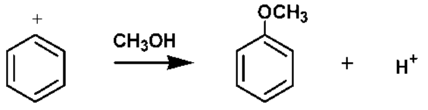
spectrometry. The major products that were identified by their masses were benzene (78 amu), thiophene, (88 amu), anisole (108 amu) and a sulfur-containing species corresponding to the molecular formula; C_6H_5-S-C_4H_7 (164 amu). We propose the complex mechanism shown in Scheme 1 to explain these results. In this mechanism, the anion is omitted for simplicity.

In this mechanism, the sulfonium salt is excited by the irradiating light. All photolyses and photopolymerizations conducted during the course of this work were carried out in ambient air. Since photolysis of the sulfonium salts does not appear to be appreciably quenched in the presence of oxygen, there is a high probability that the excited singlet state is initially produced on irradiation. The sulfonium salt then undergoes cleavage of a carbon-sulfur bond via the excited singlet or after intersystem crossing to the excited triplet. With S-aryl-S,S-cycloaliphatic sulfonium salts there are three possible modes of bond cleavage. Pathway **a** of Scheme 1 depicts the cleavage of one of the two carbon-sulfur bonds of the five membered ring. Subsequent loss of a proton by an elimination reaction as shown in equation (3) would give **8** and account for the 164 amu photolysis product and simultaneously generate a Brönsted acid. Two possible pathways for the cleavage of the sulfur-carbon bond to the aromatic ring are shown respectively involving a homolytic bond cleavage (pathway **b**) and a heterolytic bond cleavage (pathway **c**). While photolysis by pathway **b** would explain the observed formation of tetrahydrothiophene and benzene via the well known (21–23) tetrahydrothiophene cation-radical and the phenyl radical, other expected free radical products such as biphenyl are notably absent in the GC-mass spectrometry analysis. This suggests that pathway **b** is not operative. The observation of anisole among the major photolysis products of **1** can be rationalized by considering pathway **c** of Scheme 1. The expected products of pathway **c** are: tetrahydrothiophene, benzene and anisole. This latter product (**9**) is produced by interaction of the phenyl cation with methanol as depicted in equation (4).



8

(3)



9

(4)

In addition to the organic photolysis products produced by pathways **a** and **c** of Scheme 1, the strong Brönsted acids, $HMtX_n$, are generated that initiate the cationic polymerizations of a wide variety of vinyl and heterocyclic monomers represented by **M** in equation (5).

$$HMtX_n + M \longrightarrow HM^+MtX_n^- \qquad (5)$$

Conclusions

S-aryl-S,S-cycloalkylsulfonium salts can be conveniently prepared by the direct, copper-catalyzed arylation of the appropriate cyclic sulfides by diaryliodonium salts. Several novel compounds were prepared using this route and characterized using conventional methods. Kinetic studies using real-time infrared spectroscopy and optical pyrometry demonstrated that these compounds are rather poor photoinitiators for the cationic polymerization using UV light at wavelengths greater than 300 nm. However, it was observed that these sulfonium salts can be efficiently electron-transfer photosensitized in this spectral region through the use of 9,10-dialkoxyanthracenes. Using these photosensitizers, the cationic photopolymerizations of both heterocyclic and vinyl monomers were readily carried out at low light intensities.

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