

ADVANCES IN THE DESIGN OF PHOTOINITIATORS, PHOTSENSITIZERS AND MONOMERS FOR CATIONIC UV CURING

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Abstract

This paper will focus on recent developments made in this laboratory in the areas of the synthesis of novel cationic photoinitiators, photosensitizers and monomers. Dialkylphenacylsulfonium salts are excellent photoinitiators for cationic UV curing that are readily prepared in high yields by simple, straightforward reactions. Carbazole compounds are excellent and highly general photosensitizers for onium salts used in cationic UV curing. Especially, interesting and useful is the observation that polymers and copolymers of N-vinylcarbazole are excellent photosensitizers. Epoxy-functional silicone monomers and oligomers have been prepared that exhibit outstanding reactivity in cationic UV curing. These materials have been synthesized by a novel process and show much promise for use in a number of application areas.

Introduction

Interest and research activity in cationic UV curing has increased rapidly as this technology has found broad use in many industrial applications. Decorative and protective coatings, printing inks and adhesives are just a few examples of those applications in which photoinitiated cationic polymerizations have experienced the most commercial growth.¹ There are several major motivating factors driving the adoption of this technology. First, the ability to conduct these crosslinking polymerizations very rapidly, with low energy and without the use of an inert atmosphere provides important economic incentives. Second, since solvents are not employed, there are no emissions and consequently, the environmental consequences of these polymerizations are minimal. Lastly, the thermal, mechanical, chemical resistance, low shrinkage and adhesion characteristics of the network polymers that are formed are excellent. The industrial impact of cationic UV curing is predicted to increase markedly in the future as this technology undergoes further maturation.²

This paper focuses on recent developments originating from this laboratory that are directed towards advancement in the field of cationic UV curing in three key areas. The first of these areas is the development of new

photoinitiators. Until recently, two classes of onium salt photoinitiators, diaryliodonium and triarylsulfonium salts have dominated the field of cationic UV curing. While these photoinitiators display excellent photosensitivity and thermal latency, they are not easily modified to improve their solubility, toxicity or their spectral sensitivity. In addition, diaryliodonium salts are relatively expensive while the cheaper commercially available triarylsulfonium salts are impure and have variable compositions.

All cationic photoinitiators have a limited range of spectral sensitivity. The overall sensitivity of these onium salts can be markedly improved through the use of photosensitizers. This is commercially advantageous since higher throughput rates can be realized in the presence of a photosensitizer at the same light intensity than in its absence. There is, therefore, a need for the development of strongly absorbing efficient photosensitizers that are inexpensive and possess no human toxicological effects.

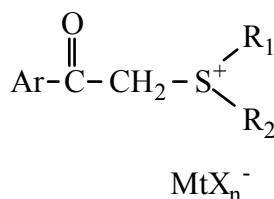
Early work in the field of cationic photopolymerization took advantage of commercially available epoxide monomers. These epoxide monomers were and still are widely employed in thermally induced condensation polymerizations together with coreactants such as amines, anhydrides and thiols for such purposes as coatings, adhesives, potting and encapsulating resins. They were not intended for use in cationic ring-opening addition polymerizations. Consequently, such monomers are not optimally designed for nor in many cases do they possess sufficient purity for this purpose. As the uses of photoinitiated cationic polymerizations in advanced applications increase, in many cases, these epoxides no longer meet the required higher performance characteristics that are demanded. For these reasons, there has been a long-standing interest in this laboratory in the design and synthesis of novel epoxide monomers expressly for use in cationic photopolymerizations.

In this paper we report recent research advances made in these three major areas of cationic UV curing in our laboratory.

Results and Discussion

Synthesis and Reactivity of Dialkylphenacylsulfonium Salt Photoinitiators

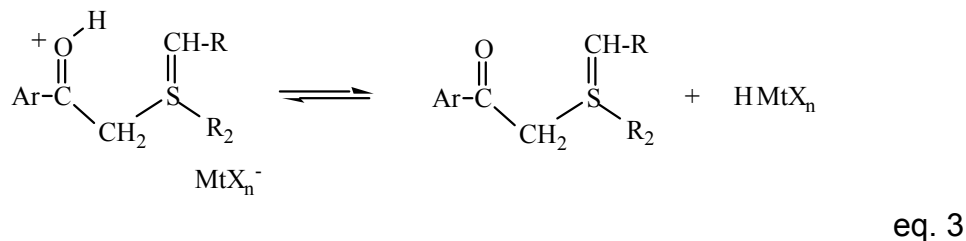
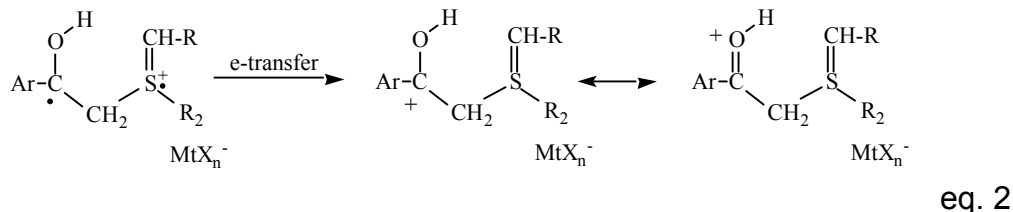
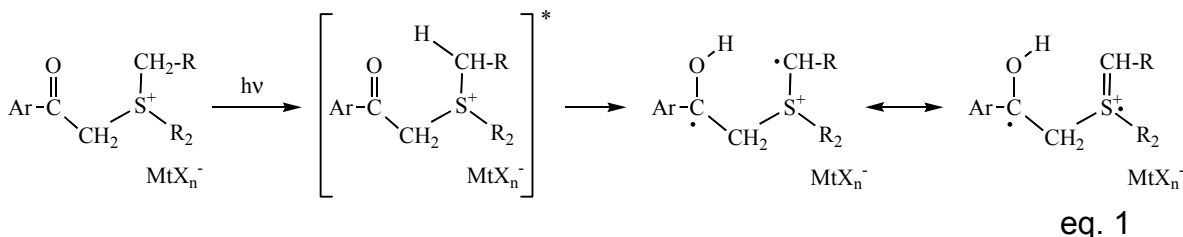
A class of interesting photoinitiators is dialkylphenacylsulfonium salts (DPS) having the general structure I shown below.^{3,4}



I

Preliminary investigations in this laboratory have shown that DPS are excellent photoinitiators for the cationic polymerization of reactive monomers such as multifunctional epoxides, oxetanes and vinyl ethers. Mechanistic studies⁵ have revealed that unlike diaryliodonium and triarylsulfonium salt photoinitiators, DPS compounds mainly undergo reversible photolysis to generate an ylide and a strong protonic acid. This mechanism, which resembles a Norrish type II process, is depicted in Scheme 1.

Scheme 1

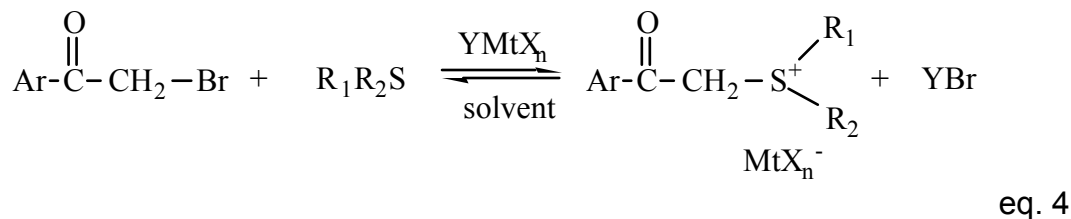


Prolonged irradiation results in fragmentation of the photoinitiator by secondary photolysis processes to give a variety of free radical derived products.^{6,7} A further useful property of these photoinitiators is their ability to undergo facile electron-transfer photosensitization with a variety of electron donor compounds.⁸ Using photosensitization, the spectral sensitivity of these photoinitiators can be readily broadened to include the long wavelength UV and visible spectral regions.

Despite the many attractive features of DPS, until now the general use of these photoinitiators has languished for several reasons. Several methods for the preparation of DPS have been reported.^{9,10} However, using the available synthetic methods, reasonable yields have been obtained of only those DPS with low solubility and high ionic character. For this reason, non-polar monomers such as epoxidized vegetable oils, vinyl, 1-propenyl or 1-butenyl ethers and epoxy-functional silicones could not be effectively polymerized using these

photoinitiators. Even in the case of polar monomers, the poor solubility of DPS photoinitiators results in partial and erratic polymerizations and, in some cases, the polymerizations fail altogether. For these reasons, compared to diaryliodonium and triarylsulfonium salts, research in DPS has been essentially inactive until recently.

A new simplified synthetic procedure for the preparation of DPS has been developed in this laboratory.¹¹ As shown in equation 4, the new synthesis involves the one-pot reaction of phenacyl bromides (2-bromoacetophenones) or their aryl (naphthyl, anthracenyl or pyrenyl) counterparts with an appropriate dialkyl sulfide in the presence of an alkali metal salt of the desired non-nucleophilic anion. Typically, this reaction is carried out in the presence of a solvent such as acetone, 2-butanone or 4-methyl-2-pentanone. Although represented as an equilibrium process, the reaction is strongly driven to the right by precipitation of the insoluble alkali metal halide, YBr. When the reaction is complete, the reaction mixture is simply filtered to remove the alkali metal halide and the desired photoinitiators isolated by removal of the solvent. Thereafter, the photoinitiators can be rigorously purified by conventional crystallization techniques.



Shown in Table 1 are the structures, yields and physical characteristics of the various DPS prepared during the course of this work. As may be noted, this synthetic method may be applied to the preparation in good yields of a wide variety of DPS including those bearing the same or different aryl groups, alkyl groups of differing chain lengths and structures and with different anions. Manipulation of the structure of these photoinitiators permits control of their melting points and solubility characteristics. Through optimization of the structure, it is possible to produce highly photosensitive photoinitiators that are both very soluble in a wide variety of polar and non-polar monomers, yet are readily purified through crystallization techniques.

DPS salts prepared by this method are stable, colorless, light-sensitive compounds. Crystalline DPS salts do not appear to undergo thermal decomposition at temperatures up to their melting points. Accordingly, these photoinitiators display excellent thermal latency in the presence of reactive monomers and oligomers. DPS salts which differ only in the length and type of alkyl groups bonded to the positively charged sulfur atom share identical UV absorption characteristics. This is indicative of the fact that the aryl ketone group in these DPS is the primary light absorbing chromophore. The major absorption

Table 1
Structures and Characteristics of Dialkylphenacylsulfonium Salts
 $C_6H_5-CO-CH_2-S^+R_1(R_2) MtX_n^-$

Note	R ₁	R ₂	MtX _n ⁻	m.p. (°C)	Yield (%)	Note	R ₁	R ₂	MtX _n ⁻	m.p. (°C)	Yield (%)
1	C ₄ H ₉	C ₄ H ₉	SbF ₆ ⁻	88-89	60	12	CH ₃	C ₁₂ H ₂₅	AsF ₆ ⁻	48-50	87
2	C ₆ H ₁₃	C ₆ H ₁₃	SbF ₆ ⁻	oil	85	13	CH ₃	C ₁₂ H ₂₅	SbF ₆ ⁻	58.5-60	50
3	C ₈ H ₁₇	C ₈ H ₁₇	SbF ₆ ⁻	oil	67	14	CH ₃	C ₁₄ H ₂₉	SbF ₆ ⁻	65-66.5	60
4	C ₁₀ H ₂₁	C ₁₀ H ₂₁	SbF ₆ ⁻	oil	53	15	CH ₃	C ₁₆ H ₃₃	SbF ₆ ⁻	74.75.5	63
5	C ₁₂ H ₂₅	C ₁₂ H ₂₅	SbF ₆ ⁻	46-47	17	16	CH ₃	C ₁₈ H ₃₇	SbF ₆ ⁻	80-82	62
6	C ₁₄ H ₂₉	C ₁₄ H ₂₉	SbF ₆ ⁻	60-61	26	17	C ₂ H ₅	C ₁₂ H ₂₅	SbF ₆ ⁻	oil	90
7	CH ₃	C ₈ H ₁₇ [*]	SbF ₆ ⁻	51-52	63	18	C ₂ H ₅	C ₁₄ H ₂₉	SbF ₆ ⁻	50-52	77
8	CH ₃	C ₈ H ₁₇	SbF ₆ ⁻	75-76	84	19	C ₂ H ₅	C ₁₆ H ₃₃	SbF ₆ ⁻	60-62	67
9	CH ₃	C ₁₀ H ₂₁	SbF ₆ ⁻	oil	53	20	C ₂ H ₅	C ₁₈ H ₃₇	SbF ₆ ⁻	70-71	70
10	CH ₃	C ₁₂ H ₂₅	B(C ₆ F ₅) ₄ ⁻	oil	66	21	C ₃ H ₇	C ₁₈ H ₃₇	SbF ₆ ⁻	72-74	67
11	CH ₃	C ₁₂ H ₂₅	PF ₆ ⁻	49-51	82	22	C ₄ H ₉	C ₁₈ H ₃₇	SbF ₆ ⁻	50-51	72

^{*}(C₈H₁₇) = -CH₂-CH(C₂H₅)C₄H₉.

maxima (in CH₃CN) of these compounds are: 206, 251 and 281 nm with molar extinction coefficients of 11,000, 12,000, and 1600, respectively. In addition, the UV spectra of these photoinitiators characteristically exhibit a low intensity tail absorption that extends out to approximately 320 nm.

A comparative study of the photoinitiated cationic polymerization of bisepoxide PC-1000 was carried out using S,S-di-n-docecyl-S-phenacylsulfonium hexafluoroantimonate (C₁₂C₁₂-DPS SbF₆⁻), S-n-decyloxyphenyl-S,S-diphenylsulfonium hexafluoroantimonate (SOC-10 SbF₆⁻) and (4-n-undecyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC-11 SbF₆⁻) as photoinitiators. The polymerizations were monitored by real-time infrared spectroscopy and the results are shown in Figure 1. Over the course of a 200 second continuous irradiation period, the differences between these three photoinitiators are rather small despite the fact that the quantum yields and absorption spectra of these three photoinitiators are different.

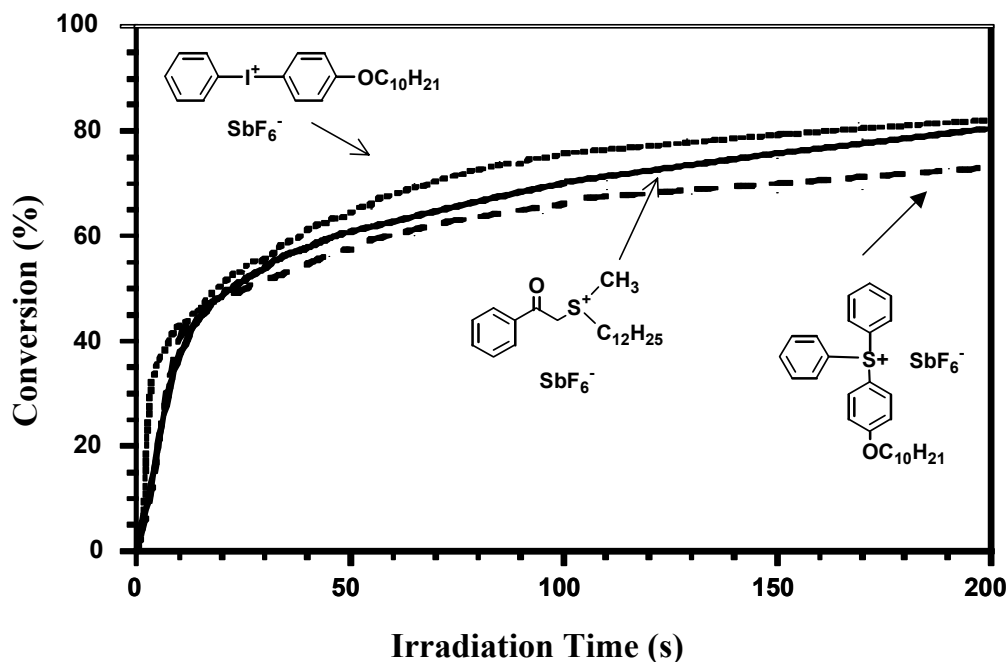
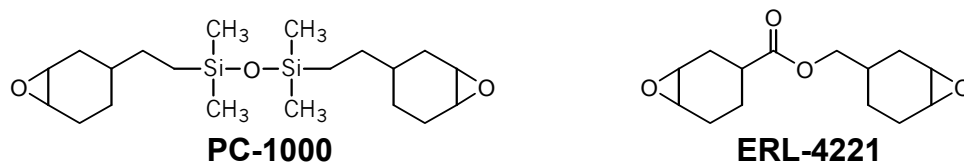


Figure 1. Comparison of the C₁₂C₁₂-DPS SbF₆⁻, SOC-10 SbF₆⁻ and IOC-11 SbF₆⁻ photoinitiated polymerizations of PC-1000. (1.0 mol % photoinitiator; light intensity 1300 mJ/cm²·min).



DPS photoinitiators can be readily structurally modified both by variation in the aryl ketone and alkyl portions of the molecule. Figure 2 shows a study of the effect of modifying the aryl ketone portion of these photoinitiators. The simple

dialkylphenacylsulfonium salt C_1C_{12} -DPS SbF_6 shows the lowest rate of polymerization of the epoxide monomer, ERL-4221. Higher rates are realized for both the photoinitiator containing the longer wavelength indanone and 4-methoxyphenacyl moieties. Examination of the UV spectra of these DPS photoinitiators shows that the observed order of reactivity correlates well with the shift of the λ_{max} of these compounds to longer wavelengths.

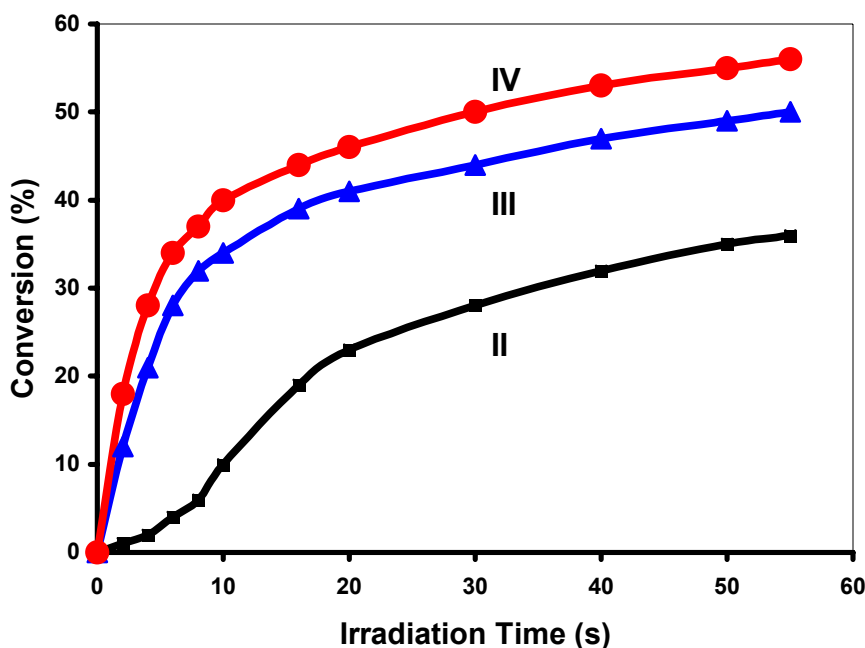
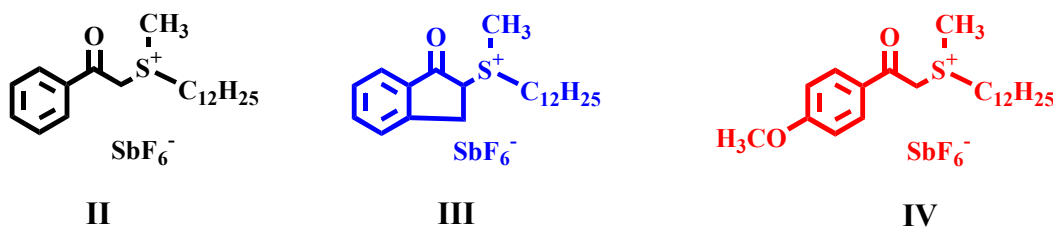


Figure 2. Comparison of the photopolymerizations of ERL-4221 in the presence of 0.5 mol% of photoinitiators II, III and IV (light intensity 1300 $mJ/cm^2 \cdot min$).

Similarly, the introduction of long alkyl groups into a DPS confers considerable nonpolar or lipophilic character. Such photoinitiators can be used to carry out the polymerization of highly nonpolar monomers. In Figure 3 is depicted the photopolymerization of 1,2-epoxytetradecane. The polymerization of this α -olefin epoxide is not easily achieved using other types of cationic photoinitiators due to their insolubility.

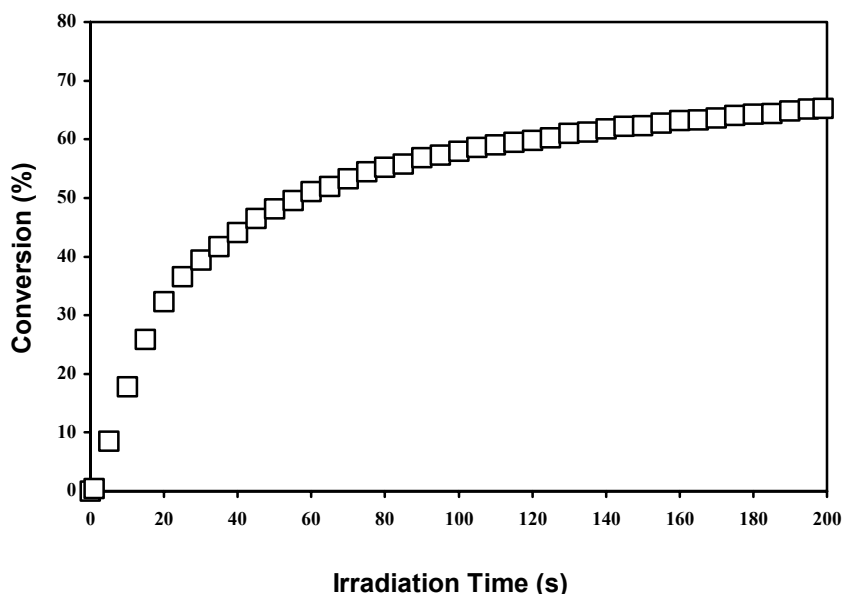


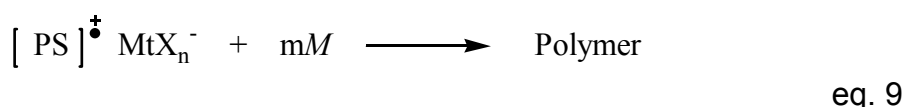
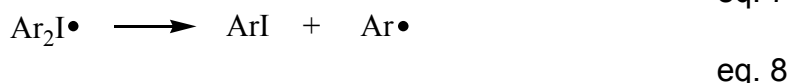
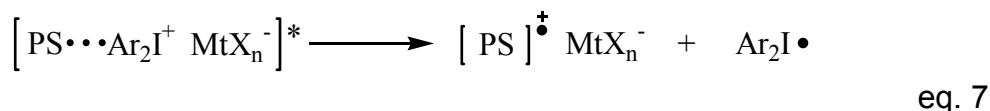
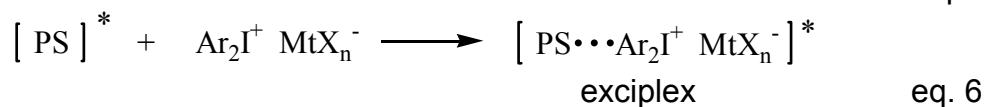
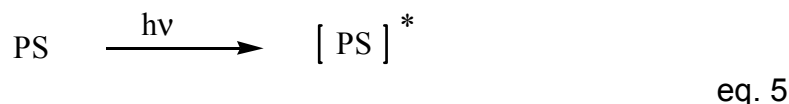
Figure 3. Photopolymerization of 1,2-epoxytetradecane using 1.0 mol% C₁₄C₁₄-DPS SbF₆ (light intensity 840 mJ/cm²·min).

Photosensitization of Cationic Photopolymerization

A particularly effective means of affecting a substantial increase in the rate of a cationic ring-opening polymerization is through the use of photosensitizers.^{12,13} Diaryliodonium, triarylsulfonium and dialkylphenacylsulfonium salt cationic photoinitiators typically possess major absorption bands in the short wavelength region (< 300 nm) of the UV spectrum. For this reason, much of the energy emitted by these light sources is not absorbed by the onium salt photoinitiator and, therefore, wasted. The use of photosensitizers can dramatically improve the speed of onium salt induced cationic photopolymerizations by broadening the range of the spectral absorption of these photoinitiators.

Particularly effective in expanding the spectral sensitivity of the photolysis of onium salts are electron-transfer photosensitizers. Shown in Scheme 2 is a generalized mechanism for the electron-transfer photosensitization of diaryliodonium salts.

Scheme 2.



Analogous mechanisms can be written for the photosensitization of triarylsulfonium and dialkylphenacylsulfonium salts. Electron-transfer photosensitization involves first, the absorption of light by the photosensitizer to give the corresponding excited species $[\text{PS}]^*$ (eq. 5). An excited state complex (exciplex) is often formed as an intermediate between the onium salt and the excited photosensitizer (eq. 6). Subsequently, the onium salt is reduced by a formal electron-transfer between the two reaction partners (eq. 7). The rapid decomposition of the resulting unstable diaryliodonium free radical (eq. 8) prevents back electron-transfer and renders the overall process irreversible. Cationic polymerization (eq. 9) takes place by direct interaction of the monomer with the photosensitizer cation-radical $[\text{PS}]^{\dagger} \text{MtX}_n^-$ or by first, radical dimerization of the initially formed photosensitizer cation-radical and then polymerization by the resulting dication.

Recently, Chen, et al.¹⁰ and ourselves^{14,15} have described studies of the photosensitized photolysis of onium salts by various monomeric and polymeric compounds containing the carbazole nucleus. For example, Figure 4 shows the polymerization of limonene dioxide in the presence of 9-ethylcarbazole and 9-phenylcarbazole. A curve for the photopolymerization conducted in the absence of a photosensitizer is also included in this figure for comparison.

While carbazole compounds are highly effective in accelerating the cationic photopolymerization of epoxides, these compounds display some undesirable effects such as skin irritation. In Figure 5 is shown one means of circumventing this problem. Poly(N-vinylcarbazole) displays excellent photosensitizing activity for the cationic photopolymerization of cyclohexene oxide.¹⁶ As shown in Figure 5, the activity of the polymeric carbazole on the basis of total amounts of carbazole groups is the same as observed for its lower molar mass analogue, 9-ethylcarbazole.

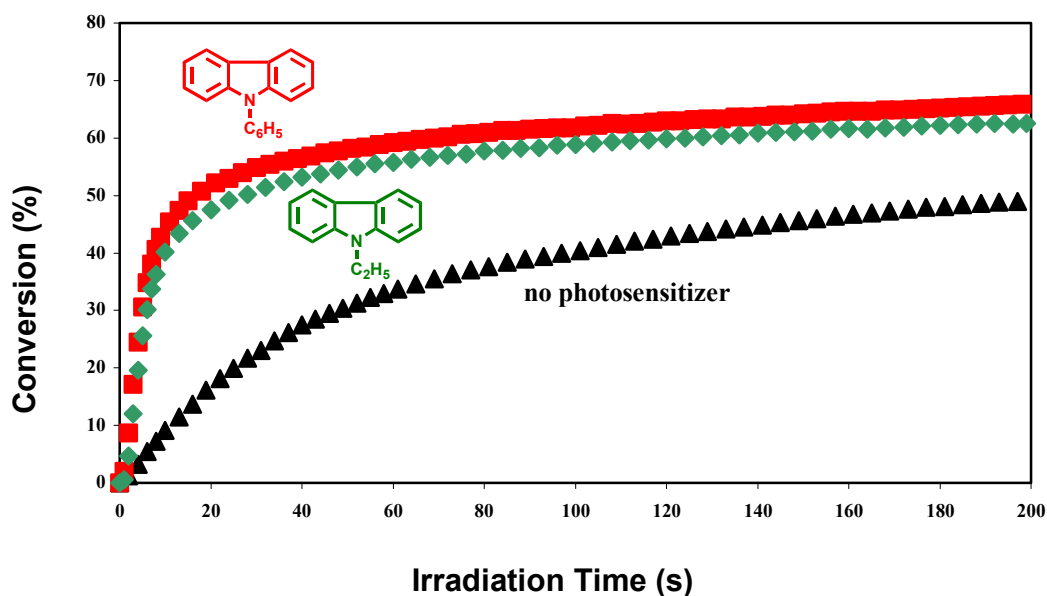


Figure 4. Photopolymerization of limonene dioxide using 0.5% C₁C₁₂-DPS SbF₆ using 0.2% carbazole photosensitizers (light intensity 256 mJ/cm² min).

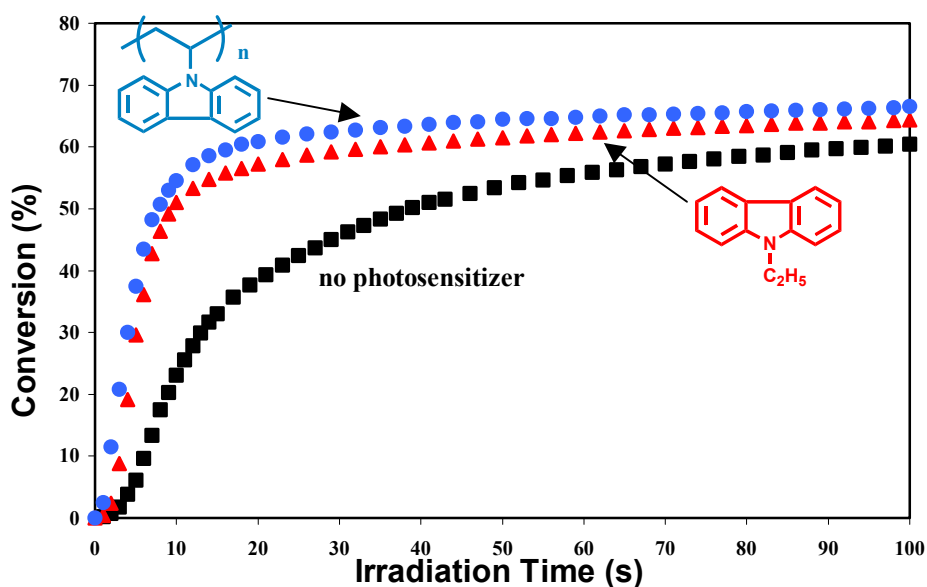


Figure 5. FT-RTIR study of the photopolymerization of cyclohexene oxide in the presence of 0.5 % IOC10 alone (■) and using 0.2% PVK (●) and 0.2% NEK (▲). (light intensity 103 mJ/cm² min)

In Figure 6 is depicted another approach to the photosensitization of ring-opening polymerizations. Shown in this figure is the cationic photopolymerizations of cyclohexene oxide in the presence of a small amount of a carbazole monomer bearing a polymerizable epoxy group. During polymerization this monomeric photosensitizer becomes bonded into the matrix of the polymer that is formed. Thus, this interesting monomer photosensitizes the photopolymerization before, during and after its polymerization. Alternatively as shown in Figure 6, the epoxy-carbazole monomer can be first independently polymerized and the resulting polyether bearing pendant carbazole groups used to photosensitize the photopolymerization of cyclohexene oxide. It is noteworthy, that both approaches are approximately equally effective.

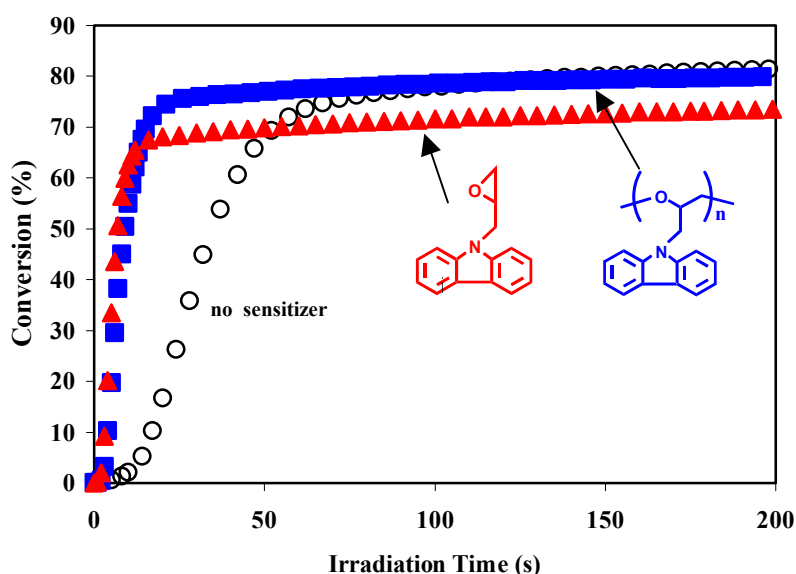
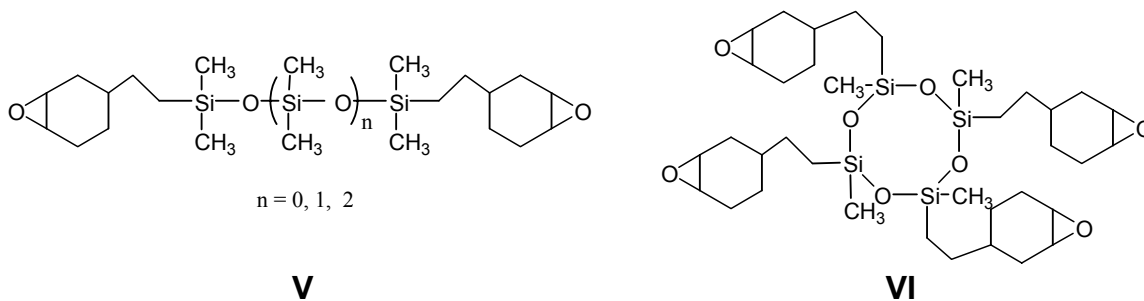


Figure 6. Comparison of the polymerization of cyclohexene oxide in the presence of 1.0% 9-(2,3-epoxypropyl)carbazole (▲) and poly[9-(2,3-epoxypropyl)carbazole] (■). Polymerization in the absence of a photosensitizer (*). (light intensity 200 mJ/cm² min; 1.0 % IOC10)

Synthesis of Novel Epoxy Monomers

As pointed out in the at the outset of this article, there is a dearth of epoxy monomers that possess both high reactivity and high chemical and mechanical performance characteristics available for use in photoinitiated cationic polymerization. As a result, it has been an objective of the ongoing work in this laboratory to prepare such monomers. One class of monomers that fills the above stated requirements are epoxy functional siloxanes. Over the course of several years,^{17,18} we have prepared monomers as such **V** and **VI** shown below

that display outstanding reactivity in photoinduced cationic ring-opening polymerization.



These monomers can be prepared by the straightforward hydrosilylation of α,ω -Si-H polydimethylsiloxanes such as 1,1,3,3-tetramethyldisiloxane and 1,3,5,7-tetramethylcyclotetrasiloxane with 4-vinyl cyclohexene oxide (eq. 10).

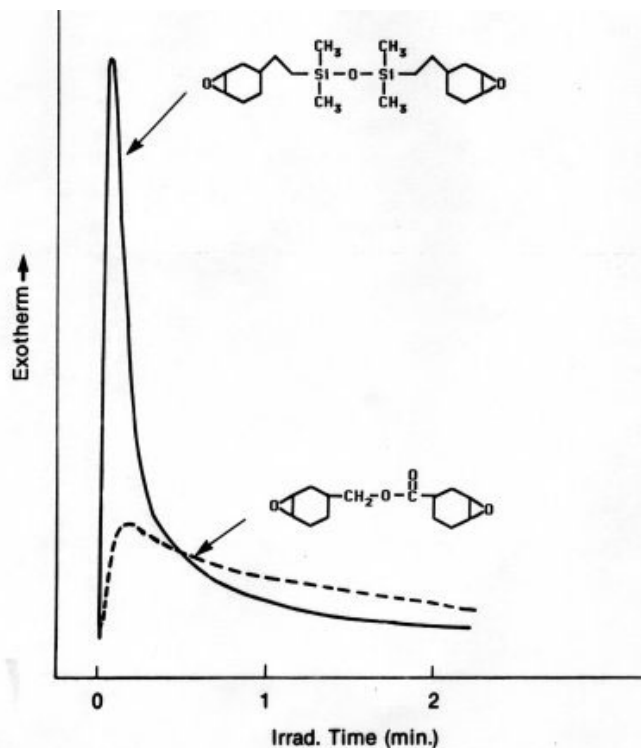
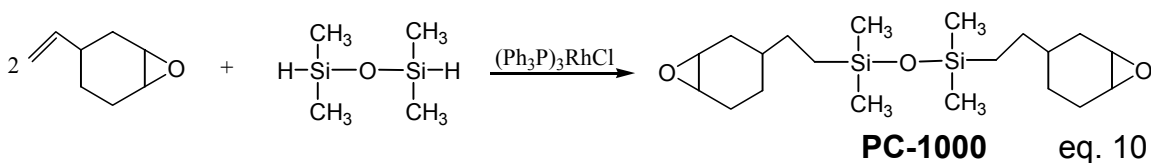
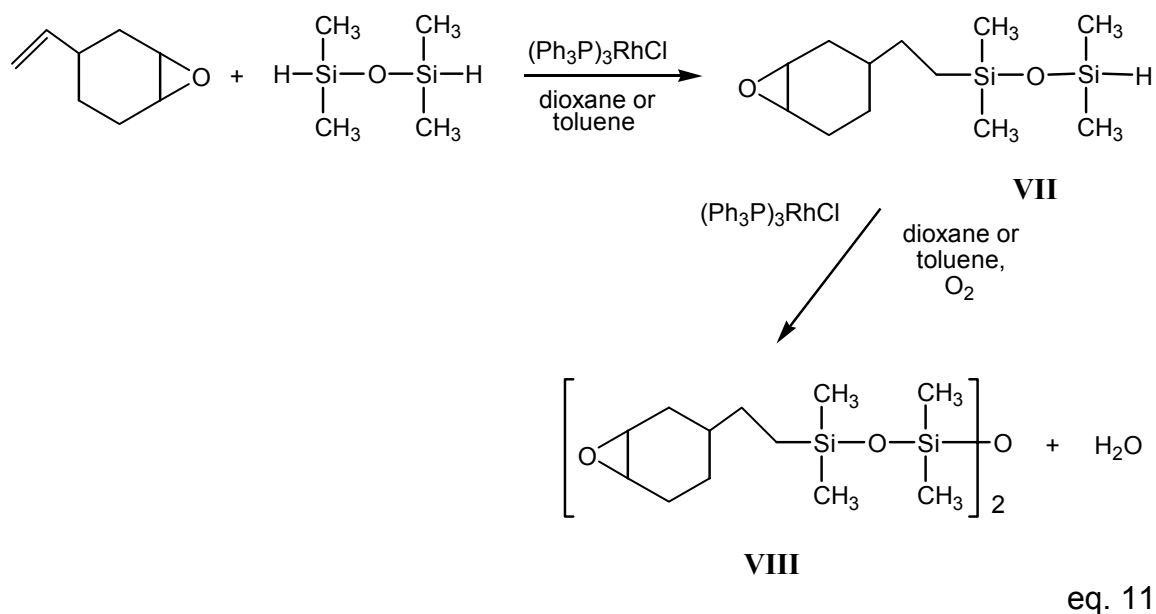


Figure 7. Comparative DSP study of the photopolymerizations of PC-1000 and ERL-4221 using 1.0 % (4-n-octyloxyphenyl)phenyliodonium hexafluoroantimonate.

Figure 7 shows a comparison of the cationic ring-opening polymerizations of two bicycloaliphatic epoxy monomers; the epoxy silicon PC-1000 and ERL-4221 using differential scanning calorimetry (DSC). The much higher reactivity of PC-1000 is clearly evident from the sharper reaction exotherm produced with this monomer. **VI** and other related monomers bearing the epoxy-silicone structure display similar high rates of UV cure.

Recently, we have shown that it is possible to modify the synthesis shown in equation 10 to prepare other interesting epoxy-silicone monomers.¹⁹ The synthesis of **VII** can be carried out in >98% yield by a controlled hydrosilylation reaction. Further, when **VII** is subjected to treatment with oxygen (air), coupling occurs to give high yields of difunctional epoxy monomer **VIII** with a long siloxane spacer.



Using this two-step, one-pot reaction a series of interesting and novel epoxy siloxane monomers can be prepared. Depicted in Figure 8 is the cationic photopolymerization of several monomers prepared using the above route. All the monomers display high reactivity, but the monomer with the highest epoxy content or the shortest siloxane spacer between the epoxy groups exhibits the highest reactivity. These studies demonstrate that it is possible to purposefully design and prepare monomers with high rates of photocure using simple reaction chemistry.

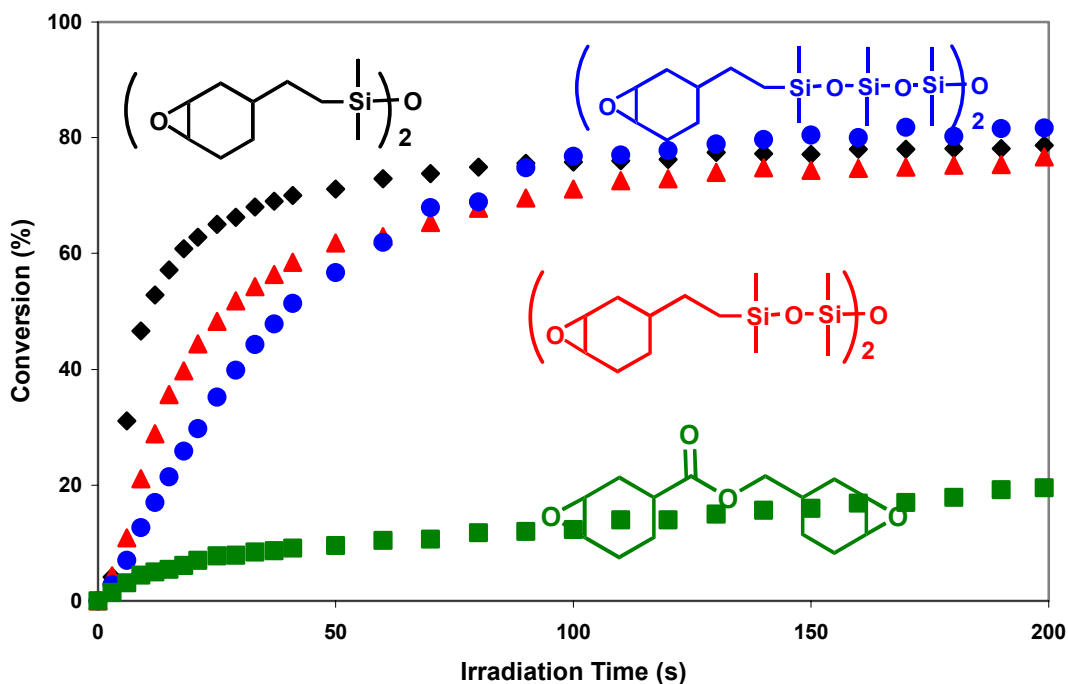


Figure 8. RTIR study of the photoinitiated cationic ring-opening polymerizations of four diepoxides using 1.0 mol% IOC10 as the photoinitiator. (light intensity 410 mJ/cm² min).

Conclusions

Cationic UV curing is still in its initial development stages. This article has focused on recent results from this laboratory in three key areas of this technology. Novel photoinitiators continue to be developed that provide many advantages in terms of their activity, spectral absorption and solubility characteristics. The photosensitivity and spectral response of these systems can be adjusted through the synthesis of novel low molar mass and polymeric photosensitizers. Lastly, the rational design of novel high reactivity epoxy monomers has been demonstrated.

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