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Photoinduced and Thermally Induced Cationic Polymerizations Using Dialkylphenacylsulfonium Salts

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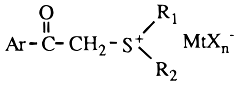
ABSTRACT: A study of the photoinitiated and thermally initiated cationic polymerizations of several monomer systems using dialkylphenacylsulfonium salt (DPS) photoinitiators bearing different alkyl chains and anions has been conducted. DPS compounds are capable of photoinitiating the cationic polymerization of a wide variety of epoxy and vinyl ether monomers directly on irradiation with UV light or by using visible light irradiation in the presence of photosensitizers. Kinetic studies show that DPS photoinitiators compare favorably with respect to their reactivity to diaryliodonium and triarylsulfonium salt photoinitiators in the polymerization of epoxides. The photopolymerizations of vinyl and 1-propenyl ethers display a marked induction period consistent with termination of the growing chains by reaction with the photogenerated ylides. Preliminary studies have demonstrated that DPS can also be employed as thermal initiators for the cationic ring-opening polymerization of epoxides at moderate temperatures.

Introduction

Dialkylphenacylsulfonium salts (DPS) are highly attractive photoinitiators for cationic polymerization.[1−3] These compounds are prepared from readily available and inexpensive starting materials by a straightforward synthetic method. As photoinitiators, these compounds are advantageous since they are thermally stable at room temperature yet are highly photosensitive. DPS possess absorption maxima in the mid region of the UV spectrum. However, the spectral sensitivity of these photoinitiators can be readily modified and broadened to include the long wavelength UV and visible wavelength regions through the use of electron-transfer photosensitizers.[4] Despite the above-enumerated advantages, these photoinitiators have seen little use in practical applications. This is because DPS photoinitiators thus far available by conventional routes have displayed very poor solubility in most cationically polymerizable monomers and especially those of commercial interest.

In a companion paper,[5] we have described the recent development of a new generally applicable synthetic method which makes possible the facile preparation of a novel series of second-generation DPS with the general structure shown below.



$\mathrm{Ar-\overset{O}{\overset{\|}{C}}-CH_2-\overset{+}{S}\begin{smallmatrix}R_1\\ R_2\end{smallmatrix}\ MtX_n^-}$

This new synthetic method makes it possible to prepare soluble, crystalline DPS photoinitiators in high yields which may be exhaustively purified by conventional methods. The solubility of these photoinitiators may be readily tailored to a specific monomer system through the modification of alkyl groups (R_1, R_2). Further, the spectral sensitivity of these photoinitiators can be adjusted through the use of various aryl ketone chromophors or by electron-transfer photosensitization.

The present paper describes the evaluation of a number of novel, second-generation DPS photoinitiators in the polymerizations of several different monomer systems. In addition, direct comparisons with previously prepared DPS photoinitiators and with other types of cationic photoinitiators are also presented.

Experimental Section

Materials. 3,4-Epoxycyclohexylmethyl 3′,4′-epoxycyclohexanecarboxylate (ERL 4221E) was used as obtained from the Union Carbide Corp. 1,3-Di(3,4-epoxycyclohexylethyl)-1,1,3,3-tetramethyldisiloxane (PC-1000), was a gift from the Polyset Co., Mechanicville, NY. 3,6,9,12-Tetraoxatetradeca-1,13-diene (RapiCure DVE−3) was provided by International Specialty Products, Wayne, NJ. General Electric Silicones contributed UV9315 epoxy silicone oligomer as a gift. 9-(2-Hydroxyethyloxy)-11-oxatetracyclo $[6.2.1.0^{2,7}0.^{4,6}]$ undecane) used for the synthesis of monomer **VIII,** epoxidized linseed oil (Vikoflex 7190). and epoxidized poly(1,4-butadiene) (Ricon 130) were gifts from the Elf-Atochem Co., Blooming Prairie, MN. Epoxidized soybean oil (Kronox-S) was obtained from the FMC Corp., New York, NY.

The syntheses of the DPS photoinitiators used in this article are described in a companion paper.[5] The photoinitiators, (4-(*n*-decyloxy)phenyl)phenyliodonium hexafluoroantimonate (IOC-10(SbF_6)), (4-(*n*-undecyloxy)phenyl)phenyliodonium hexafluoroantimonate (IOC-11(SbF_6)) and (4-(*n*-octyloxy)phenyl)diphenylsulfonium hexafluoroantimonate (SOC-8(SbF_6)) were prepared as described previously.[6,7] $(4\text{-}i\text{-}C_3H_7{-}C_6H_4)I^+(4\text{-}CH_3{-}C_6H_4)B(C_6F_5)_4^-$ (Rhodosil 2074) was obtained from the Rhone-Poulenc Company, Lyon, France. 2,2-Dimethoxy-2-phenylacetophenone (Esacure KB-1) was obtained as a gift from the Sartomer Corp., Exton, PA.

Synthesis of 9-(2-Ethoxyethyloxy)-11-oxatetracyclo-$[6.2.1.0^{2,7}0.^{4,6}]$undecane) (VIII). To a solution of 9-(2-hydroxyethyloxy)-11-oxatetracyclo$[6.2.1.0^{2,7}0.^{4,6}]$undecane, 10.5 g, 0.05 mol), iodoethane (15.6 g, 0.10 mol), and sodium hydroxide (4.0 g, 0.10 mol) in 15 mL of toluene was added tetra-*n*-butylammonium bromide (0.16 g, 0.5 mmol). The reaction mixture was stirred at 70 °C overnight and filtered. The organic solution was then washed with water, dried over sodium sulfate, and filtered. After solvent removal under reduced pressure, the crude product was distilled at 120−125 °C/0.05 mmHg to give 8.9 g (74% yield) of 9-(2-ethoxyethyloxy)-11-oxatetracyclo$[6.2.1.0^{2,7}0.^{4,6}]$undecane (**VIII**) as a colorless oil.

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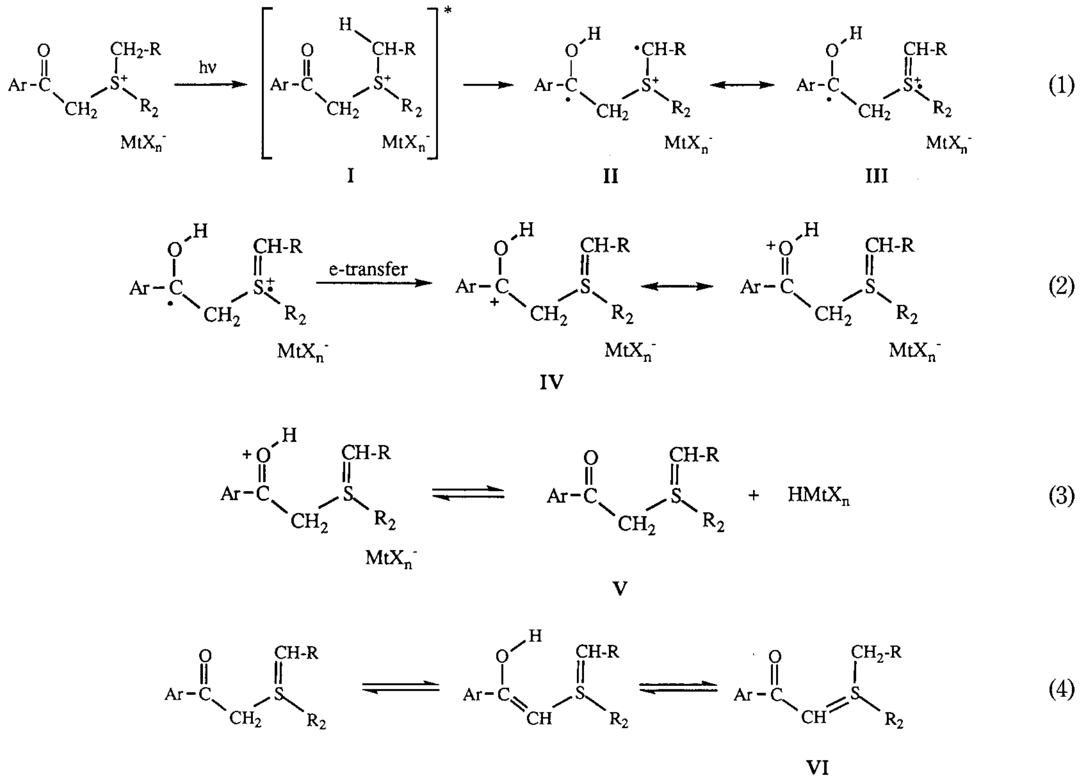
Scheme 1



^{1}H NMR (300 MHz, CDCl$_3$) (ppm): 3.70−3.20 (m, 13H, epoxy−CH, CH$_2$−O and CH−O), 2.60−1.30 (m, 6H, CH$_2$ and CH on dicyclopentadiene skeleton), 1.30−1.10 (m, 3H, CH$_3$).

Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.68; H, 9.28.

Photopolymerization Studies Using Real-Time Infrared Spectroscopy (RTIR). A Midac M-1300 FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT detector was used. The instrument was fitted with a UVEXS model SCU-110 mercury arc lamp equipped with a flexible liquid optic wand. The end of this wand was placed at a distance of 5 cm and directed at an incident angle of 45° onto the sample window. UV light intensities were measured with the aid of a International Light Co. Control-Cure radiometer at the sample window. The light intensity used for each polymerization reaction is noted in the figure caption.

Photopolymerizations were carried out at room temperature in bulk monomers containing 1 mol % of the designated DPS photoinitiator. The monomer/photoinitiator solutions were coated onto a 12 μm oriented and corona-treated polypropylene film, covered with an identical polypropylene film, and then mounted in a 5 cm × 5 cm slide frame. Infrared spectra were collected at a rate of 1−2 spectra per second using LabCalc data acquisition software obtained from the Galactic Corp. and were processed using GRAMS-386 software from the same company. During irradiation, the decrease of the absorbance due to the vinyl ether double bonds centered at 1620 cm^{-1} and the absorbances due to the epoxy groups centered at 838 cm^{-1} (**VIII**) and 885 cm^{-1} (**VII**) of the two monomers were monitored. In all cases, experiments were performed in triplicate to verify reproducibility. Data reduction and subsequent conversion vs time plots were obtained using KaleidaGraph (Synergy Software) software.

Photopolymerization Studies Using Differential Scanning Photocalorimetry (DSP aka Photo-DSC). The photoinitiated polymerization of selected monomers were carried out using a Perkin-Elmer DSC-7 differential scanning calorimeter equipped with a DPA-7 photocalorimeter module fitted with a 200-W high-pressure Hg arc lamp. Polymerizations were conducted isothermally in static air at 30 °C on samples of the monomer containing 0.5−1.0 mol % of the desired photoinitiator. For direct comparison purposes, all the samples had nearly identical (~20 mg) sample weights. Broad-band, unfiltered UV light was used in all cases. Samples were allowed to equilibrate for 30 s and then the shutter opened to start the polymerization and irradiation continued until the termination of the experiment. The heat flow data collected were normalized with respect to the sample mass and then the curves integrated using a baseline correction. Conversion vs time plots were drawn assuming an enthalpy of polymerization of 96.7 kJ/mol based upon recent literature values for the ring-opening polymerization of epoxycyclohexane.[8]

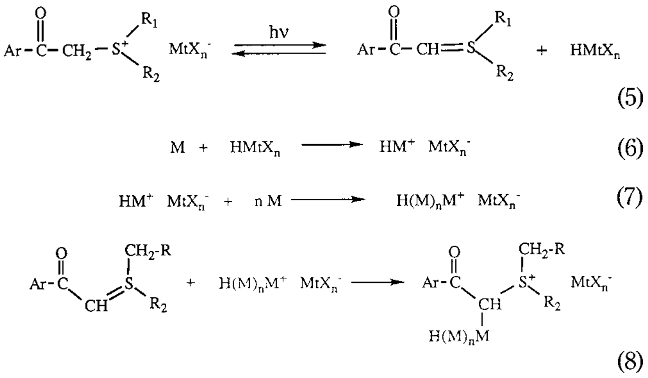
Thermally Initiated Cationic Polymerizations. Studies of thermally initiated cationic polymerizations were carried out using a Perkin-Elmer DSC-7 differential scanning calorimeter. Samples (10 mg) containing 1 mol % of the DPS dissolved in the appropriate monomer were heated in the calorimeter from 30 to 200 °C in static air at a rate of 10 °C/min. Isothermal studies were conducted by placing the sample in the DSC preheated to 70 °C and then heating at a rate of 500 °C/min to the desired set temperature. The sample was held at the set temperature for 20 min and then cooled to room temperature. Conversions were calculated from the integrated areas of the exothermic curves assuming a value of 96.7 kJ/mol for the enthalpy of the ring-opening epoxide polymerization.

Discussion of Results

General Considerations. The mechanism by which DPS photoinitiators undergo photolysis is markedly different than that of diaryliodonium and triarysulfonium salt photoinitiators. Whereas the two latter photoinitiator types undergo an irreversible photolysis leading to complete fragmentation of the photoinitiator, the photolysis of DPS compounds proceeds by a reversible process which is outlined in Scheme 1.

Details of the experiments carried out to elucidate this mechanism were published previously.[1,2,3] Briefly, the mechanism proceeds by a Norish type II process (eq 1) involving excitation of the aryl ketone chromophor. This is followed by the triplet carbonyl abstraction of hydrogen atoms attached to one of the carbons adjacent to

Scheme 2

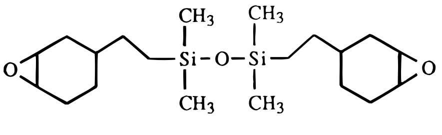


the positively charged sulfur atom via a six-membered ring transition state, **I**. The resulting diradical, **II**, is in resonance equilibrium with the sulfur cation-radical species, **III**. Internal electron transfer (eq 2) takes place within the molecule leading to the protonated species, **IV**. Deprotonation gives the corresponding sulfur ylide, **V**, and a protonic acid (eq 3). Prototropic shift (eq 4) converts the initially formed ylide, **V**, to the more stable ylide, **VI**. It is important to note that in the presence of the protonic acid, the ylides may undergo a spontaneous back-reaction to afford the starting DPS (eq 3).

The mechanism shown above implies that when irradiation ceases, the Brønsted acid generated by photolysis is rapidly scavenged by the ylide to regenerate the DPS. Thus, when DPS salts were photolyzed in inert solvents, no change could be detected by ^{1}H NMR. However, when reactive deuterated solvents (e.g., DMSO-d_6) were employed, the replacement of the protons with deuterium at the all carbon atoms adjacent to the positively charged sulfur atom during photolysis could be observed using ^{1}H NMR spectroscopy. Using this indirect method, we obtained an estimated quantum yield of 0.43 for these compounds.[3]

Cationic polymerization as shown in Scheme 2 takes place during irradiation of DPS (eq 5) by protonation of a suitable monomer (eq 6) followed by the sequential addition of additional monomer units (eq 7). It should also be noted that termination can occur (eq 8) by reaction of the growing chain with the ylide.

DPS photoinitiators are shelf-stable in the presence of even highly reactive monomers and oligomers, and long pot-lives are observed provided that the solutions are stored in the dark. For example, a 3% solution of a DPS(SbF$_6$) photoinitiator dissolved in the highly reactive biscycloaliphatic epoxy monomer **VII** showed no tendency toward spontaneous polymerization even after 3 months storage in the dark at room temperature.



VII

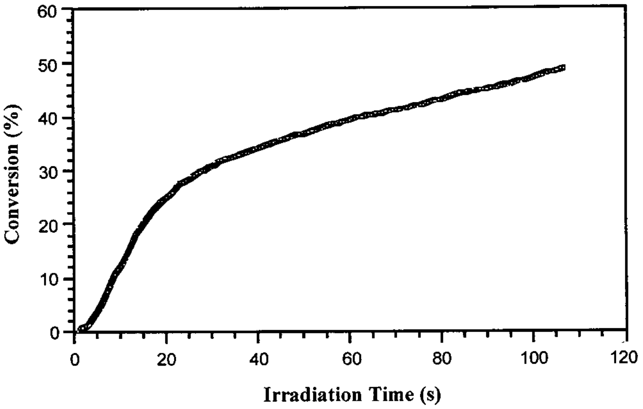
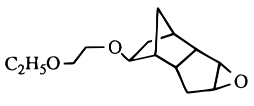


Figure 1. RTIR average curve for the photopolymerizations of monomer **VII** using 1.0 mol % of photoinitiators: $\mathrm{C_1C_{18}{-}DPS(SbF_6)}$; $\mathrm{C_2C_{18}{-}DPS(SbF_6)}$; $\mathrm{C_4C_{18}{-}DPS(SbF_6)}$; $\mathrm{C_{14}C_{14}{-}DPS(SbF_6)}$ (light intensity: 960 mJ/cm^2·min).

Effect of DPS Structure on Photoinitiated Cationic Polymerizations. Although the DPS compounds described in this investigation display excellent latency when stored in the dark even in the presence of highly reactive monomers, they are highly efficient photoinitiators for the cationic polymerization of a wide variety of mono- and multifunctional vinyl and heterocyclic monomers. Pioneering work by Decker and co-workers[9,10] and also investigations carried out in this laboratory[11] have demonstrated the utility of real-time infrared spectroscopy (RTIR) for following the course of very rapid free radical and cationic photopolymerizations. RTIR was also employed in the present investigation to characterize the reactivity of various DPS photoinitiators in the polymerization of several typical monomers. For simplicity, we have chosen to represent DPS photoinitiators in the shorthand form $\mathrm{C}_a\mathrm{C}_b$–DPS(MtX$_n$), where a and b represent the number of carbon atoms in each alkyl group and MtX$_n$ represents the anion. Thus, $\mathrm{C_1C_{12}{-}DPS(SbF_6)}$ is *S*-*n*-dodecyl *S*-methyl phenacylsulfonium hexafluoroantimonate.

When a homologous series of $\mathrm{C_1C}_b$–DPS(SbF$_6$) photoinitiators (b = 8–18) were compared in the photopolymerization of monomer **VII**, identical kinetic curves were obtained using the RTIR technique. This suggests that the photosensitivity of the corresponding DPS salts are identical and independent of the chain length of the alkyl group. Given in Figure 1 is a conversion vs time plot that represents an average of the data taken from the individual kinetic curves for a series of four related DPS photoinitiators in which the lengths of both alkyl groups are varied. It is interesting to note that the response of these four photoinitiators is the same despite the fact that when the methyl group (R$_1$) is replaced with a longer alkyl group, the number of abstractable hydrogens at that carbon atom decreases from three to two. In these two studies we have employed the highly reactive difunctional epoxy monomer **VII** and monitored its epoxide band at 885 cm^{-1}. Although simple variation in the alkyl chain lengths does not affect the rate of the polymerization of **VII**, the melting points and solubility characteristics of the DPS are greatly influenced by the modifications of these groups as noted previously.[5]

A comparison of the photoinitiated epoxide ring-opening polymerization of monomer **VIII** using $\mathrm{C_1C_{12}}$–



VIII

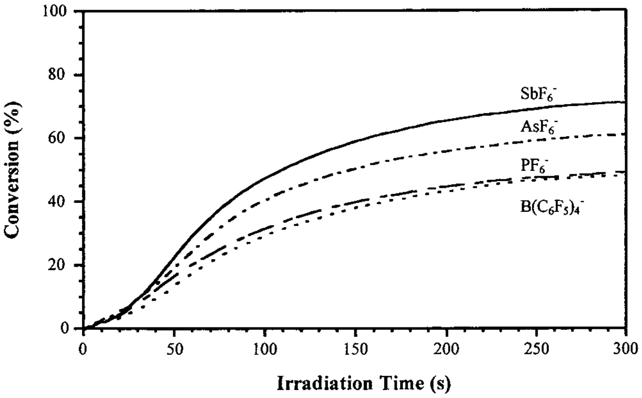


Figure 2. RTIR study of the photopolymerization of monomer **VIII** using 1.0 mol % C_1C_{12}–$DPS^+MtX_n^-$ salts: SbF_6^-, (—); AsF_6^-, (- — -); PF_6^-, (– —); $B(C_6F_5)_4^-$, (- - -) (light intensity 1350 mJ/cm²·min).

DPS(MtX_n) photoinitiators bearing four different anions is shown in Figure 2. Dicyclopentadiene epoxide monomer **VIII** was selected for this study because all of the DPS salts are readily soluble in this monomer and because the epoxide band at 838 cm^{-1} is sharp and easy to monitor by RTIR. In addition, the polymerization of this monomer takes place at a sufficiently slow rate which allows for ready comparison of the effects of the various anions. The synthesis of this monomer is described in the experimental portion of this paper. In the polymerization of monomer **VIII**, the order of increasing reactivity of the C_1C_{12}–$DPS^+(MtX_n)$ photoinitiators is as follows: $B(C_6F_5)_4^-$, PF_6^-, AsF_6^-, and SbF_6^-. Since the same sulfonium cation was employed in all cases, the quantum yields of photolysis of these photoinitiators can also be assumed to be the same. The observed order of reactivity can be ascribed to the degree of association within the propagating cation–anion ion pair during the ring-opening polymerization which is determined by the nucleophilicity of the respective anions.

Comparison with Diaryliodonium and Triarylsulfonium Salt Photoinitiators. It has already been mentioned that the mechanism of the photolysis of DPS salts involves the reversible formation of an ylide (Scheme 1) while diaryliodonium salts and triarylsulfonium salts undergo photolysis by an irreversible photofragmentation process. Consideration of the mechanism shown in Scheme 1 leads to two conclusions. First, there will always be a competition between the monomer and the ylide for the initially formed Brønsted acid as well as for the growing cationic chain end. Effective polymerization will take place in those instances where the protonation of monomer is favored by its greater concentration, basicity and nucleophilicity or due to thermodynamic factors such as the relief of ring strain. Second, in all cases, the polymerizations initiated by these photoinitiators would be expected to self-terminate by addition of an ylide to the growing chain end as shown in eq 8.

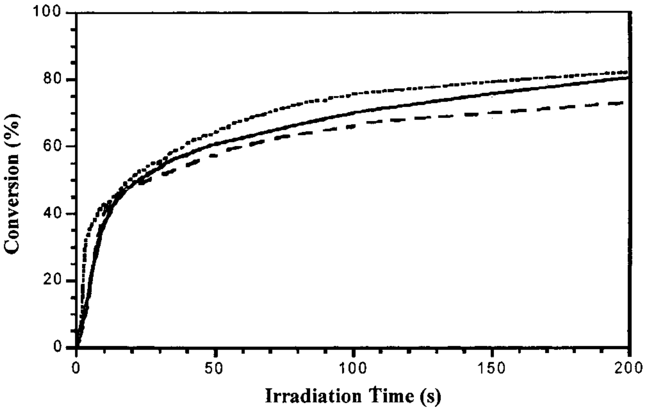


Figure 3. Comparison of the photopolymerizations of **VII** in the presence of 1.0 mol % of C_1C_{12}–DPS(SbF_6) (—), IOC-10-(SbF_6) (···), and SOC-8(SbF_6) (- - -) (light intensity 1380 mJ/cm²·min).

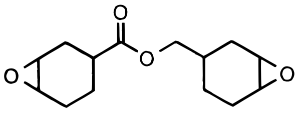
Table 1. UV Absorption Characteristics of Cationic Photoinitiators

photoinitiator	solvent	λ_{max} (ϵ), nm
$PhCOCH_2S^+CH_3(C_{12}H_{25})SbF_6^-$	CH_3CN	251 (12000) 281 (1630)
$4(n\text{-}C_{10}H_{21}O-C_6H_4)(C_6H_5)I^+SbF_6^-$	CH_3OH	247 (15000)
$4(n\text{-}C_8H_{17}O-C_6H_4)(C_6H_5)_2S^+SbF_6^-$	CH_3OH	262 (18200)

An RTIR comparison of the photopolymerizations of monomer **VII** in the presence of 1 mol % of C_1C_{12}–DPS-(SbF_6), IOC-10(SbF_6), and SOC-8(SbF_6) is shown in Figure 3. It should be noted that, in this case, the quantum yields and absorption spectra of these three photoinitiators are different. Therefore, Figure 3 provides a comparison between these three photoinitiators under identical UV irradiation conditions. Table 1 gives a comparison of the UV absorption spectra for all three photoinitiators.

It is interesting to observe that over the course of a 200 s continuous irradiation period, the differences between these three photoinitiators are rather small. However, a close examination of the first 10 s of the photolysis shows that the initial polymerization rate using the diaryliodonium salt is considerably higher than observed for the other two photoinitiators. The polymerization rates for the two sulfonium salts are comparable.

Using differential scanning photocalorimetry (DSP), a DPS salt (C_4C_4–DPS(SbF_6)) was compared with IOC-10(SbF_6) in the polymerization of biscycloaliphatic monomer **IX** (3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexanecarboxylate). **IX** is a commercially available monomer which is employed in many applications using photoinitiated cationic polymerization. The curves shown in Figure 4 indicate that polymerizations using these two photoinitiators proceed at very similar rates and to nearly the same extents of reaction. A slightly slower polymerization rate was observed for the DPS photoinitiator.



IX

The photoinitiated cationic polymerization of 3,6,9,-12-tetraoxatetradeca-1,13-diene (triethylene glycol divinyl ether) was carried out using $C_{12}C_{12}$–DPS(SbF_6) and IOC-11(SbF_6) as photoinitiators, and the results are compared in Figure 5. There are marked differences between these two polymerizations. Using the iodonium salt photoinitiator, the polymerization takes place without an induction period and reaches high conversion. In contrast, the polymerization using the DPS photoinitiator displays a marked induction period followed

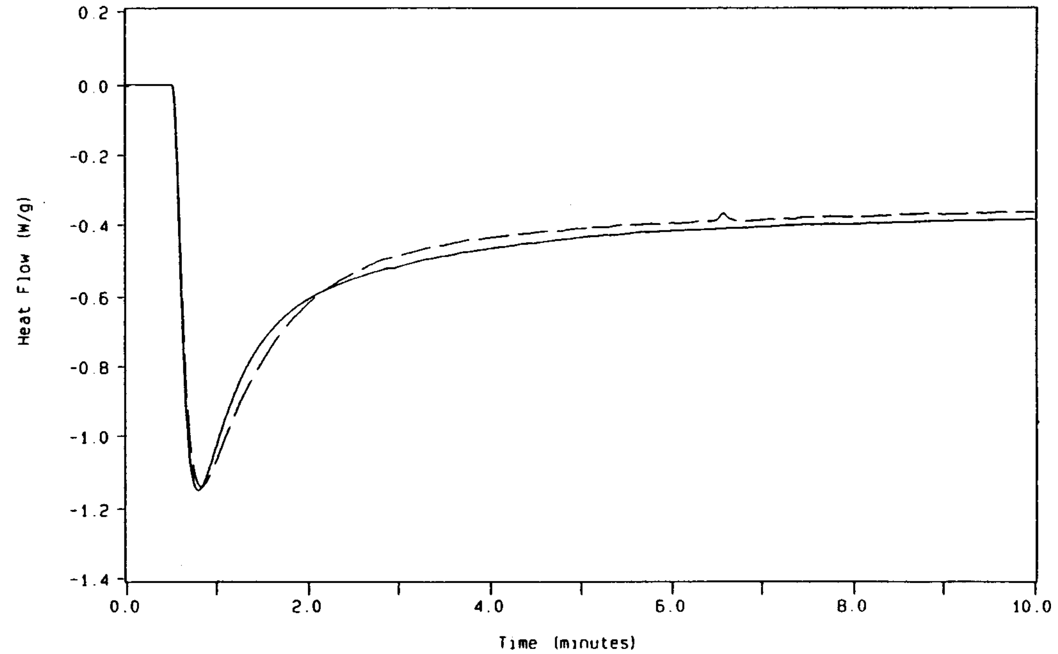


Figure 4. DSP comparison of the photopolymerizations of **IX** in the presence of 0.5 mol % of C_4C_4−DPS(SbF_6) (- - -) and IOC-10(SbF_6) (—) (light intensity 650 mJ/cm^2•min).

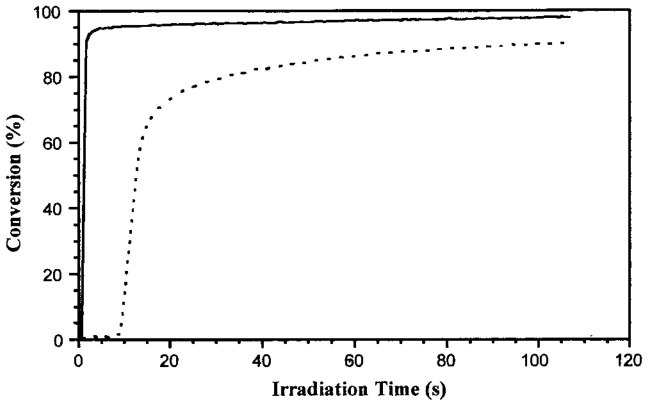
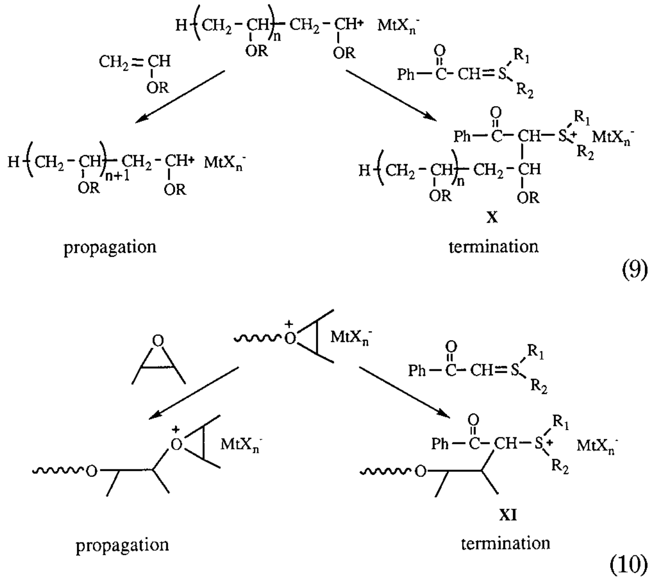


Figure 5. Comparison of the $C_{12}C_{12}$−DPS(SbF_6) (- - -) and IOC-11(SbF_6) (—) photoinitiated polymerizations of 3,6,9,12-tetraoxatetradeca-1,13-diene (0.5 mol % photoinitiator; light intensity 720 mJ/cm^2•min).

Scheme 3



by rapid conversion of the monomer to polymer. Analogous results were observed when octyl 1-propenyl ether was used as the monomer. An explanation for the behaviors of the two respective photoinitiators derives from the basic difference in their mechanisms of photolysis. Photolysis of the diaryliodonium salt results in a high quantum yield irreversible fragmentation of the photoinitiator into products (principally Brønsted acids), which are highly active for the initiation of polymerization. In this case, which involves the polymerization of a vinyl ether monomer, the polymerization is nonterminating and, once initiated, proceeds to high conversion without an induction period. In contrast, the DPS photoinitiator reversibly generates an ylide and a Brønsted acid (Scheme 2). As already pointed out, initiation using these photoinitiators always consists of a competition between the ylide and the monomer for the protonic acid. This competition depends on the relative basicity of the respective two species. In the case of epoxide monomers, polymerization is favored since the difference in basicity between the two species is relatively small. The reverse is the case for vinyl ethers, due to the considerable difference in basicity between the ylide and vinyl ether. In this case, initiation would be expected to be slow. Furthermore, once initiation has occurred, there is an additional competition between the vinyl ether and the nucleophilic ylide for the growing alkoxycarbenium ion chain end. Termination of the polymerization by the ylide is favored since the sulfonium salt formed is expected to be more stable than the propagating alkoxycarbenium ion. This is depicted in eq 9 of Scheme 3. In an analogous fashion, the termination of epoxide and other types of cationic ring-opening polymerizations would occur to yield polymers with DPS end groups (eq 10). Since there is less gain in stability in the conversion of the propagating oxonium ion to a sulfonium ion, termination of the epoxide polymerization by the ylide is a less significant process than the vinyl ether case.

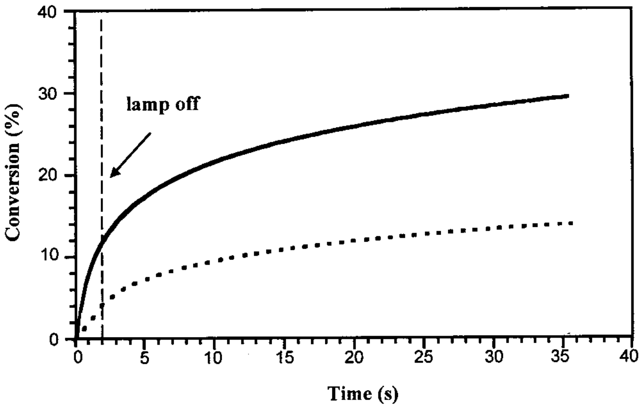
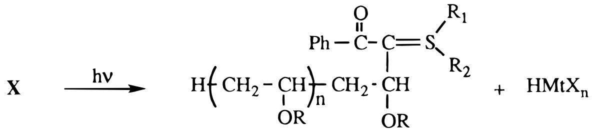


Figure 6. RTIR study of the postpolymerizations of **VII** using 1 mol % $C_1C_{12}-DPS(SbF_6)$ (- - -) and IOC-11(SbF_6) (—) (2 s irradiation at an intensity of 1450 mJ/cm^2·min).

Polymers **X** and **XI** containing DPS terminal groups are photosensitive and on continued irradiation, will initiate polymerization as depicted in eq 11.

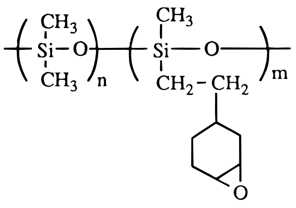


(11)

As noted in Scheme 1, photolysis of the DPS can involve all of the protons on the carbons adjacent to the positively charged sulfur atom. Therefore, in principle, the process of photolysis and termination may occur until all the protons are replaced by polymer chains. Thus, the DPS salt functions as an initiator and terminator and a coupling agent in a polymerization. This would result in polymers having a starlike architecture. However, as polymer chains become bound to the DPS moiety, there is a corresponding increase in the steric hindrance about the ylide carbon−sulfur double bond, and consequently, the rate of termination should decrease markedly. The pronounced induction period observed for the $C_{12}C_{12}-DPS(SbF_6)$ photoinitiator followed by rapid polymerization as shown in Figure 5 may be ascribed to the above two effects.

As a consequence of the above termination mechanisms, it may be predicted that cationic polymerizations catalyzed using DPS photoinitiators should display rapid termination when the UV irradiation is extinguished; i.e., they should exhibit very limited dark polymerization. In contrast, polymerizations employing diaryliodonium or triarylsulfonium salts exhibit considerable dark polymerization due to the lack of such termination processes. Shown in Figure 6 is a study in which the photopolymerization of **VII** using 1.0 mol % $C_1C_{12}-DPS(SbF_6)$ is compared with the polymerization of the same monomer in the presence of an equivalent amount of IOC-11(SbF_6). The samples were irradiated with UV light at an intensity of 1450 mJ/cm^2·min for 2 s in each case and then allowed to proceed in the dark. While both photoinitiators displayed dark polymerizations, as expected, the dark polymerization initiated by IOC-11(SbF_6) proceeded more rapidly and to a much greater extent than that initiated by $C_1C_{12}-DPS(SbF_6)$. These observations also suggest that while termination does take place in epoxide polymerizations with the DPS, the rate of termination is considerably suppressed by steric hindrance.

Photoinitiated Cationic Polymerizations of Selected Monomer/Oligomer Systems Using DPS Photoinitiators. DPS photoinitiators bearing anions derived from superacids (Hammet acidities $H_0 = -12$ or greater) are capable of initiating the polymerization of virtually every known type of cationically polymerizable monomer. Of particular interest in this investigation was the use of the novel second-generation DPS photoinitiators to carry out the photopolymerization of monomers and oligomers which are problematic using other types of cationic photoinitiators due to their poor solubility. Especially important and useful are epoxy functional poly(dimethylsiloxane)s (silicones). For example, silicones bearing pendant epoxycyclohexyl groups such as shown below are of interest as release coatings for pressure-sensitive adhesives.



The cationic photopolymerization of epoxy silicones is problematic since the solubility of most onium salt cationic photoinitiators in these oligomers is poor. Currently, iodonium hexafluoroantimonate salts bearing long, branched alkyl groups are used.[12,13] Alternatively, diaryliodonium salts with the tetra(pentafluorophenyl)borate anion can be employed.[14,15]

We have conducted a differential scanning photocalorimetry (DSP) study of the photopolymerization of an epoxycyclohexane functional silicone oligomer (General Electric Silicones UV9315) having an epoxy equivalent weight of 1000 using two different photoinitiators. This technique was employed in this instance because the low concentration of epoxy functional groups and their weak absorption render the usual RTIR method insensitive. Compared were the borate salt, $C_1C_{12}-DPS(B(C_6F_5)_4)$, with $(4\text{-}i\text{-}C_3H_7-C_6H_4)I^+(4\text{-}CH_3C_6H_4)B(C_6F_5)_4^-$ (Rhodorsil 2074) and the results are shown in Figures 7 and 8. The apparent higher reactivity observed using the diaryliodonium salt photoinitiator is due, as previously mentioned, to the better spectral absorption characteristics, higher quantum yield, and the nonterminating character of this photoinitiator. In addition, the higher rate of polymerization observed using this photoinitiator is a result of autoacceleration effects due to the increase of the sample temperature during the polymerization. This effect is also reflected in the difference in the extents of polymerization (ultimate conversion) of both samples after 9 min irradiation. The rapid polymerization observed with the diaryliodonium salt photoinitiator produces a higher reaction temperature which results in greater conversion.

Nonpolar monomers such as epoxidized vegetable oils and epoxidized diene polymers are difficult to polymerize with conventional onium salt photoinitiators due to the poor solubility of the photoinitiator. The polymerization of these monomers is only possible using modified onium salts such as IOC-11(SbF_6). Figure 9 gives the DSP curves for epoxidized soybean oil, linseed oil and poly(1,4-butadiene) using 1.0 wt % $C_{12}C_{12}-DPS(SbF_6)$. Also included for comparison is the polymerization of epoxidized linseed oil with 0.95 wt % IOC-11(SbF_6) (same molar equivalent as $C_{12}C_{12}-DPS(SbF_6)$). In all

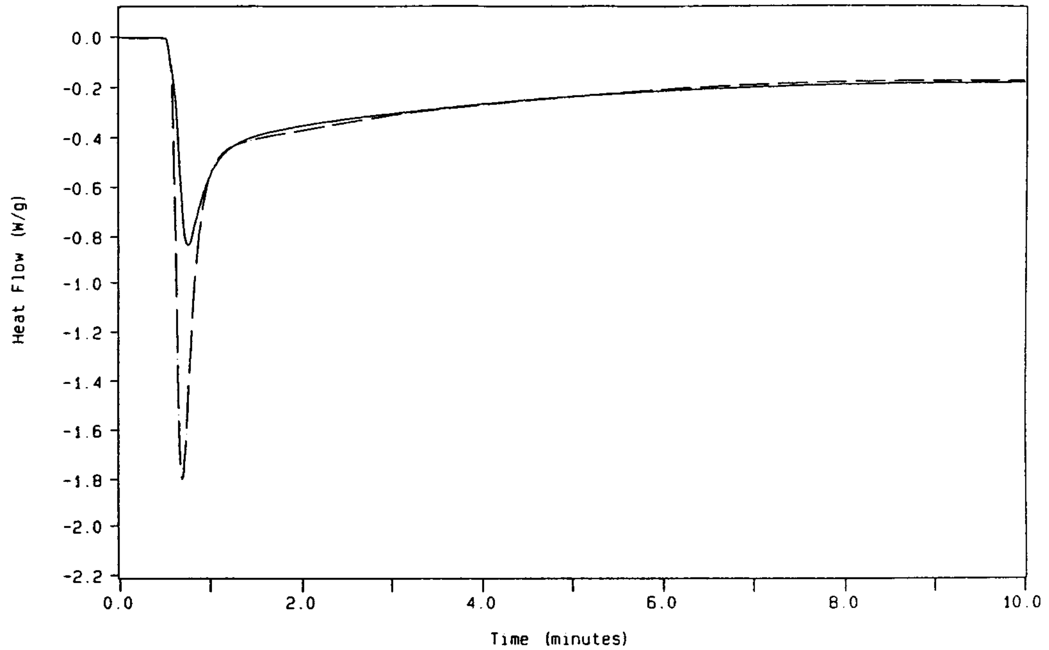


Figure 7. DSP comparison of $C_1C_{12}-DPS(B(C_6F_5)_4)$ (—) with $(4\text{-}i\text{-}C_3H_7-C_6H_4)I^+(4\text{-}C_6H_4-CH_3)B(C_6F_5)_4^-$ (Rhodorsil 2074) (- - -) in the polymerization of epoxy silicone oligomer (UV9315) (1 mol % photoinitiator; light intensity 900 mJ/cm^2·min; shutter opened after 0.5 min).

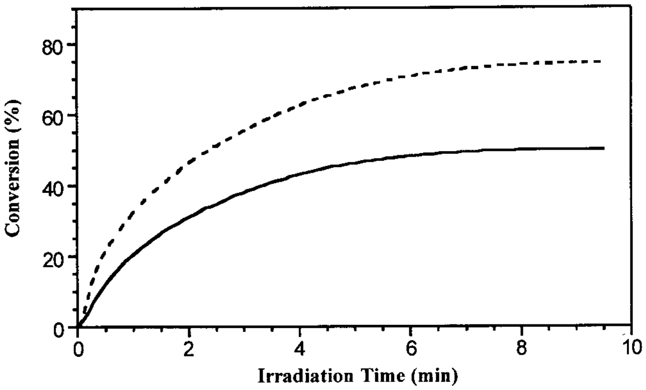


Figure 8. Conversion vs time plot of DSP data from Figure 7. $(4\text{-}i\text{-}C_3H_7-C_6H_4)I^+(4\text{-}C_6H_4-CH_3)B(C_6F_5)_4^-$ (- - -) and $C_1C_{12}-DPS(B(C_6F_5)_4)$ (—).

cases, the photoinitiators were completely soluble in the liquid monomer or oligomer. In contrast to **VII**, the polymerizations of these three monomers/oligomers are much slower as indicated by the considerably broader exothermic peaks. Comparison of the curves for the photopolymerizations of epoxidized linseed oil using $C_{12}C_{12}-DPS(SbF_6)$ and IOC-11(SbF_6) shows that the latter photoinitiator is only slightly more active than the former.

Free-Radical-Promoted Cationic Polymerization. The ability of free radicals to induce the decomposition of diaryliodonium salt photoinitiators has been reported by Ledwith,[16] Yagci et al.,[17,18,19] Neckers,[20] and ourselves.[21,22,23] At the same time, triarylsulfonium salts do not undergo this reaction. The difference in the behavior of these two classes of cationic photoinitiators can be attributed to the marked difference in their reduction potentials. Whereas diaryliodonium salts have low reduction potentials ($E_{1/2} = -0.2$ V), allowing their facile reduction by many types of carbon-centered free radicals, the higher reduction potential of triarylsulfonium salts ($E_{1/2} = -1.01$ to -1.46 V) obviates this reaction.[24] The reduction potential of DPS salts has been found to be intermediate ($E_{1/2} = -0.6$ to -0.7 V)[25] between these two classes of onium salts. This raised the possibility that they may undergo free-radical-induced decomposition. Accordingly, the $C_1C_{12}-DPS(SbF_6)$-catalyzed photopolymerization of **VII** was carried out in the presence and absence of the free radical photoinitiator 2,2-dimethoxy-2-phenylacetophenone (Esacure KB-1). The results of this study are shown in Figure 10 together with a control study in which IOC-11(SbF_6) was included for comparison. While the rate enhancement effect of the free radical initiator on the IOC-11(SbF_6) polymerization appears to be greater, the effect in the case of the DPS salt is also considerable. The redox mechanism shown in Scheme 4 is proposed to account for this rate enhancement.

In addition to the direct photolysis of the DPS, as shown in eq 12 of Scheme 4, simultaneous photolysis of the free radical photoinitiator also takes place yielding an acyl radical, **XII**, and a dimethoxyphenylmethyl radical, **XIII**. This latter species which has an oxidation potential (E_r^{ox}) of approximately -0.8 V[25] interacts with the DPS as shown in eq 13 to undergo a redox reaction in which the radical is oxidized to the cation, **XV**, while the DPS is reduced to the corresponding sulfur centered free radical, **XIV**. Finally, **XIV** species undergoes irreversible fragmentation (eq 14) to yield the resonance-stabilized phenacyl radical, **XVI**, and a dialkyl sulfide. Cationic polymerization can occur by attack of the dimethoxyphenylmethylcarbenium ion on the monomer as well as by the generation of a strong Brønsted acid by direct photolysis of the DPS. This mechanism results in an apparent acceleration of the rate of polymerization due to the rapid generation of reactive cations by a free-radical-induced irreversible decomposition of the photoinitiator.

Thermally Initiated Cationic Polymerizations Using DPS Salts. The use of sulfonium salts to conduct thermally initiated cationic polymerizations has been investigated recently by several authors.[26−29] Typically, the mechanism of initiation involves a transalkylation

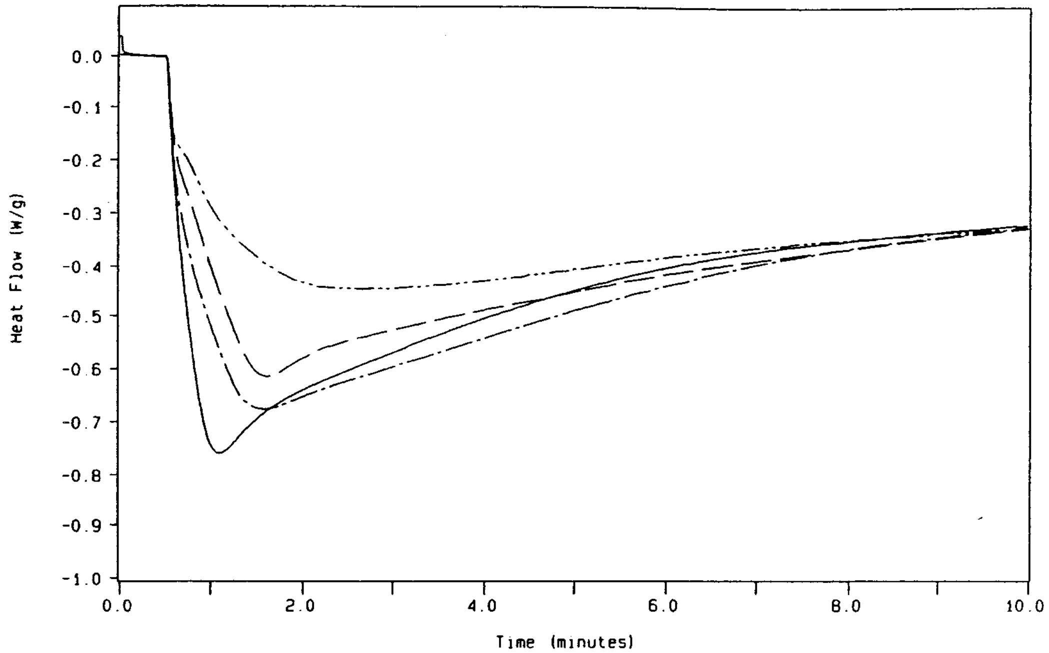


Figure 9. DSP curves for the photopolymerization of epoxidized soybean oil with 1.0 wt % $C_{12}C_{12}$−DPS(SbF_6) (—), epoxidized linseed oil with 1.0 wt % $C_{12}C_{12}$−DPS(SbF_6) (— —), epoxidized linseed oil with 0.95 wt % IOC-10(SbF_6) (— • —), and epoxidized poly(1,4-buta-diene) with 1.0 wt % $C_{12}C_{12}$−DPS(SbF_6) (— • • —) (light intensity 1100 mJ/cm^2•min)

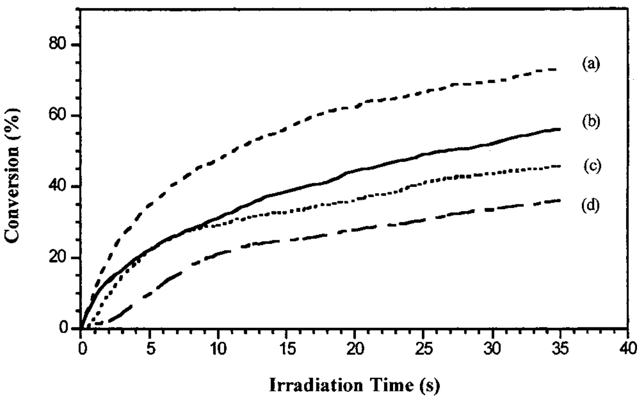
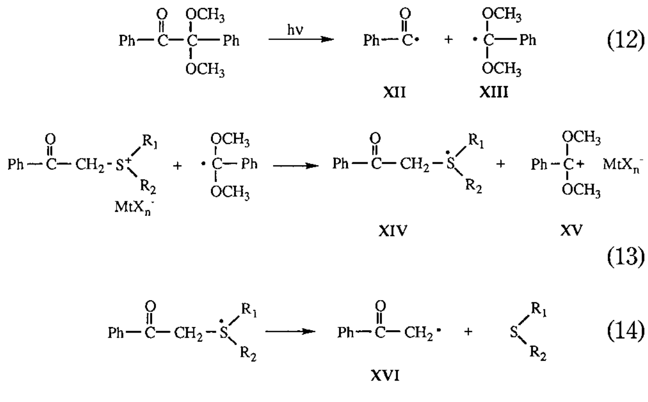


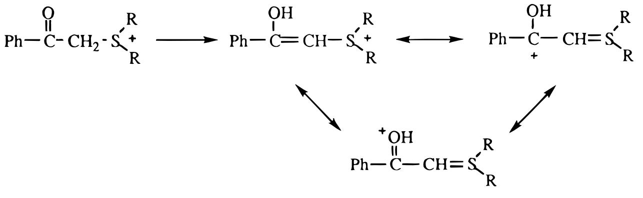
Figure 10. Free-radical-promoted cationic polymerization of **VII** using (a) 1.0 mol % IOC11(SbF_6) and 1.0 mol % Esacure KB-1; (b) 1.0 mol % IOC11(SbF_6); (c) 1.0 mol % C_1C_{12}−DPS (SbF_6) and 1.0 mol % Esacure KB-1; and (d) 1.0 mol % C_1C_{12}−DPS(SbF_6) (light intensity 950 mJ/cm^2•min).

Scheme 4



or a transarylation from the sulfonium salt to the monomer to form the propagating cationic species. There is a great difference in the reactivity of sulfonium salts as thermal initiators which can be related to their structure. Trialkylsulfonium salts will initiate the cationic polymerizations of some monomers at room temperature while triarylsulfonium salts initiate polymerizations only at temperatures approaching 200 °C. Thus, the incorporation of aryl or other groups, which can stabilize the positive charge on sulfur by resonance, results in an increased thermal stability of the sulfonium salt and in a higher onset temperature of the thermally induced cationic polymerization.

DPS salts represent a potential compromise in thermal stability between trialkyl- and triarylsulfonium salts. These compounds bear a phenacyl group which stabilizes the sulfonium salt by resonance via the enol structure as shown below (anion omitted for clarity).



(15)

It was of some interest, therefore, to determine the thermal stability of DPS salts in the presence of nucleophilic, cationically polymerizable monomers.

A DSC investigation of the thermally induced polymerization of several DPS(SbF_6) salts bearing different alkyl groups was carried out using the highly reactive silicone diepoxide monomer **VII**. The studies were conducted using 1 mol % of the respective DPS at a heating rate of 10 °C/min. The behavior of these DPS salts is very similar and independent of the nature of the alkyl groups. The onset of polymerization typically occurs at 85 ± 5 °C and the peak temperature at 95 ± 5 °C. Figure 11 gives a comparison of DSC curves for **VII** and **IX**. As shown in this figure, the thermal stability of a DPS salt is a function of the monomer used. Table 2 gives the DSC data collected for four different monomers studied during this investigation. The results correlate well with the reactivity of the corresponding

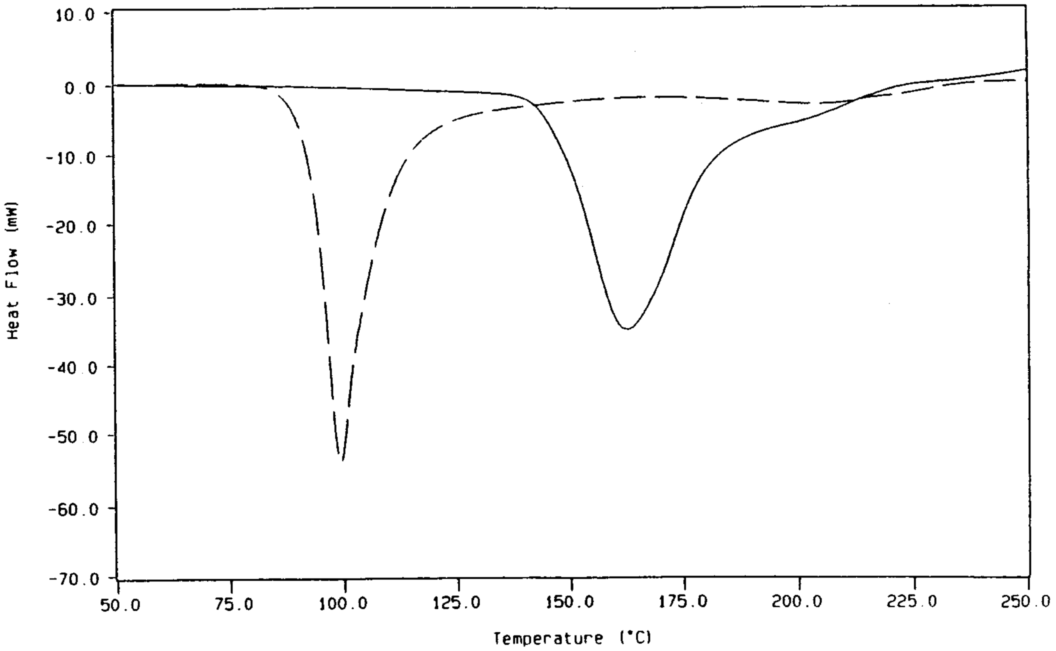


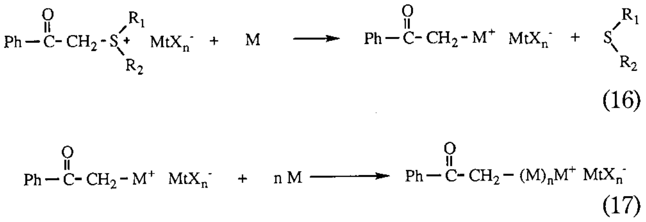
Figure 11. DSC study of the thermally induced polymerization of **VII** (- - -) and **IX** (—) using 1.0 mol % C_1C_{18}–DPS(SbF_6) (heating rate 10 °C/min in air).

Table 2. Thermally Induced Cationic Polymerization of Various Monomers by DPS[a]

monomer	initiator	onset (peak)
VII	C_1C_{12}–DPS(SbF_6)	86 (96)
VIII	$C_{14}C_{14}$–DPS(SbF_6)	161 (166)
IX	C_1C_{18}–DPS(SbF_6)	149 (162)
octyl 1-propenyl ether	$C_{14}C_{14}$–DPS(SbF_6)	90 (100)

[a] 1 mol % DPS used at a heating rate of 10 °C/min in air.

Scheme 5



$$\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}\overset{+}{S}\begin{smallmatrix}R_1\\R_2\end{smallmatrix}\ MtX_n^-} + \mathrm{M} \longrightarrow \mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}M^+\ MtX_n^-} + \mathrm{S\begin{smallmatrix}R_1\\R_2\end{smallmatrix}} \qquad (16)$$

$$\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}M^+\ MtX_n^-} + n\,\mathrm{M} \longrightarrow \mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}(M)_nM^+\ MtX_n^-} \qquad (17)$$

monomers (i.e., octyl 1-propenyl ether and **VII** are the most reactive monomer while **VIII** is the least).

As the onset and peak temperatures indicate, the DSC scans consist of sharp exothermic peaks indicating that there is a thermal threshold followed by very rapid polymerization. We propose that the thermally induced polymerization takes place via the transalkylation mechanism shown in Scheme 5.

An isothermal DSC study was also conducted using monomer **VII** at several temperatures, and the results are depicted in Figure 12. At 80 °C, the photoinitiator is stable and no reaction takes place. As the temperature is progressively raised, polymerization sets in at increasingly shorter times, until at 120 °C polymerization ensues almost immediately. The conversions were calculated to be above 90% for the polymerizations carried out at 100 and 120 °C.

Recently, we have observed that the temperature of the onset of thermally induced polymerizations of epoxides can be increased by the addition of free radical inhibitors such as 4-*tert*-butylcatechol. This is suggestive of the possible participation of free radicals in the mechanism of the decomposition of DPS compounds. Further studies are in progress, and the results will be presented at a later time.

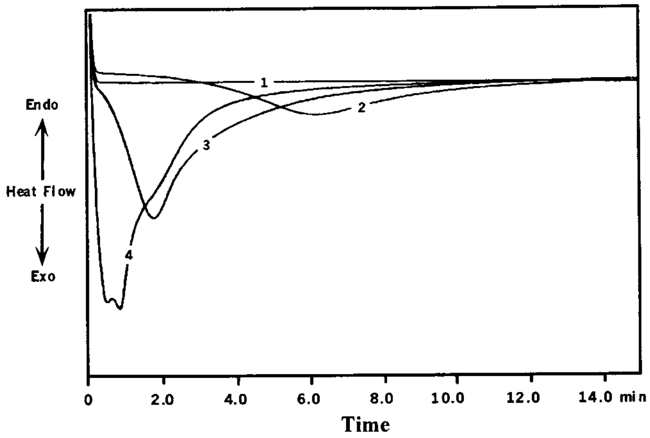


Figure 12. Isothermal DSC study of the thermally induced polymerization of **VII** using 1.0 mol % C_1C_{18}–DPS(SbF_6) at (1) 80 °C, (2) 90 °C, (3) 100 °C, and (4) 120 °C.

The results of the temperature-programmed and isothermal studies indicate that DPS photoinitiators have sufficient thermal stability to ensure good shelf lives at room temperature in the presence of even very reactive monomers. Yet, they exhibit excellent photosensitivity when irradiated with UV or visible light in the presence of photosensitizers. Alternatively, DPS can be employed as effective thermal cationic initiators at temperatures from 100 to 170 °C depending on the monomer used.

Conclusions

Employing a new synthetic methodology, a series of second-generation dialkylphenacylsulfonium salts (DPS) have been prepared which display a desirable combination of high photosensitivity and excellent solubility characteristics in both polar and nonpolar monomers. An investigation of the cationic photopolymerization of several different monomer systems using DPS showed interesting behavior. While epoxide monomers polymerize rapidly and without inhibition, the polymerization of vinyl ethers takes place rapidly only after an appreciable induction period. In the case of the vinyl ether photopolymerization, these results were attributed to termination during the early stages by reaction of the growing vinyl ether polymer chains ends with the photogenerated ylide. When DPS photoinitiators are compared to diaryliodonium and triarylsulfonium salts in the polymerization of epoxy monomers, they display a very similar level of photosensitivity and efficiency as these latter onium salt cationic photoinitiators. Of particular interest is the use of these photoinitiators for the photopolymerization of highly nonpolar monomers and oligomers such as epoxy-functional silicones, epoxidized hydrocarbon elastomers and epoxidized vegetable oils.

DPS can also be employed as thermally activated initiators for the cationic polymerizations of epoxides. Investigations of the thermolysis of DPS salts have shown that the threshold for their decomposition is highly dependent on the monomer employed. This suggests that the primary mode of initiation of polymerization takes place by a transalkylation mechanism in which nucleophilic monomer displaces a phenacyl group in the DPS.

DPS have many benefits as photoinitiators which are attractive for laboratory and commercial uses. First, they are readily prepared in high yields by a straightforward synthetic method which employs readily available, inexpensive starting materials. DPS photoinitiators can be photosensitized to allow for spectral broadening to provide sensitivity in both the long wavelength UV and the visible regions. They are especially attractive for the polymerization of epoxides and generally compare well with existing cationic photoinitiators in both photosensitivity and efficiency of initiation. Since DPS photoinitiators become bound to the polymer chain ends and are, therefore, held within the matrix, they are not extractable. This may be important for medical and food contact applications. These novel photoinitiators are useful in many applications including the following: UV-curable abrasion-resistant coatings, release coatings, inks, adhesives, fiber-reinforced composites and pressure-sensitive adhesives, and fiber optic coatings. Thermally curable compositions using these sulfonium salts may be useful for electronic encapsulations and electrical insulation.

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