

**Redox Initiated Cationic Polymerization: Reduction of Dialkylphenacylsulfonium  
Salts by Silanes**

by

Max Molleo

A Thesis Submitted to the Graduate  
Faculty of Rensselaer Polytechnic Institute

in Partial Fulfillment of the  
Requirements for the Degree of  
MASTER OF SCIENCE  
Major Subject: CHEMISTRY

Approved:

---

James V. Crivello, Thesis Adviser

---

Chang Ryu, Professor

Rensselaer Polytechnic Institute  
Troy, New York

May, 2009

# CONTENTS

LIST OF TABLES.....	iii
LIST OF FIGURES.....	iv
ACKNOWLEDGMENTS.....	v
ABSTRACT.....	vi
1. INTRODUCTION AND HISTORICAL REVIEW.....	1
2. APPARATUS .....	4
3. MATERIALS.....	6
4. DISCUSSION.....	10
5. CONCLUSIONS.....	18
LITERATURE CITED.....	19

## LIST OF TABLES

1)	Names, Abbreviations, and Structures of Monomers.....	7
2)	Names, Abbreviations, and Structures of Organosilanes.....	8
3)	Names, Abbreviations, and Structures of Phenacylsulfonium Salts.....	9

## LIST OF FIGURES

1)	Optical pyrometry apparatus modified for redox cationic polymerization studies.....	5
2)	OP study of the polymerization of cyclohexene oxide with 3.0% DPS-C <sub>1</sub> C <sub>16</sub> SbF <sub>6</sub> and 8 ppm Karstedt catalyst using 1,1,3,3-tetramethyldisiloxane (TMDS) as the reducing agent.....	10
3)	Proposed mechanism for the DPS-silane redox couple; MtX <sub>n</sub> <sup>-</sup> = BF <sub>4</sub> <sup>-</sup> , PF <sub>6</sub> <sup>-</sup> , AsF <sub>6</sub> <sup>-</sup> , SbF <sub>6</sub> <sup>-</sup> , (C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> B <sup>-</sup> ; M = Cationically Polymerizable Monomer; R <sub>1</sub> ,R <sub>2</sub> = Alkyl Groups; R <sub>3</sub> ,R <sub>4</sub> ,R <sub>5</sub> = Alkyl or Alkoxy groups.....	12
4)	OP study of the polymerization of VCHDO with 3.0% DPS-C <sub>1</sub> C <sub>16</sub> SbF <sub>6</sub> and 8 ppm Karstedt catalyst using TMDS as the reducing agent.....	13
5)	Effect of the Karstedt catalyst concentration on the polymerization of VCHDO using 3.0% DPS-C <sub>1</sub> C <sub>16</sub> SbF <sub>6</sub> and TMDS as the reducing agent.....	14
6)	OP study of the polymerization of VCHDO with 3.0% DPS-C <sub>1</sub> C <sub>16</sub> SbF <sub>6</sub> and 8 ppm Cl <sub>2</sub> (COD)Pd(II) using TMDS as the reducing agent.....	14
7)	Polymerization of VCHDO with 3.0% DPS-C <sub>1</sub> C <sub>16</sub> SbF <sub>6</sub> , 8 ppm Karstedt catalyst using triethoxysilane (TEOS), n-hexylsilane (HS), triethylsilane (TES) and 1,1,3,3-tetramethyldisiloxane (TMDS) as reducing agents.....	15
8)	Comparison of the polymerization of VCHDO with 3.0% DPS-C <sub>1</sub> C <sub>12</sub> SbF <sub>6</sub> , DPS-C <sub>1</sub> C <sub>12</sub> AsF <sub>6</sub> , and DPS-C <sub>1</sub> C <sub>12</sub> PF <sub>6</sub> , using 8 ppm Karstedt catalyst with TMDS as the reducing agent.....	16
9)	Comparison of the polymerization of VCHDO with 3.0% of various DPS SbF <sub>6</sub> salts using 8 ppm Karstedt catalyst with TMDS as the reducing agent.....	16
10)	Polymerizations of DVE-3 and triethyleneglycol methyl vinyl ether with 3.0 % DPS-C <sub>1</sub> C <sub>16</sub> SbF <sub>6</sub> , 16 ppm Cl <sub>2</sub> (COD)Pd(II) using TMDS as the reducing agent.....	17

## ACKNOWLEDGEMENT

I would like to thank all of the people who have helped and inspired me while I have earned both my bachelor's and master's degree at Rensselaer Polytechnic Institute.

Foremost, I would like to thank my research professor, Dr. James V. Crivello, for his unwavering support and guidance with my research. He has dedicated immense amounts of time to help me succeed at Rensselaer, and has intensified my ambition to continue researching polymers in graduate school. A world-renown scientist and all-around remarkable individual, I will always remember the friendship that has grown this past year.

To my family and friends... without you, my work would be meaningless. You inspire me to achieve greatness, and it is this inspiration that perpetuates by desire to change the world. I would especially like to thank my parents, Edward and Marion Molleo, and my brothers, Ed and Kane, for their unconditional love and support through all of my endeavors.

The work for this master's thesis was submitted for publication to *Macromolecules*, an ACS publication, in March of 2009.

## ABSTRACT

Silanes bearing Si-H groups reduce S,S-Dialkyl-S-phenacylsulfonium salts while in the presence of a noble metal catalyst. The resulting redox couple may be used as an initiator for the cationic polymerizations of epoxides, oxetanes, and vinyl ethers. The polymerizations of these monomers can be carried out in a conventional manner with neat monomer or under solution conditions. These polymerizations are normally rapid and exothermic. An original two-component redox system in which vaporized silane is delivered to a thin film of monomer, sulfonium salt, and noble metal catalyst is studied. Optical pyrometry (infrared thermography) is used to examine and optimize the kinetics of the abovementioned cationic polymerizations. The structural variations of sulfonium salts, silanes, and noble metal catalysts on the polymerizations of various vinyl and heterocyclic monomers were studied.

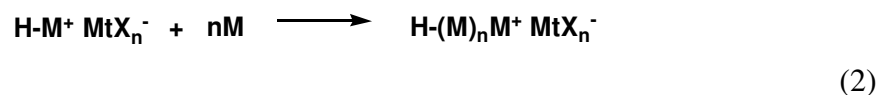
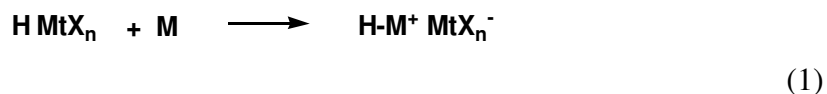
## 1. Introduction and Historical Review

Radical polymerizations are a class of chain-growth polymerizations in which the polymer propagates by means an unpaired electron (a free-radical). Unpaired electrons are extremely reactive, making radicals very likely to react with neighboring compounds. A typical radical polymerization consists of three stages: initiation, propagation, and termination. During the initiation stage, a free-radical is formed and attacks a monomer; this process converts the monomer into a reactive radical group. The radical attacks a neighboring monomer and transfers its radical, thereby bonding to the monomer and propagating the polymer chain. This process continues until the radical reacts in a way that terminates propagation. Termination often occurs when two radicals react and couple with each other, creating a molecule that lacks a reactive radical component. Termination may also transpire by means of disproportionation, a process in which a radical group transfers a proton to another radical; this again eliminates both radicals and ends propagation.

It is widely accepted that reduction-oxidation systems can generate free radical initiators<sup>1</sup>. These processes are used in the commercial manufacturing of vinyl polymers and styrene polyesters such as countertops and other furnishings for bathrooms and kitchens. Free radical redox initiating systems have numerous beneficial properties. Because the redox reactions have low activation energies, they are conveniently conducted at room temperature. The redox systems are often inorganic salts that are capable of polymerizing monomers in aqueous solvents. Additionally, the redox systems are very stable and do not require refrigeration during storage. The overall process of using free radical redox systems is highly cost effective.

Reduction-oxidation systems have also been used as initiators for cationic polymerizations. Unlike its free radical counterpart, cationic polymerizations propagate by means of a positively-charged Lewis acid (cation) rather than a radical. Professor James Crivello's research group has previously shown that diaryliodonium salts react as oxidants with reducing agents such as ascorbic acid<sup>2</sup>, benzoin<sup>3</sup>, or stannous octoate<sup>4</sup> to initiate cationic polymerizations at temperatures as low as 25 °C. The diaryliodonium salts are selected to produce a strong Brønsted acid such as  $\text{HPF}_6$ ,  $\text{HBF}_4$ , or  $\text{HSbF}_6$ .

These acids, which are commonly referred to as “super acids,” are known to initiate both cationic vinyl and heterocyclic ring-opening polymerizations<sup>5,6</sup> (eq. 1 and 2).

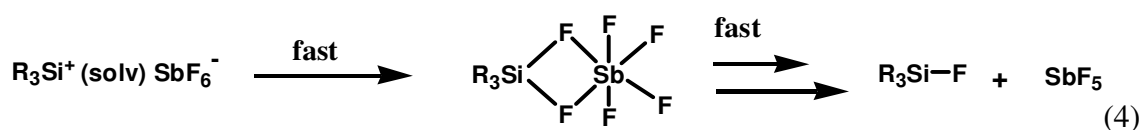
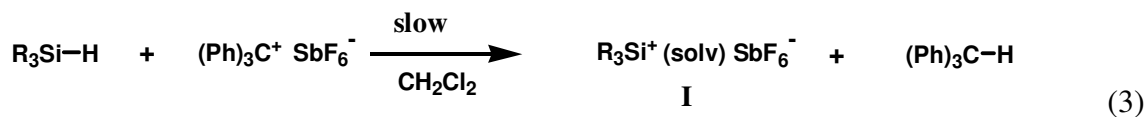


**Scheme 1.** Mechanism of a cationic polymerization using a super acid produced by a redox system

The research groups of Ledwith<sup>7</sup>, Timpe and Baumann<sup>8,9,10,11,12</sup>, Yagci<sup>13,14,15,16,17</sup> and Fouassier<sup>18,19,20</sup> have demonstrated that thermolytic and photolytic free radical-generating molecules act as reducing agents for diaryliodonium salts. There has been limited success using similar systems to reduce triarylsulfonium salts for cationic polymerizations; this is because the reduction of triarylsulfonium salts ( $E_{\text{red}} = -28 \text{ k-cal mol}^{-1}$ )<sup>21</sup> is significantly more difficult than that of diaryliodonium salts ( $E_{\text{red}} = -5 \text{ k-cal mol}^{-1}$ ). However, heat or light is needed to initiate the reduction of both salts.

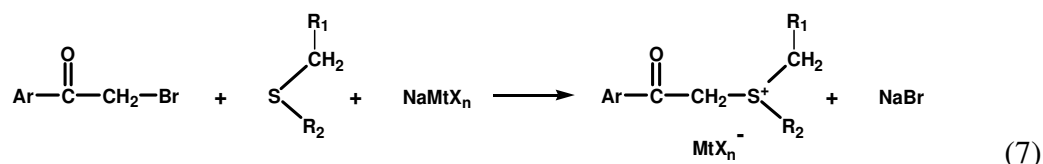
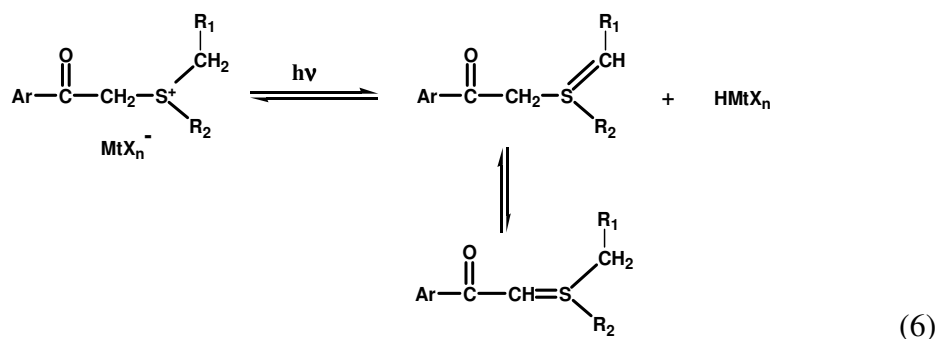
Crivello has recently verified the existence of redox systems that can initiate cationic polymerizations at room temperature<sup>22,23</sup>. These systems are comprised of a diaryliodonium or triarylsulfonium salt as the oxidizing agent and an organosilane with the functional group Si-H as the reducing agent. This redox reaction is catalyzed by noble metal complexes such as those of platinum, palladium and rhodium. The proposed mechanism by which these onium salts are reduced is expected to be similar to the reduction of trityl salts by silanes<sup>24</sup>. As observed in Scheme 2, Chojnowski et al. proposes that in the absence of a catalyst, the organosilane reduces the trityl salt. The mechanism proceeds through steps involving the formation of solvated silicenium ion intermediates, which may be observed in equations 3 and 4. Triphenylmethane and the corresponding fluorosilane are produced by this reaction and continue to react, creating unspecified products (eq. 5).





**Scheme 2** – Mechanism of the reduction of a trityl salt by an organosilane

The excellent photosensitivity and photoinitiating characteristics of S,S-dialkyl-S-phenacylsulfonium salts (DPS) bearing anions,  $\text{MtX}_n^-$ , of low nucleophilic character has previously been reported by Crivello and Lam<sup>25</sup>. They are considered a useful class of cationic photoinitiators due to their ability to undergo a photoinduced elimination reaction by a Norrish Type II process and yield an ylide and a Brønsted acid. These two products are able to recombine and reform the original salt by means of a dark reaction (eq. 6). DPS may easily be synthesized from phenacylhalides, a dialkyl sulfide and an inorganic salt by reaction in acetone or methyl ethyl ketone, producing high yields of pure DPS. The synthetic pathway is shown in equation 7.



**Scheme 3** – Degradation, recombination, and synthetic pathway of DPS

Since the nomenclature of DPS salts is lengthy and complex, a system of abbreviations was developed and is used throughout this communication. The abbreviation is in the form, DPS-C<sub>a</sub>C<sub>b</sub> MtX<sub>n</sub>, where DPS signifies the phenacylsulfonio group, C<sub>a</sub> and C<sub>b</sub> represent the two alkyl groups and MtX<sub>n</sub> is the accompanying anion. For example, DPS-C<sub>1</sub>C<sub>8</sub> SbF<sub>6</sub> denotes the compound, S-methyl-S-n-octyl-S-phenacylsulfonium hexafluoroantimonate. The alkyl groups are assumed to be unbranched unless otherwise specified.

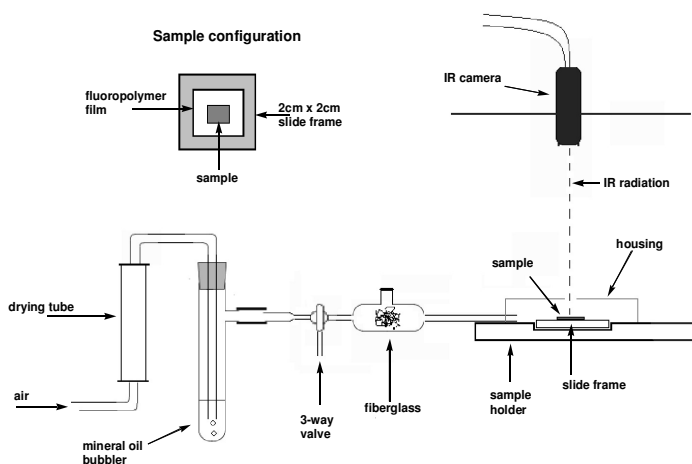
It is of interest to examine the ability of organosilanes to reduce other onium salts and, by means of a redox reaction similar to Scheme 2, create initiators for cationic polymerizations. Additionally, it is important to understand the extent to which the kinetics of these reactions may be controlled. In this thesis, we investigate redox initiator systems comprised of organosilanes, S,S-dialkyl-S-phenacylsulfonium salts, and noble metal catalysts and explore their use in the polymerizations of vinyl and heterocyclic monomers.

## 2. Apparatus

Optical pyrometry is a useful technique for monitoring the heat that evolves during a polymerization. The apparatus sampling, configuration, and analytical techniques are thoroughly discussed in previous publications by Falk, Vallinas, and Crivello<sup>26,27,28</sup>. Figure 1 illustrates a schematic diagram of the optical pyrometry apparatus used in this experiment.

Samples for OP analysis were prepared by dissolving the sulfonium salt in the appropriate monomer and adding the noble metal catalyst to the resulting solution by syringe. The liquid sample is absorbed into a thin (0.2 mm) 15 mm x 15 mm sheet of nonwoven polyester fabric (veil) placed on a thin (0.25 mm) fluorinated polyethylene film mounted in a plastic 2 cm x 2 cm slide frame. The slide frame was placed into a recessed sample holder and a 8.5 cm dia. x 1.0 cm circular glass housing was placed over the sample. The housing serves to confine the silane vapor to the area about the sample. The housing serves to confine the silane vapor to the area about the sample. A 1 cm dia. aperture was cut into the top of the housing to permit direct line-of-sight access to the sample by the infrared camera and to function as a vent. The sample was positioned at the center of the aperture and at such a distance that it lies at the focal

point of the infrared camera. This was accomplished with the aid of a laser sighting device.



**FIGURE 1.** Optical pyrometry apparatus modified for redox cationic polymerization studies.

The sensitivity of the OP technique is largely determined by the infrared camera that was used. In these experiments, an Omega Corp. Model OS 552-V1-6 infrared camera with a sensitivity of  $\pm 0.5$  °C over the range of -18-538 °C was employed. Reactions that produce a sample temperature change of at least 1 °C/min can be monitored with this instrument.

To initiate polymerization, a small amount (0.3 ml) of the designated silane reducing agent was injected into a cell filled with glass wool. The wool increases the surface area of the organosilane, thereby enhancing its vaporization. A slow stream of dry air passing through the cell carries the vapors of the silane into the sample cell via a glass tube that was positioned with the end at a distance of 2.5 cm from the sample. All polymerizations were carried out at an initial temperature of 23-25 °C. During kinetic runs, the temperature of the sample was monitored at a rate of one measurement per second after an initial equilibration period of 20 s.

Gas chromatography and  $^{29}\text{Si}$  NMR were used to determine the mechanism by which an organosilane reacts with a *S,S*-dialkyl-*S*-phenacylsulfonium salt to produce a cationic polymerization initiator. The Shimadzu QP5000 Gas Chromatograph-Mass Spectrometer equipped with 10 m phenyl silicone capillary columns was used to analyze

the redox system. A similar redox system in a deuterated solvent was analyzed via  $^{29}\text{Si}$  NMR on a Varian Unity 500 MHz Nuclear Magnetic Resonance Spectrometer.

Gel permeation chromatography is a technique commonly used to determine the molecular weight of a polymer. Into a clean dry 4 dram amber screw cap vial equipped with a Teflon microstirbar and fitted with a polyethylene liner were placed 1.96 g (0.02 mol) distilled cyclohexene oxide, 0.0284 g ( $5 \times 10^{-5}$  mol) DPS- $\text{C}_1\text{C}_8$   $\text{SbF}_6$  and 1.0 g dichloromethane. There were added by syringe 100  $\mu\text{l}$  1,1,3,3-tetramethyldisiloxane (TMDS) and 4 ppm of the Karstedt catalyst and the vial capped and immersed in an ice-water bath at room temperature. The reaction mixture was allowed to stir at room temperature for 2 hr and then poured into 50 ml methanol to precipitate the polymer. The polymer was collected by vacuum filtration, washed twice with fresh methanol and allowed to dry overnight at room temperature. After drying, 1.03 g solid polymer (53 % yield) was obtained as a white powder. Molecular weight analysis by GPC in high grade THF gave a  $M_n = 11000$  g/mol based on polystyrene standards.

### 3. Materials

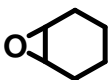
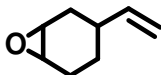
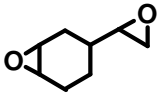
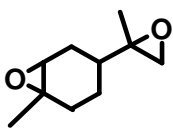
Limonene dioxide (1-methyl-4-(2-methyloxiranyl)-oxabicyclo[4.1.0]-heptane), and 1,2-epoxydecane was received as a gift from the Viking Chemical Co., Minneapolis, MN. Bis(3-ethyloxetanylmethyl) ether (DOX) was kindly provided as a gift from the Toagosei Chemical Company, Ltd. Nagoya, Japan. 3,4-Epoxy cyclohexylmethyl 3',4'-epoxycyclohexane carboxylate (ERL-4221) was purchased from Dow Chemical, Midland, MI. DVE-3 (triethyleneglycol divinyl ether, CAS name: 3,6,9,12-tetraoxatetradeca-1,13-diene) was obtained from ISP Technologies, Inc. Wayne, NJ. Triethyleneglycol methyl vinyl ether was provided as a sample by the BASF Corporation, Ludwigshaven, Germany. Organosilanes, the Karstedt (2.1-2.4% Pt in xylene) and Lamoreaux (2.0-2.5 % Pt in octanol) catalysts were purchased from Gelest, Inc., Morrisville, PA. All other metal complexes used as catalysts in this work were purchased from Strem Chemicals, Inc., Newburyport, MA. All other monomers, reagents and chemicals were used as purchased from the Aldrich Chemical Co., Milwaukee, WI. Cyclohexene oxide was purified prior to use by distillation over  $\text{CaH}_2$ .

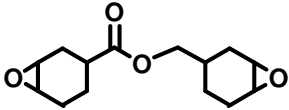
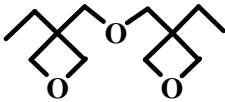
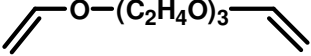
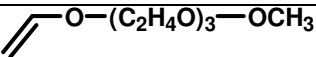
The S,S-dialkyl-S-phenacylsulfonium salts (DPS)<sup>29</sup> and S(4-n-decyloxyphenyl)-S,S-diphenylsulfonium hexafluoroantimonate (SOC-10 SbF<sub>6</sub>)<sup>30</sup>, were synthesized and purified by a method used by Crivello. Triphenylsulfonium SbF<sub>6</sub> was prepared according to the method of Potratz et al<sup>31</sup>.

The commercially available Karstedt and Lammoreau catalysts were purchased as solutions in which the platinum contents were listed as 2.0 % in both cases. Thus, when these solutions were used, the amounts used are given in ppm Pt. When the well characterized Cl<sub>2</sub>(COD)Pd(II) was used, the concentrations were calculated on the basis of weight% complex. Thus, when these latter solutions were employed, the amounts used are given in ppm metal complex.

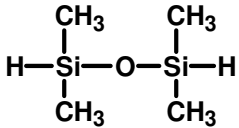
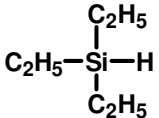
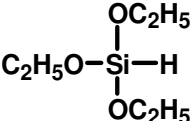
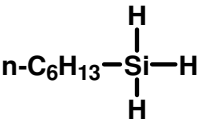
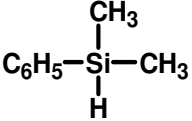
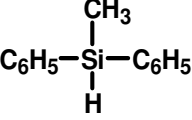
The names, abbreviations, and structures of all the monomers, silanes and the phenacylsulfonium salts described in this thesis are given in Tables 1, 2, and 3.

**Table 1**  
**Names, Abbreviations, and Structures of Monomers**

Name	Abbreviation	Structure
cyclohexene oxide	CHO	
4-vinylcyclohexene-1,2-oxide	VCHO	
4-vinylcyclohexene-dioxide	VCHDO	
limonene dioxide	LDO	

epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate	ERL-4221	
bis(3-ethyloxetanylmethyl) ether	DOX	
triethylene glycol divinyl ether	DVE-3	
triethyleneglycol methyl vinyl ether	N/A	

**Table 2**  
**Names, Abbreviations, and Structures of Organosilanes**

Name	Abbreviation	Structure
1,1,3,3,-tetramethyldisiloxane	TMDS	
triethylsilane	TES	
triethoxysilane	TEOS	
n-hexylsilane	n-HS	
dimethylphenylsilane	N/A	
diphenylmethylsilane	N/A	

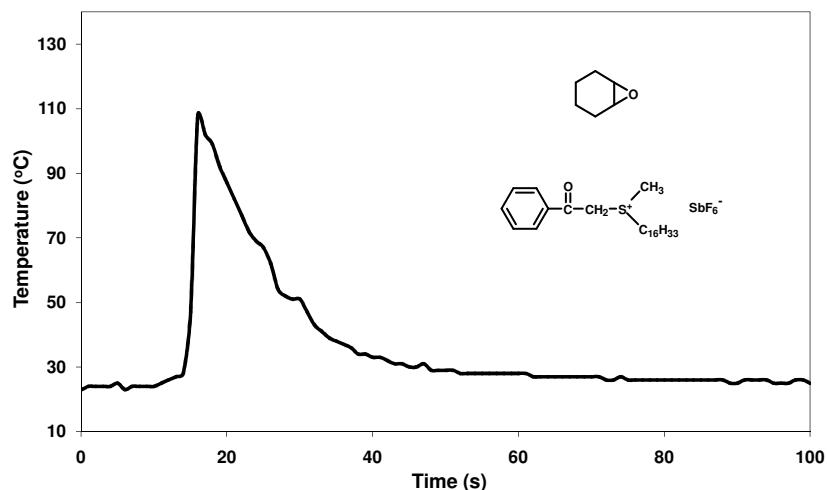
1,3,5,7-tetramethylcyclotetrasiloxane	N/A	
1,3,5,7,9-pentamethylcyclopentasiloxane	N/A	

**Table 3**  
**Names, Abbreviations, and Structures of Phenacylsulfonium Salts**

Name	Abbreviation	Structure
S-methyl-S-n-octyl-S-phenacylsulfonium SbF <sub>6</sub>	DPS-C <sub>1</sub> C <sub>8</sub> SbF <sub>6</sub>	
S-methyl-S-n-hexadecyl-S-phenacylsulfonium SbF <sub>6</sub>	DPS-C <sub>1</sub> C <sub>16</sub> SbF <sub>6</sub>	
S-methyl-S-n-dodecyl-S-phenacylsulfonium SbF <sub>6</sub>	DPS-C <sub>1</sub> C <sub>12</sub> SbF <sub>6</sub>	
S-methyl-S-n-dodecyl-S-phenacylsulfonium PF <sub>6</sub>	DPS-C <sub>1</sub> C <sub>16</sub> PF <sub>6</sub>	
S-methyl-S-n-dodecyl-S-phenacylsulfonium AsF <sub>6</sub>	DPS-C <sub>1</sub> C <sub>16</sub> AsF <sub>6</sub>	
S-pentamethylene-S-phenacylsulfonium SbF <sub>6</sub>	N/A	
S(4-n-decyloxyphenyl)-S,S-diphenylsulfonium SbF <sub>6</sub>	SOC-10 SbF <sub>6</sub>	
Triphenylsulfonium SbF <sub>6</sub>	TPS SbF <sub>6</sub>	

#### 4. Discussion

It was of great interest to determine whether DPS, together with an organosilane, can act as a reduction-oxidation system to create a cationic initiator. Because the reduction potential of DPS ( $E_{\text{red}} = -14.5 \text{ k-cal/mol}$ )<sup>32</sup> is between that of triarylsulfonium and diaryliodonium salts, it was reasonable to predict that DPS would undergo facile reduction by silanes. Because DPS dissolved in inert solvents such as dichloromethane did not spontaneously react with silanes, we attempted to catalyze the redox reactions with noble metals. Parts per million levels of Karstedt catalyst, composed of a platinum(0) complex with two moles of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane in xylene, were observed to catalyze the redox reaction. A highly acidic solution was formed when DPS- $\text{C}_1\text{C}_8 \text{SbF}_6$  was combined with 1,1,3,3-tetramethyldisiloxane (TMDS) in the presence of 8 ppm of the Karstedt catalyst at room temperature. When a small amount of this solution was added to bulk cyclohexene oxide, almost immediate, exothermic polymerization occurred. An OP study of this polymerization is shown in Figure 2; following a 16 second induction period, TMDS was added as a vapor to a thin (0.2 mm) film of solution containing monomer, DPS- $\text{C}_1\text{C}_8 \text{SbF}_6$ , and Karstedt catalyst. The polymerization of cyclohexene oxide monomers had finished in approximately 25 s and had reached a maximum temperature of 110 °C.



**FIGURE 2.** OP study of the polymerization of cyclohexene oxide with 3.0% DPS- $\text{C}_1\text{C}_{16} \text{SbF}_6$  and 8 ppm Karstedt catalyst using 1,1,3,3-tetramethyldisiloxane (TMDS) as the reducing agent.

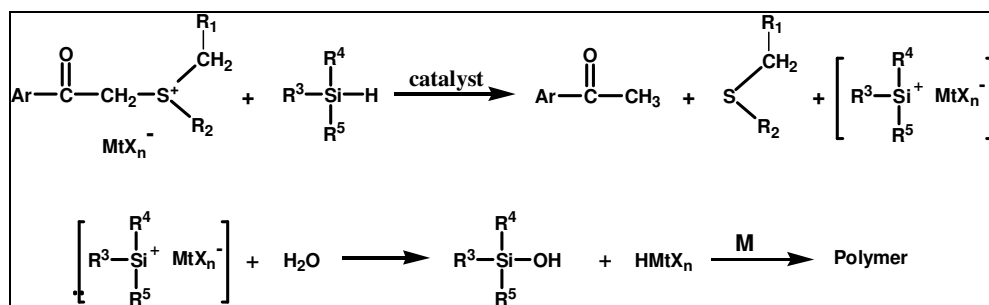


These results suggest that the species that initiates polymerization is long-lived, thereby ruling out silicenium or carbenium ions as the initiating species. It also provides evidence to suggest that a Lewis or Brønsted acid acts as the initiating species. When nitrobenzene was substituted for dichloromethane in the aforementioned polymerization, an identical thermographic analysis (OP diagram) was obtained. Nitrobenzene is a well-known inhibitor/retarder for free radical reactions; this provides strong evidence for the existence of an ionic, rather than a radical, reaction. Additionally, when 0.5% 2,6-di-*t*-butylpyridine, a compound known as a proton trap, was present in a solution containing triethylsilane, cyclohexene oxide, 2.0 % of DPS-C<sub>1</sub>C<sub>8</sub> SbF<sub>6</sub> and 4 ppm Karstedt catalyst, polymerization did not occur; this also supports the conclusion that the initiating species is a Brønsted acid. Further evidence to refute radical initiators may be provided by placing acrylate monomers in the presence of DPS-silane-catalyst redox systems; epoxides and vinyl ethers are readily polymerized by these systems, whereas acrylate monomers (e.g. trimethylolpropane triacrylate) did not react under the same conditions.

To provide insight into the mechanism of the cationic redox initiator system, a dichloromethane solution containing 2% DPS-C<sub>1</sub>C<sub>8</sub> SbF<sub>6</sub>, 0.020 g triethylsilane and 4 ppm Cl<sub>2</sub>(COD)Pd(II) as a catalyst was prepared, allowed to react for 1 hr at room temperature and then subjected to analysis on a Shimadzu QP5000 Gas Chromatograph-Mass Spectrometer equipped with 10 m phenyl silicone capillary columns. GC peaks at 120 and 160 M/e were identified respectively as acetophenone and methyl *n*-octyl sulfide by direct comparison with authentic samples of these compounds. A similar solution was prepared in CDCl<sub>3</sub> and then analyzed by <sup>29</sup>Si NMR on a Varian Unity 500 MHz Nuclear Magnetic Resonance Spectrometer; the NMR results were inconclusive.

Considering the aforementioned evidence and the work of Chojnowski et al.<sup>24</sup>, we propose the mechanism displayed in Scheme 3 for the redox interaction between DPS and Si-H containing silanes and the subsequent ability of this redox couple to initiate cationic polymerizations. Initially, the noble metal complex catalyst mediates the attack of the hydride anion derived from silane on the DPS. This attack fragments the DPS, forming the corresponding aryl methyl ketone, dialkyl sulfide, and an intermediate species that exhibits “silicenium ion-like” behavior. Reports have indicated the formation of silicenium ions from similar reduction reactions<sup>33</sup>. It is reasonable to

assume the formation of a fleeting silicenium ion rather than its carbenium ion counterpart due to its increased stability<sup>34</sup>. However, the formation of free silicenium ions remains controversial<sup>35,36,37</sup>. The “silicenium-like ion” rapidly reacts with traces of water or other protonic impurities to create Brønsted acid, HMtX<sub>n</sub>. We propose that this acid acts as the initiator for cationic polymerizations.

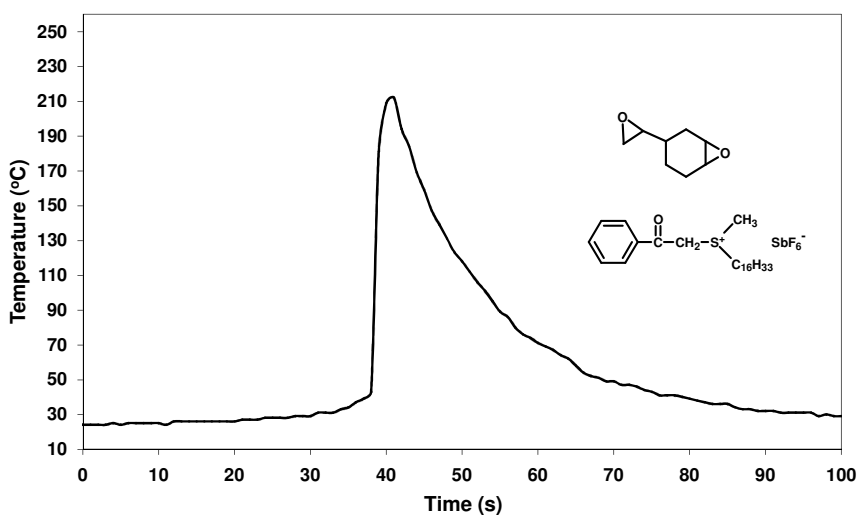


**FIGURE 3.** Proposed mechanism for the DPS-silane redox couple; MtX<sub>n</sub><sup>-</sup> = BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, (C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>B<sup>-</sup>; M = Cationically Polymerizable Monomer; R<sub>1</sub>,R<sub>2</sub> = Alkyl Groups; R<sub>3</sub>,R<sub>4</sub>,R<sub>5</sub> = Alkyl or Alkoxy groups.

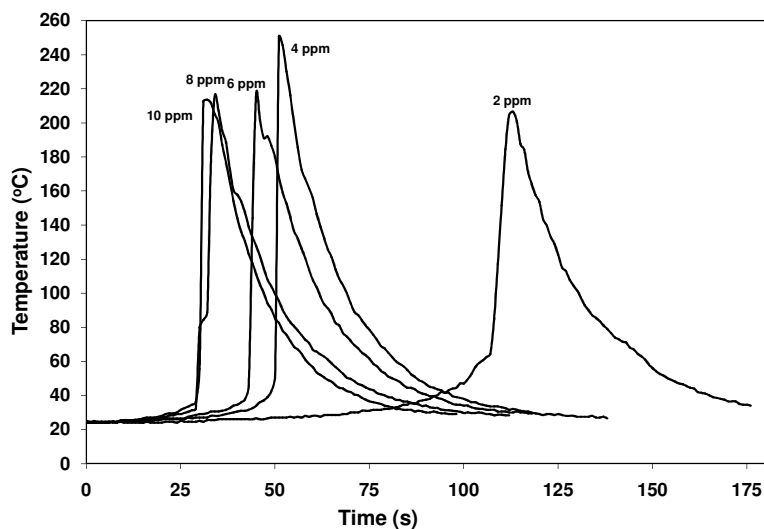
The DPS-organosilane redox couple is a complex three-component system consisting of a DPS, an organosilane and a noble metal complex that acts as a catalyst. Investigation and optimization of the influences of the structures and concentrations of these three components is of considerable importance. One must also consider the influence of a monomer, reaction temperature and other various experimental factors. Optical pyrometry was used as a rapid screening method to detail the effects of the reaction parameters.

Using a stock solution of 3.0 % DPS-C<sub>1</sub>C<sub>16</sub> SbF<sub>6</sub> in 4-vinyl-1,2-cyclohexene dioxide (VCHDO), 0.5 ml aliquots of various noble metal complexes were screened by means of optical pyrometry. The heat released by the polymerization of the monomer was monitored; this was used to investigate the extent to which the noble metal complexes affected the polymerizations. Due to its commercial availability, stability and ease of use, we screened Karstedt catalyst as the noble metal catalyst. As the OP study of this polymerization illustrates (Figure 4), the Karstedt catalyst<sup>38</sup> at the 2-8 ppm Pt level is an excellent catalyst for the reduction of DPS-C<sub>1</sub>C<sub>16</sub> SbF<sub>6</sub> by 1,1,3,3-tetramethyldisiloxane (TMDS). As shown by Figure 5, there is a clear trend associated

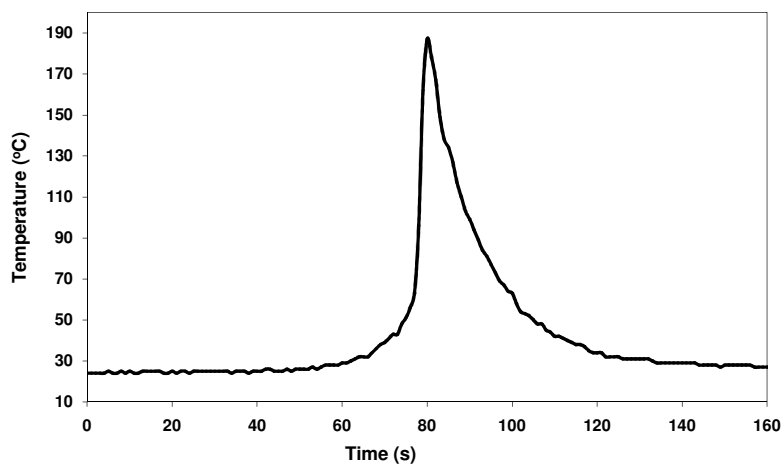
with the concentration of Karstedt catalyst to the induction period; as the concentration of catalyst increases, the length of the induction period decreases. The trend appears to reach a maximum around 8 ppm because additional increments of the concentration of catalyst did not significantly decrease the induction period. Another excellent catalyst is the palladium complex  $\text{Cl}_2(\text{COD})\text{Pd}(\text{II})$ ; an OP study of this noble metal complex catalyzing the silane reduction of DPS salts is shown in Figure 6. Some catalysts, such as the dimeric rhodium and iridium complexes,  $[\text{Cl}(\text{CO})_2\text{Rh}(\text{I})]_2$ ,  $[\text{Cl}(\text{NBD})\text{Rh}(\text{I})]_2$  and  $[\text{Cl}(\text{COD})\text{Ir}(\text{I})]_2$  displayed high activity, while the ruthenium complex  $\text{Cl}_2(\text{CO})_2(\text{Ph}_3\text{P})_2\text{Ru}(\text{II})$  was inactive as a catalyst.



**FIGURE 4.** OP study of the polymerization of VCHDO with 3.0% DPS- $\text{C}_{16}\text{SbF}_6$  and 8 ppm Karstedt catalyst using TMDS as the reducing agent.



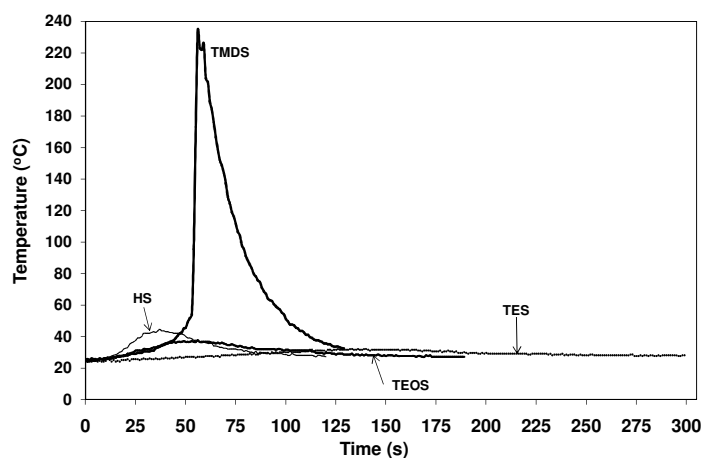
**FIGURE 5.** Effect of the Karstedt catalyst concentration on the polymerization of VCHDO using 3.0% DPS-C<sub>1</sub>C<sub>16</sub> SbF<sub>6</sub> and TMDS as the reducing agent.



**FIGURE 6.** OP study of the polymerization of VCHDO with 3.0% DPS-C<sub>1</sub>C<sub>16</sub> SbF<sub>6</sub> and 8 ppm Cl<sub>2</sub>(COD)Pd(II) using TMDS as the reducing agent.

Figure 7 shows the compilation of our OP investigations into the effect of the structure of the organosilanes used in this redox initiator. Each OP study focuses on a distinct silane vapor inducing the polymerization of VCHDO with DPS-C<sub>1</sub>C<sub>16</sub> SbF<sub>6</sub> and Karstedt catalyst. As illustrated by Figure 7, TMDS is clearly the most superior reducing agent; this could be because of its high volatility and low boiling point (b.p. 70-71 °C) or

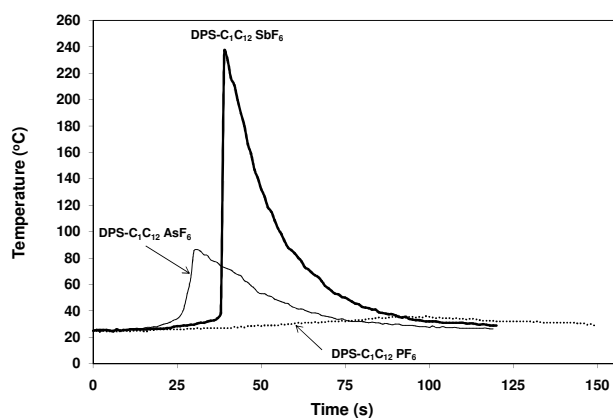
because the molecule bears two Si-H bonds instead of one. Even though there are three Si-H groups per molecule on n-Hexylsilane (HS), its lower volatility and higher boiling point (b.p. 114-115 °C) could account for why the polymerization did not proceed to completion. This same reasoning could account for the low order of reactivity of both triethoxysilane (TEOS, 134-135 °C) and triethylsilane (TES, b.p. 107-108 °C). However, when TMDS is added as a liquid to VCHDO monomer, DPS-C<sub>1</sub>C<sub>16</sub> SbF<sub>6</sub> and Karstedt catalyst, the polymerizations proceeded very rapidly and vigorously. Other organosilanes, including dimethylphenylsilane, diphenylmethylsilane, 1,3,5,7-tetramethylcyclotetrasiloxane and 1,3,5,7,9-pentamethylcyclopentasiloxane, were also found to be active reducing agents for DPS in the presence of a noble metal catalyst.



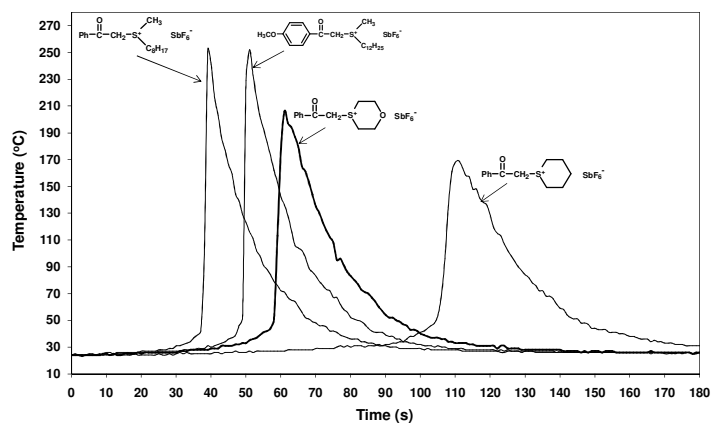
**FIGURE 7.** Polymerization of VCHDO with 3.0% DPS-C<sub>1</sub>C<sub>16</sub> SbF<sub>6</sub>, 8 ppm Karstedt catalyst using triethoxysilane (TEOS), n-hexylsilane (HS), triethylsilane (TES) and 1,1,3,3-tetramethyldisiloxane (TMDS) as reducing agents

It was also of interest to evaluate the relative reactivity of each phenacylsulfonium salt. Using VCHDO as the monomer in addition to TMDS and Karstedt catalyst, we compared the OP studies of DPS-C<sub>1</sub>C<sub>12</sub> salts bearing different anions. As shown in Figure 8, DPS-C<sub>1</sub>C<sub>12</sub> SbF<sub>6</sub> is clearly more reactive than the corresponding AsF<sub>6</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup> salts. A similar trend was found in photopolymerizations of epoxides that used the same onium salts<sup>28</sup>. Again using TMDS and Karstedt, we examined the effects of differentiating the DPS cation on the polymerizations of VCHDO. As illustrated in Figure 9, each of the four DPS salts nearly had the same

effect on the polymerizations; the reasons for the slight differences in reactivity are unknown.



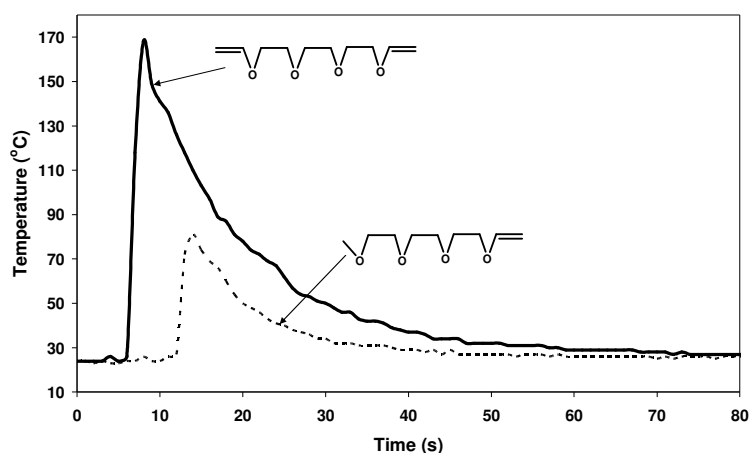
**FIGURE 8.** Comparison of the polymerization of VCHDO with 3.0% DPS-C<sub>1</sub>C<sub>12</sub> SbF<sub>6</sub>, DPS-C<sub>1</sub>C<sub>12</sub> AsF<sub>6</sub>, and DPS-C<sub>1</sub>C<sub>12</sub> PF<sub>6</sub>, using 8 ppm Karstedt catalyst with TMDS as the reducing agent.



**FIGURE 9.** Comparison of the polymerization of VCHDO with 3.0% of various DPS SbF<sub>6</sub> salts using 8 ppm Karstedt catalyst with TMDS as the reducing agent.

We also examined the effects that monomers have on the polymerization system. Similar to the other cycloaliphatic epoxide monomers CHO, VCHO, and VCHDO, the polymerization of limonene dioxide is exothermic and has a very short induction period.

In comparison, the bicyclic aliphatic ester containing monomer, 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate (ERL-4221) and the dioxetane monomer, bis(3-ethyloxetanylmethyl) ether (DOX) are considerably less reactive. However, both monomers polymerize violently and rapidly when TMDS is added to the neat monomers containing 3.0 %. DPS-C<sub>1</sub>C<sub>12</sub> SbF<sub>6</sub> with 16 ppm of the Karstedt catalyst. Figure 10 shows an OP study of the TMDS vapor-induced cationic polymerizations of triethyleneglycol divinyl ether (DVE-3) and triethyleneglycol methyl vinyl ether carried out using 3.0 % DPS-C<sub>1</sub>C<sub>12</sub> SbF<sub>6</sub> with 16 ppm of Cl<sub>2</sub>(COD)Pd(II) as a catalyst. The polymerizations of these two vinyl ether monomers are rapid, exothermic and proceed with only a short induction period. The more rapid and exothermic polymerization of DVE-3 is due to the fact that it is a difunctional vinyl ether monomer.



**FIGURE 10.** Polymerizations of DVE-3 and triethyleneglycol methyl vinyl ether with 3.0 % DPS-C<sub>1</sub>C<sub>16</sub> SbF<sub>6</sub>, 16 ppm Cl<sub>2</sub>(COD)Pd(II) using TMDS as the reducing agent.

There are multiple applications for redox systems that are initiators for cationic polymerizations; these applications revolve around their ability to polymerize as thin crosslinked polymer films. Among these are the application and cure of surface coatings such as paints and lacquers, the formation of pressure sensitive adhesives and the rapid cure of ink jet and conventional printing inks. Included is the application and cure of fiber optic coatings. Also of interest is the deposition and cure of dielectric films on electronic components, the encapsulation of microelectronic components and for thin film composite applications. Each of these areas of potential use takes advantage of the

separable two-component systems described in this paper in which the silane is delivered in the vapor state to the monomer containing a triarylsulfonium salt and a noble metal complex catalyst.

## **5. Conclusions**

Catalyzed by noble metals, silanes reduce S,S-dialkyl-S-phenacylsulfonium salts to produce a Brønsted acid that acts as the initiator of cationic vinyl and ring-opening polymerizations under solution and bulk conditions. This novel cationic polymerization also offers the possibility of being triggered by exposure to the vaporized silane. As previously discussed, the polymerization of the monomers is rapid and exothermic. Optical pyrometry (infrared thermography) is used to monitor the progress of these cationic polymerizations.



## LITERATURE CITED

1. Moad, G.; Solomon, D.H. *The Chemistry of Radical Polymerization*; Elsevier, New York, 2006; pp. 85-106.
2. Crivello, J.V.; Lam, J.H.W. *J. Polym. Sci. Part A: Polym. Chem.* **1981**, *19*, 539.
3. Crivello, J.V.; Lee, J.L. *J. Polym. Sci. Part A: Polym. Chem.* **1983**, *21*(4), 1097.
4. Crivello, J.V.; Lee, J.L. *Makromol Chem* **1983**, *184*, 463.
5. Gandini, A.; Cheredame, H. *Cationic Polymerization of Alkenyl Monomers, Adv. Polym. Sci.* *34/35*, Springer-Verlag, New York, 1980, pp. 6-9.
6. Penczek, S.; Kubisa, P.; Matyjaszewski, K. *Cationic Ring-Opening Polymerization of Heterocyclic Monomers, Adv. Polym. Sci.* *37*, Springer-Verlag, New York, 1980, pp. 8-10.
7. Ledwith, A. *Polymer* **1978**, *19*, 1217.
8. Klemm, E.; Flammersheim, H.-J.; Märtin, R.; Hörhold, H.-H. *Angew Makromol Chem.* **1985**, 135.
9. Baumann, H.; Timpe, H.-J. *Z. Chem.* **1984**, *24*, 18.
10. Baumann, H.; Timpe, H.-J. *J. Prakt. Chem.* **1984**, *326*, 529.
11. Timpe, H.-J.; Merckel, C.; Baumann, H. *Makromol. Chem.* **1986**, *187*, 187.
12. Yagci, Y.; Ledwith, A. *J. Polym. Sci. Part A: Polym. Chem.* **1988**, *26*, 1911.
13. Dursun, C.; Degirmenci, M.; Yagci, Y.; Jockusch, S.; Turro, N.J. *Polymer* **2003**, *44*, 7389.
14. Degirmenci, M.; Hepuzer, Y.; Yagci, Y. *J. Appl. Polym. Sci.* **2002**, *85*, 2389.
15. Yagci, Y.; Kminek, I.; Schnabel, W. *Eur. Polym. J.* **1992**, *28*, 387.
16. Yagci, Y.; Kminek, I.; Schnabel, W. *Polymer*, **1993**, *34*, 426.
17. Durmaz, Y.Y.; Moszner, N.; Yagci, Y. *Macromolecules* **2008**, *41*, 6714.
18. Lalevéé, J.; Blanchard, N.; El-Roz, M.; Graff, B.; Allonas, X.; Fouassier, J.P. *Macromolecules* **2008**, *41*, 4180.
19. Lalevéé, J.; El-Roz, M.; Graff, B.; Allonas, X.; Fouassier, J.P. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*(9), 3042.

20. Lalevée, J.; Dirani, A.; El-Roz, M.; Allonas, X.; Fouassier, J.P. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*(6), 2008.
21. Crivello, J.V.; Lee, J.L. *Polym. J.* **1985**, *17*(1), 73.
22. Crivello, J.V. *J. Polym. Sci., Part A: Polym. Chem.* *in press*.
23. Crivello, J.V. *Silicon*, *submitted*.
24. Chojnowski, J.; Fortuniak, W.; Stanczyk, W. *J. Am. Chem. Soc.* **1987**, *109*, 7776.
25. Crivello, J.V.; Lam, J.H.W. *J. Polym. Sci. Part A: Polym. Chem.* **1979**, *17*, 2877.
26. Falk, B.; Vallinas, S. M; Crivello, J.V. *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *41*(4), 579.
27. Crivello, J.V.; Falk, B.; Vallinas, S.M *Polym. Mater. Sci. Eng. Prepr.* **2003**, *88*, 209.
28. Crivello, J.V.; Falk, B.; Jang, M.; Zonca, Jr., M.R.; Vallinas, S. M *RadTech Report*, **2004**, *May/June*, 36-43.
29. Crivello, J.V.; Kong, S. *Macromolecules*, **2000**, *33*(3), 825.
30. Akhtar, S.R.; Crivello, J.V.; Lee, J.L.; Schmitt, M.L. *Chem. Mater.* **1990**, *2*(6) 732.
31. Wildi, D.S.; Taylor, S.W.; Potratz, H.A. *J. Am. Chem. Soc.* **1951**, *73* 1965.
32. Saveant, J.M. *C.R. Hebd. Seances. Acad. Sci. Ser. C* **1964**, *258*, 585.
33. Kursanov, D.N.; Parnes, Z.N.; Loim, N.M. *Synthesis*, **1974**, *9*, 633.
34. Carey, F.A.; Tremper, H.S. *J. Am. Chem. Soc.* **1968**, *90*, 2578.
35. Eaborn, C. *J. Organomet. Chem.* **1991**, *405*, 173
36. Lambert, J.B.; Zhang, S.; Stern, C.L.; Huffman, J.C. *Science* **1993**, *260*, 1917
37. Karstedt, B.D. U.S. Patent 3,715,334 (Feb. 6, 1973) to General Electric Corp.