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ARTICLE

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

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ABSTRACT: *S*,*S*-Dialkyl-*S*-phenacylsulfonium salts undergo facile reduction by silanes bearing Si−H groups in the presence of a noble metal catalyst. This redox couple can be employed as a convenient initiator system 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. In this communication we also report the novel use of a two-component redox system in which the silane is delivered as a vapor to a thin film monomer sample containing the sulfonium salt. Typically, the polymerizations are rapid and exothermic. The use of optical pyrometry (infrared thermography) as a convenient method with which to monitor and optimize the aforementioned cationic polymerizations is described. Studies of the effects of variations in the structures of the *S*,*S*-dialkyl-*S*-phenacylsulfonium salt, the silane and the type of noble metal catalyst on the polymerizations of typical vinyl and heterocyclic monomers were carried out.

Introduction

Redox systems that generate free radicals are well-known[1] and in widespread use for a number of commercial applications including the production of vinyl polymers by emulsion polymerizations and in the manufacture of composite boats, bathroom enclosures, countertops, etc. by the cross-linking polymerization of unsaturated polyester-styrene mixtures The virtues of free radical redox initiating systems are many. Since redox reactions proceed with low activation energies, these initiators can be used at room temperature and below. In many cases, inorganic salts can be used as the components of a redox couple which allows polymerizations to be conducted in aqueous media. The oxidant and reducing agents used in redox initiator systems are very stable and can be stored without refrigeration. Lastly, typical free radical redox systems are highly cost-effective.

In contrast to their free radical counterparts, redox systems capable of initiating cationic polymerization are less well-known. Early work in this laboratory showed that diaryliodonium salts can be employed as oxidants together with reducing agents such as ascorbic acid,[2] benzoin,[3] or stannous octoate[4] to initiate cationic polymerizations at temperatures as low as 25 °C. As an example, the reaction of a diphenyliodonium salt with benzoin and mediated by a copper catalyst is given in eq 1 of Scheme 1. Along with the organic products produced by this redox couple, an acid, $HMtX_n$, is generated that is derived from the anion of the starting diphenyliodonium salt. Typically, diaryliodonium salts are selected so that a super acid such as HPF_6, HBF_4, or $HSbF_6$ is formed during this reaction. These strong Brønsted acids are well-known initiators of both cationic vinyl and heterocyclic ring-opening polymerizations (eqs 2 and 3).[5,6]

A number of research groups including those of Ledwith,[7] Timpe and Baumann,[8−12] Yagci,[13−17] and Fouassier[18−20] have shown that free radicals generated either by thermolytic or by photolytic methods can be used as reducing agents for diaryliodonium salts. The use of such combination systems were subsequently employed as initiators for cationic polymerization. Thus far, attempts to employ these same methods for the corresponding reduction of triarylsulfonium salts have met with limited success. This can be attributed to the considerably greater difficulty of reducing triarylsulfonium salts ($E_{red} = -28$ kcal mol^{-1})[21] as compared to diaryliodonium salts ($E_{red} = -5$ kcal mol^{-1}).[1] Although technically these methods can be classified as redox systems, they do not take place spontaneously and require an external stimulus (heat or light) for reaction to take place.

Very recently, two new cationic redox systems were described in publications from this laboratory[22,23] that are capable of initiating cationic polymerizations spontaneously at room temperature. These redox systems consist of a diaryliodonium or a triarylsulfonium salt as the oxidant with an organosilane bearing a Si−H group as the reducing agent. The reactions are catalyzed by noble metal complexes such as those of platinum, palladium and rhodium. In 1987 Chojnowski et al.[24] reported that silicon hydrides reduce trityl salts in the absence of a catalyst. The products of the reaction were triphenylmethane and the corresponding fluorosilane. On the basis of this and other evidence they proposed that the reaction proceeds through a mechanism involving the formation of solvated silicenium ion intermediates (**I**) as shown in eq 4 of Scheme 2. In the absence of other reactants, they proposed that the highly electrophilic silicenium ion abstracts a fluorine atom from the anion resulting in the formation of the observed fluorosilane and antimony pentafluoride (eq 5). Thereafter, these latter two products undergo secondary reactions to give unspecified products (eq 6).

The reduction of diaryliodonium and triarylsulfonium salts by silanes is expected to share some commonality with the work of Chojnowski et al. It was of further interest to determine whether this approach to the design of cationic redox initiator systems is limited to diaryliodonium and triarylsulfonium salts or whether it can be extended to other types of onium salts as well. In this communication we report the development of novel cationic redox initiator systems

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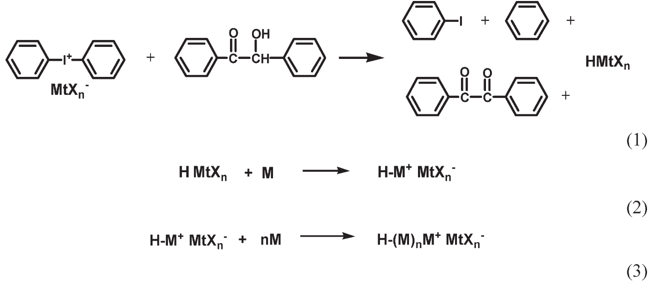
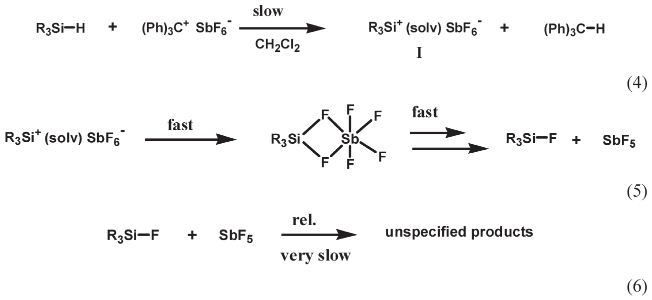
Scheme 1. Mechanism of the Initiation of Cationic Polymerization Using the Diphenyliodonium Salt−Benzoin Redox System



Scheme 2



based on silanes together with *S*,*S*-dialkyl-*S*-phenacylsulfonium salts and explore their use in the polymerizations of vinyl and heterocyclic monomers.

Experimental Section

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-Epoxycyclohexylmethyl 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 CaH_2.

The *S*,*S*-dialkyl-*S*-phenacylsulfonium salts (DPS)[25] and S(4-*n*-decyloxyphenyl)-*S*,*S*-diphenylsulfonium hexafluoroantimonate (SOC-10 SbF_6),[26] were synthesized and purified by a previously described method. Triphenylsulfonium SbF_6 was prepared according to the method of Potratz et al.[27]

The structures, names and abbreviations of all the onium salts, silanes and the monomers described in this communication are given in Table 1.

Analyses. A dichloromethane solution containing 2% DPS−C_1C_8 SbF_6, 0.020 g triethylsilane and 4 ppm $Cl_2(COD)Pd^{II}$ as a catalyst was prepared, allowed to react for 1 h at room temperature and then subjected to analysis on a Shimadzu QP5000 gas chromatograph−mass spectrometer equipped with 10 m phenyl silicone capillary columns. The products were identified by comparison with authentic samples of acetophenone and methyl *n*-octyl sulfide. A similar solution was prepared in $CDCl_3$ and then analyzed by ^{29}Si NMR on a Varian Unity 500 MHz nuclear magnetic resonance spectrometer. Molecular weight measurements were made on a Waters 2410 gel permeation chromatograph equipped with a refractive index detector and Viscotec SDVE (5 μm pores) columns. The reported molecular weights were calculated using polystyrene standards.

Solution Redox Cationic Polymerization of Cyclohexene Oxide. Into a clean dry 4 dram amber screw cap vial equipped with a Teflon microstirbar and fitted with a with a polyethylene liner were placed 1.96 g (0.02 mol) distilled cyclohexene oxide, 0.0284 g (5×10^{-5} mol) DPS−C_1C_8 SbF_6 and 1.0 g dichloromethane. There were added by syringe 100 μL 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 h 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 THF gave a M_n = 11000 g/mol based on polystyrene standards.

Optical Pyrometry (OP). General descriptions of the apparatus configuration, sampling and analytical techniques used in the optical pyrometric analysis for photopolymerization reactions were given in previous publications from this laboratory.[28−30] Figure 1 shows a schematic diagram of the basic OP apparatus together with the modifications made for conducting redox polymerization studies using a volatile silane reducing agent. The liquid sample is absorbed into a thin (0.2 mm) 15 mm × 15 mm sheet of nonwoven polyester fabric (veil) placed on a thin (0.25 mm) fluorinated polyethylene film mounted in a plastic 2 cm × 2 cm slide frame. The slide frame was placed into a recessed sample holder and a 8.5 cm diameter × 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. A 1 cm diameter 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. To initiate polymerization, a small amount (0.3 mL) of the designated silane reducing agent was injected into a cell filled with glass wool to enhance 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.

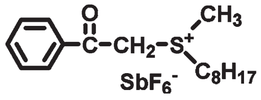
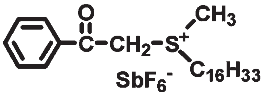
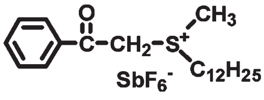
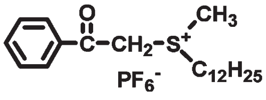
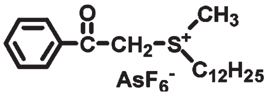
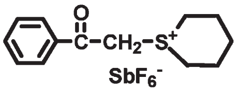
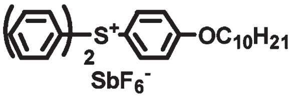
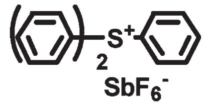
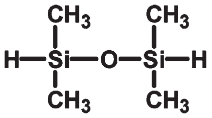
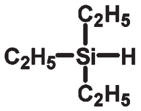
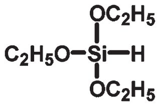
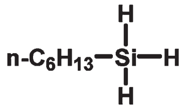
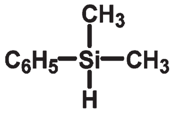
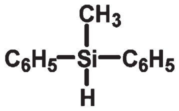
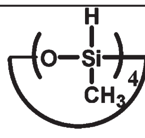
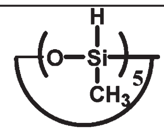
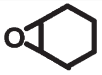
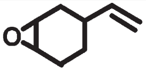
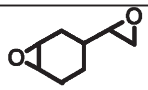
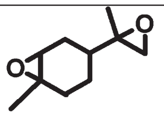
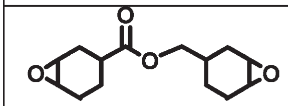
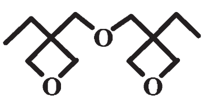
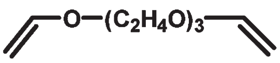
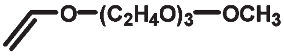
Samples for OP analysis were prepared by dissolving the sulfonium salt in the appropriate monomer and adding the noble metal catalyst to the resulting solution by syringe. The commercially available Karstedt and Lammoreau catalysts were purchased as solutions in which the platinum contents were listed as 2.0−2.5% in both cases. Thus, when these solutions were used, the amounts used are given in ppm of Pt. When the well characterized $Cl_2(COD)Pd^{II}$ 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 sensitivity of the OP technique is largely determined by the infrared camera that is used. In these experiments, an Omega Corp. Model OS 552-V1-6 infrared camera with a sensitivity of ±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.

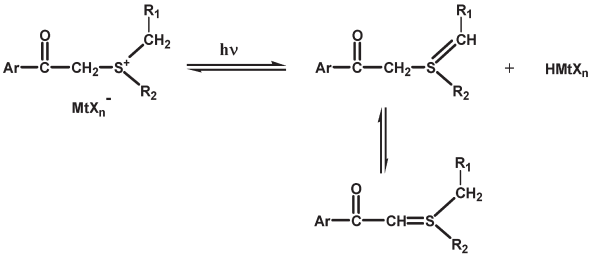
Results and Discussion

***S*,*S*-Dialkyl-*S*-phenacylsulfonium Salts.** *S*,*S*-Dialkyl-*S*-phenacylsulfonium salts (DPS) bearing anions, MtX_n^-,

Table 1. Structures of Sulfonium Salts, Silanes, and Monomer

Onium Salts			
 **DPS-C_1C_8 SbF_6** S-methyl-S-n-octyl-S-phenacylsulfonium SbF_6	 **DPS-C_1C_{16} SbF_6** S-methyl-S-n-hexadecyl-S-phenacylsulfonium SbF_6	 **DPS-C_1C_{12} SbF_6** S-methyl-S-n-dodecyl-S-phenacylsulfonium SbF_6	 **DPS-C_1C_{16} PF_6** S-methyl-S-n-dodecyl-S-phenacylsulfonium PF_6
 **DPS-C_1C_{16} AsF_6** S-methyl-S-n-dodecyl-S-phenacylsulfonium AsF_6	 S-pentamethylene-S-phenacyl-sulfonium SbF_6	 **SOC-10 SbF_6** S(4-n-decyloxyphenyl)-S,S-diphenylsulfonium SbF_6	 **TPS SbF_6** triphenylsulfoniium SbF_6
Silanes			
 **TMDS** 1,1,3,3,tetramethyldisiloxane	 **TES** triethylsilane	 **TEOS** triethoxysilane	 **n-HS** n-hexylsilane
 dimethylphenylsilane	 diphenylmethylsilane	 1,3,5,7-tetramethylcyclotetrasiloxane	 1,3,5,7,9-pentamethylcyclopentasiloxane
Monomers			
 **CHO** cyclohexene oxide	 **VCHO** 4-vinylcyclohexene-1,2-oxide	 **VCHDO** 4-vinylcyclohexene-dioxide	 **LDO** limonene dioxde
 **ERL-4221** 3,4-epoxycyclohexylmethyl 3',4'epoxycyclohexane carboxylate	 **DOX** bis(3-ethyloxetanylmethyl) ether	 **DVE-3®** triethylene glycol divinyl ether	 triethyleneglycol methyl vinyl ether

of low nucleophilic character were first reported in a publication from this laboratory to be an efficient and useful class of cationic photoinitiators.[31] An investigation of their photolysis (eq 7) showed that on UV irradiation these compounds undergo a photoinduced elimination reaction by a Norrish type II process to generate an ylide and a Brønsted acid. On standing and in the absence of a reactant, a dark reaction involving the recombination of these two products takes place to regenerate the original salt.



(7)

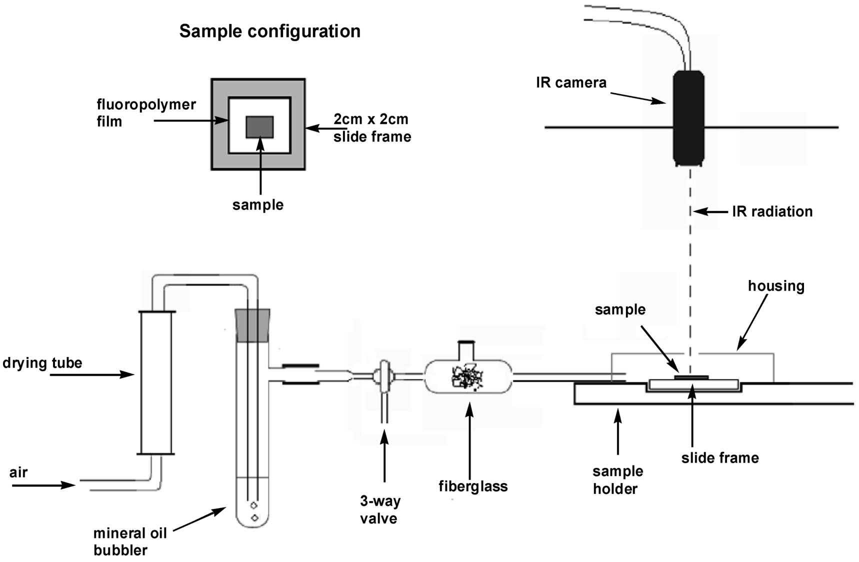
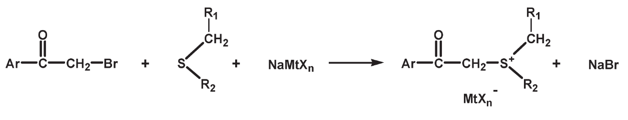


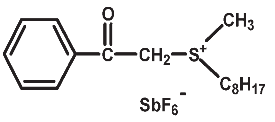
Figure 1. Optical pyrometry apparatus modified for redox cationic polymerization studies.

While the observation of the excellent photosensitivity and photoinitiating characteristics of *S*,*S*-dialkyl-*S*-phenacylsulfonium salts was interesting, these compounds received very little further interest because the synthetic route to these compounds was inconvenient, restricted only to certain members of this class of compounds and gave low yields of the desired compounds. Further, the solubility of these compounds in monomers of interest was rather poor. However, this situation radically altered when a new synthetic method for these compounds was developed which resolved all of the above issues.[25] The new synthetic pathway is shown in eq 8. The simple and direct synthesis is usually carried out in acetone or methyl ethyl ketone giving high yields of pure DPS bearing long linear or branched alkyl groups. Of particular interest are unsymmetrical DPS that display excellent solubility characteristics even in monomers of low polarity.



$$\mathrm{Ar{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}Br} + \mathrm{S(CH_2R_1)(R_2)} + \mathrm{NaMtX_n} \longrightarrow \mathrm{Ar{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}S^{+}(CH_2R_1)(R_2)\ MtX_n^{-}} + \mathrm{NaBr} \qquad (8)$$

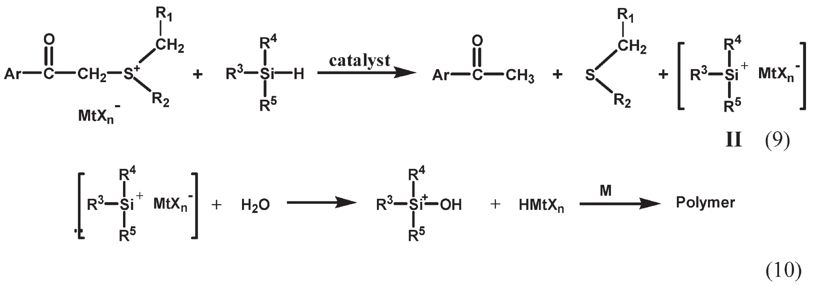
Since the nomenclature of DPS salts is lengthy and complex, a system of abbreviations was developed and is used throughout this communication. The abbreviation is in the form, DPS$-$C$_a$C$_b$ MtX$_n$, where DPS signifies the phenacylsulfonio group, C$_a$ and C$_b$ represent the two alkyl groups, and MtX$_n$ is the accompanying anion. For example, DPS$-$C$_1$C$_8$ SbF$_6$ denotes the compound *S*-methyl-*S*-*n*-octyl-*S*-phenacylsulfonium hexafluoroantimonate. The alkyl groups are assumed to be unbranched unless otherwise specified.



DPS-C$_1$C$_8$ SbF$_6$

Preliminary Evaluation of the DPS$-$Silane Redox Couple. It was of considerable interest to determine whether DPS can be incorporated as oxidants in cationic redox initiator systems with silanes as reducing agents. A search of the literature did not reveal any prior reports of attempts to carry out such reactions. The reduction potentials of DPS ($E_{\mathrm{red}} = -14.5$ kcal mol^{-1})[32] are considerably lower than comparable values for triarylsulfonium salts but higher than for diaryliodonium salts. Using this rationalé, it was predicted that these compounds should undergo facile reduction by silanes. Accordingly, several pilot reactions were carried out. It was observed that DPS dissolved in inert solvents such as dichloromethane did not react spontaneously with silanes. A similar situation was observed with the aforementioned diaryliodonium and triarylsulfonium salts and, therefore, catalysis of the redox reaction was attempted. The commercially available Karstedt catalyst consisting of a solution of a platinum(0) complex with 2 mols of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane in xylene was observed to mediate the redox reaction at levels in the range of parts per million platinum. For example, the reaction between DPS$-$C$_1$C$_8$ SbF$_6$ with 1,1,3,3-tetramethyldisiloxane (TMDS) and 8 ppm of the Karstedt catalyst proceeds very rapidly at room temperature in dichloromethane yielding a highly acidic solution. When small amounts of this solution are added to bulk monomers such as cyclohexene oxide or dodecyl vinyl ether, nearly instantaneous exothermic polymerization was observed. These results suggest that the species that initiates polymerization is long-lived. This would seem to rule out either silicenium ions or carbenium ions and favor either a Lewis or Brønsted acid as the initiating species. Further, when triethylsilane was added to neat cyclohexene oxide containing 2.0% of DPS$-$C$_1$C$_8$ SbF$_6$ and 4 ppm Karstedt catalyst with 0.5% of the proton trap, 2,6-di-*tert*-butylpyridine, no polymerization was noted. This latter experiment indicates that the primary initiators of polymerization are protonic acids rather than Lewis acids or silicenium ions. Mixtures of the DPS and the Karstedt catalyst in dichloromethane gave stable solutions that did not initiate polymerization when added to cyclohexene oxide or other monomers when the silane was omitted. As mentioned previously, DPSs also do not react with silanes in the absence of a noble metal catalyst. When nitrobenzene was substituted for dichloromethane as the solvent for the above redox couple the same results were obtained. Nitrobenzene is a well-known[33] inhibitor/retarder for free radical reactions and this observation lends support to the rationalé that the redox reaction likely takes place by an ionic rather than a free radical reaction. Additional evidence is provided by the

Scheme 3. Proposed Mechanism for the DPS−Silane Redox Couple



observation that typical monomers such as epoxides and vinyl ethers are readily polymerized in the presence of the DPS−silane redox couple whereas typical acrylate monomers (e.g., trimethylolpropane triacrylate) did not react under the same conditions.

To provide additional information about the redox couple, DPS−C_1C_8 SbF_6 was reduced with TMDS in dichloromethane and the reaction mixture analyzed by gas chromatography−mass spectrometry. GC peaks with parent peak masses of at 120 and 160 M/e were identified respectively as acetophenone and methyl *n*-octyl sulfide as products of the reaction on the basis of a comparison with authentic samples of these compounds. Attempts to identify the silicon-containing products using ^{29}Si NMR failed to give definitive results.

On the basis of the above evidence, as well as in analogy with the work of Chojnowski et al.,[24] 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. The first step (eq 9) consists of the noble metal complex catalyst mediated attack of a hydride anion derived from silane on the DPS. Fragmentation of the DPS occurs with the formation of the corresponding aryl methyl ketone, a dialkyl sulfide and a species, **II**, that exhibits "silicenium ion-like" behavior. The formation of silicenium ions in the gas phase derived from silanes has been inferred in various types of reductive reactions[34] and calculations indicate that such species are more stable than the analogous carbenium ions.[35] However, the evidence for free silicenium ions in the condensed phase remains controversial.[36−38] This includes under the conditions described previously by Chojnowski et al.[24] At the present time, we have no data in hand that allows us to unequivocally support or dismiss the formation of such species. This is indicated in 9 by the brackets enclosing **II**.

In subsequent steps (e.g., 10), **II** undergoes rapid secondary reactions with traces of water or other protonic impurities present in the reaction mixture to form the Brønsted acid, $HMtX_n$. We propose that it is this latter acid that is the ultimate initiator of cationic polymerization.

Study of Cationic Polymerizations Using the DPS−Silane Redox Couple. Initial studies of cationic epoxide ring-opening polymerizations using the DPS−silane redox couple as an initiator were carried out in solution. Cyclohexene oxide is an archetypical epoxide monomer that undergoes facile cationic ring-opening polymerization. Polymerization of this monomer proceeds smoothly at room temperature in dichloromethane as the solvent using DPS−C_1C_{16} SbF_6 and the Karstedt catalyst with TMDS as the reducing agent. As described in the Experimental Section of this paper, the poly(cyclohexene oxide) that was obtained had a M_n of 11 000 g/mol. Further optimization of this polymerization was not attempted.

The DPS−silane redox couple is a complex three component system consisting of: a DPS and a silane with a noble metal complex as a catalyst. Investigation and optimization of the influences of the structures and concentrations of these three components appeared to be a considerable task. In addition, the influence of the monomer, reaction temperature, and solvent as well as a variety of additional experimental parameters on the course of the polymerizations that are conducted with the redox couple must be considered. It was apparent that a simple, rapid screening method to facilitate the evaluation of these various parameters was desired. Previously,[22,23] we have reported the use of optical pyrometry (infrared thermography) as a remote monitoring method that takes advantage of the very high polymerization reactivity of the related diaryliodonium and triarylsulfonium salt-silane redox initiator systems. Employing optical pyrometry (OP), the temperature of a thin film liquid monomer sample is remotely and continuously monitored using an infrared camera as a function of time as the polymerization proceeds. The apparatus for conducting OP studies was originally developed for following the course of rapid free radical and cationic photopolymerizations.[28,30] This apparatus was further modified to allow the silane reducing agent to be delivered to the sample in the vapor state. Figure 1 shows a schematic drawing of the modified OP apparatus which is described in detail in the Experimental Section of this paper. When the silane vapor contacts the sample, reduction of the DPS takes place resulting in the release of a Brønsted acid with consequent polymerization of the monomer. Since it has been shown that in the early phases of the polymerization the increase in the temperature of the sample with time is directly proportional to the conversion of the monomer, this provides a simple means for monitoring the progress of the polymerization. To implement this method, a volatile silane reducing agent was required. Fortunately, most low molecular weight Si−H functional silanes are mobile liquids at room temperature with low to moderate temperature boiling points. Silanes with higher boiling points and lower vapor pressures can be accommodated in the OP apparatus by simply applying heat to the trap into which it is injected into the system. An example is shown in Figure 2 in which the polymerization of cyclohexene oxide was conducted using 3.0% DPS−C_1C_{16} SbF_6 and 8 ppm Karstedt catalyst with TMDS as the reducing agent. As can be seen in this figure, there is a brief, 16 s induction period that is followed by very rapid, autoaccelerated polymerization of the monomer. The maximum temperature attained by the thin (0.2 mm) film sample was 110 °C. Essentially, the polymerization was completed within approximately 25 s.

In a similar fashion, a stock solution consisting of 3.0% DPS−C_1C_{16} SbF_6 in 4-vinyl-1,2-cyclohexene dioxide (VCHDO) was prepared, 0.5 mL aliquots taken and various noble metal complexes were added. Each sample was then subjected to analysis by OP as described above using TMDS as the volatile reducing agent. In this manner, the exothermic

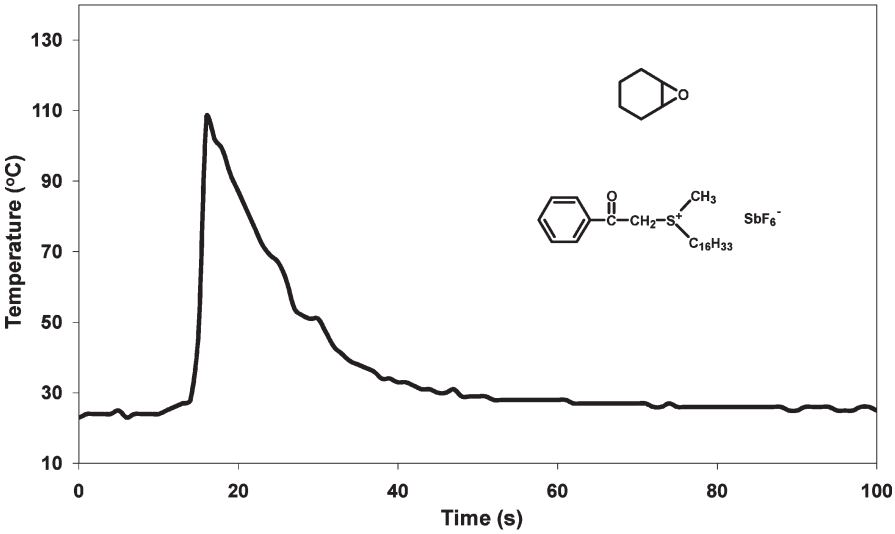


Figure 2. OP study of the polymerization of cyclohexene oxide with 3.0% DPS$-$C$_1$C$_{16}$ SbF$_6$ and 8 ppm Karstedt catalyst using 1,1,3,3-tetramethyldisiloxane (TMDS) as the reducing agent.

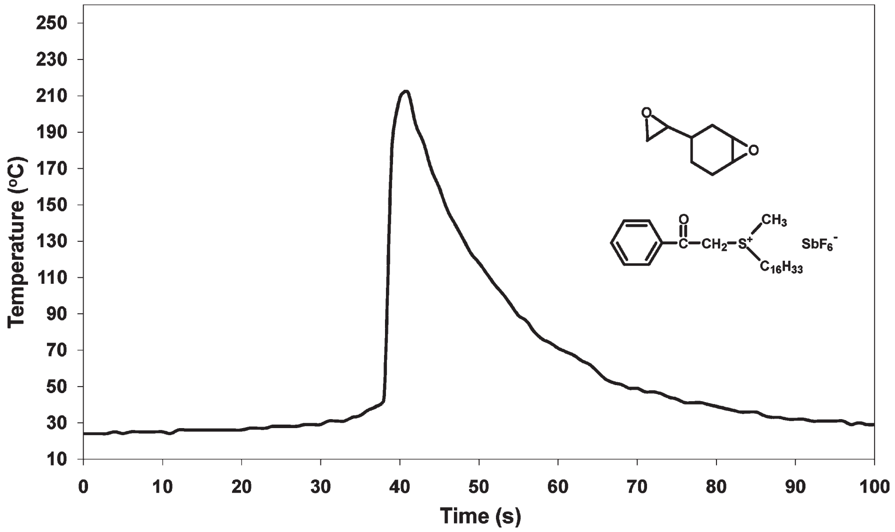


Figure 3. OP study of the polymerization of VCHDO with 3.0% DPS$-$C$_1$C$_{16}$ SbF$_6$ and 8 ppm Karstedt catalyst using TMDS as the reducing agent.

polymerization of the monomer was used as a sensitive probe to screen various noble metal complexes as catalysts for the TMDS reduction of *S*,*S*-dialkyl-*S*-phenacylsulfonium salts. The previously mentioned commercially available Karstedt catalyst[39] was an excellent catalyst at the 2$-$8 ppm Pt level for redox cationic polymerizations involving DPS. Figure 3 shows the results of an OP study using the Karstedt catalyst with VCHDO as the monomer and 1,1,3,3-tetramethyldisiloxane (TMDS) as the reducing agent. The polymerization is preceded by a 40 s induction period and then takes place by a vigorous autoacceleration process that drives the temperature of the thin film sample to an astonishing 230 °C. Other platinum complexes that were active catalysts for this reaction were H_2PtCl_6, $Cl_2(COD)Pt^{II}]_2$, $[Cl(COD)Pt^{I}]_2$ and $Cl_2[(C_2H_5)_2S]_2Pt^{II}$. Less active as catalysts were $Cl_2(C_6H_5CN)_2Pt^{II}$ and $[Cl(COD)Rh^{I}]_2$. Some of the catalysts mentioned above displayed very poor solubility in VCHDO and this may account for their low reactivity. Despite their rather poor solubility, the dimeric rhodium and iridium complexes, $[Cl(CO)_2Rh^{I}]_2$, $[Cl(NBD)Rh^{I}]_2$ and $[Cl(COD)Ir^{I}]_2$ displayed high activity. As can be seen in Figure 4, the palladium complex, $Cl_2(COD)Pd^{II}$, was an excellent catalyst for the silane reduction of DPS salts. This complex was soluble in nitromethane and a 2.0% solution of the complex in this solvent was conveniently used in both solution and bulk monomer polymerizations. The ruthenium complex and $Cl_2(CO)_2(Ph_3P)_2Ru^{II}$ was inactive as a catalyst.

Since the platinum-containing Karstedt catalyst is readily available, highly active, stable and easy to use, we have elected to use this catalyst for most of the studies reported here. Figure 5 shows the results of a study of the effects of varying the concentration of this catalyst on the TMDS vapor-induced polymerization of VCHDO with DPS$-$C$_1$C$_{16}$ SbF$_6$. There is a progressive decrease in the induction period with an incremental increase in the catalyst concentration. The effect appears to reach a maximum at 8 ppm after which little decrease in the induction period is seen. Slight differences observed in the maximum sample polymerization temperatures observed at the different concentrations can be attributed to minor experimental variations such as position and thickness of the sample during the analysis.

It was of interest to evaluate the relative reactivity of various silanes used in this new redox initiator. Accordingly, a series of vapor induced polymerizations of VCHDO with DPS$-$C$_1$C$_{16}$ SbF$_6$ was again carried out at room temperature using four different volatile silane reducing agents. The

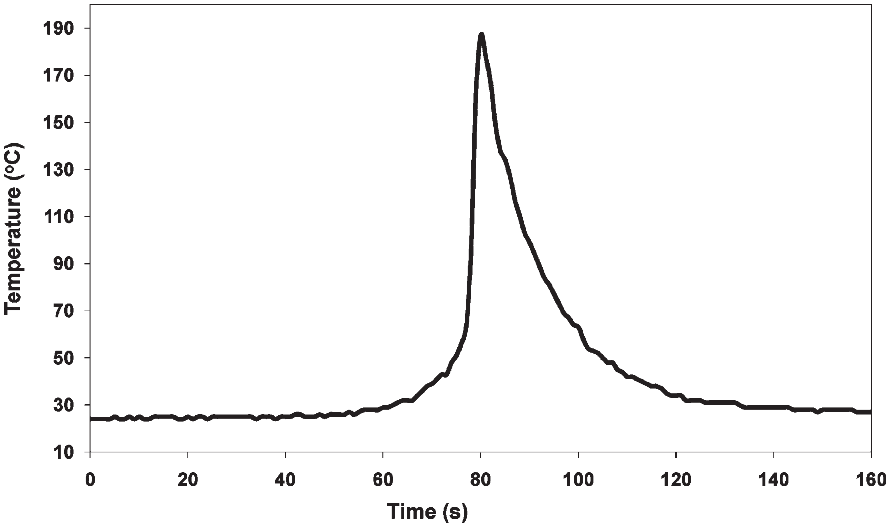


Figure 4. OP study of the polymerization of VCHDO with 3.0% DPS$-$C$_1$C$_{16}$ SbF$_6$ and 8 ppm Cl$_2$(COD)Pd^{II} using TMDS as the reducing agent.

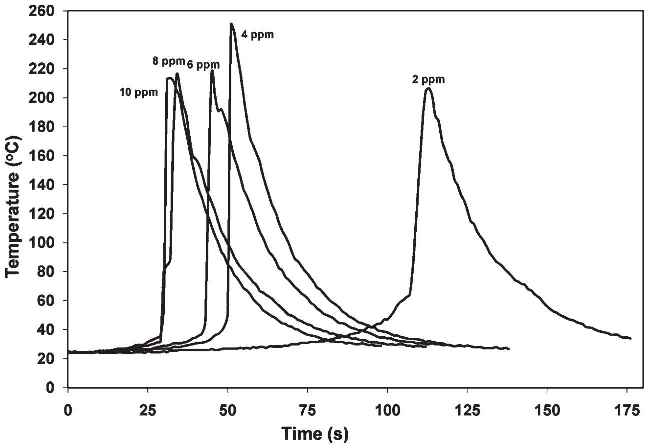


Figure 5. Effect of the Karstedt catalyst concentration on the polymerization of VCHDO using 3.0% DPS$-$C$_1$C$_{16}$ SbF$_6$ and TMDS as the reducing agent.

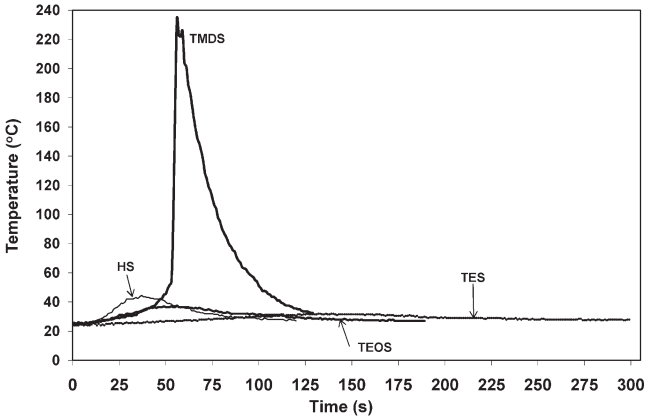


Figure 6. Polymerization of VCHDO with 3.0% DPS$-$C$_1$C$_{16}$ SbF$_6$, 8 ppm Karstedt catalyst using triethoxysilane (TEOS), *n*-hexylsilane (HS), triethylsilane (TES) and 1,1,3,3-tetramethyldisiloxane (TMDS) as reducing agents.

results obtained are depicted in Figure 6. The superiority of TMDS as a reducing agent is clearly evident in this study. This may be due to two factors; first TMDS is highly volatile with a low boiling point (bp 70−71 °C), second, the compound contains two Si$-$H bonds per molecule. *n*-Hexylsilane (HS) bears three Si$-$H groups per molecule but has a higher boiling point (bp 114−115 °C). This polymerization proceeds with a very short induction period but does not proceed to completion. Triethoxysilane (TEOS, 134−135 °C) gives similar results while triethylsilane (TES, bp 107−108 °C) generally shows a low order of reactivity. When these latter silanes are added to neat VCHDO monomer containing the same DPS and Karstedt catalyst, polymerization proceeds very vigorously after a short induction period. Similarly, we observed that a variety of other silanes containing the Si$-$H functional group were active reducing agents for DPS in the presence of a noble metal catalyst. Among those tested and found to be reactive were: dimethylphenylsilane, diphenylmethylsilane, 1,3,5,7-tetramethylcyclotetrasiloxane and 1,3,5,7,9-pentamethylcyclopentasiloxane.

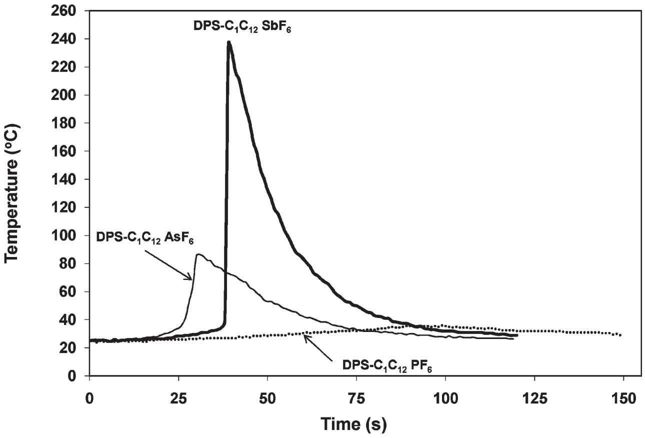


Figure 7. Comparison of the polymerization of VCHDO with 3.0% DPS$-$C$_1$C$_{12}$ SbF$_6$, DPS$-$C$_1$C$_{12}$ AsF$_6$, and DPS$-$C$_1$C$_{12}$ PF$_6$, using 8 ppm Karstedt catalyst with TMDS as the reducing agent.

In Figures 7 and 8, we show the results of our OP investigations into the structure of the DPS. In all cases, VCHDO was used as the monomer along with TMDS and the Karstedt catalyst. A study of the effect of DPS$-$C$_1$C$_{12}$ salts bearing different anions is presented in Figure 7. The outstanding reactivity of the DPS$-$C$_1$C$_{12}$ SbF$_6$ is clearly evident. The corresponding AsF$_6^-$ and PF$_6^-$ salts are considerably less reactive. We reported very similar behavior when photopolymerizations of epoxides were carried out using these same these onium salts.[31] A complementary study is given in Figure 8 in which the structure of the cation of the DPS is modified maintaining the same SbF_6^- anion. Although there are minor differences in their reactivity, all four DPS salts performed well as oxidants in the redox couple. The DPS salt bearing the tetrahydrothiopyran ring (*S*-pentamethylene-*S*-phenacylsulfonium SbF_6) appears to be slightly less reactive than the other sulfonium salts. At the present time, we have no explanation why this is the case. Shown in Figure 9 is a comparative study of DPS−C_1C_{12} SbF_6 with the triarylsulfonium salt S(4-*n*-decyloxyphenyl)-*S*,*S*-diphenylsulfonium SbF_6 in the redox initiated cationic polymerization of VCHDO Despite the difference in the reduction potentials between these two salts (approximately −14.5 versus −24 kcal/mol), it appears that the vapor phase reduction by TMDS takes place rapidly and efficiently for both sulfonium salts. Also included in Figure 9 is an OP curve in which S(4-hydroxy-3,5-dimethyl)-*S*,*S*-dimethylsulfonium SbF_6 was employed as the oxidant. This latter sulfonium salt also displays excellent reactivity as an initiator in a redox couple with TMDS.

Using the DPS−silane redox couple and employing the OP technique, the polymerizations of a number of different epoxide monomers were carried out. Like the other cycloaliphatic epoxide monomers CHO, VCHO and VCHDO, the polymerization of limonene dioxide takes place rapidly and exothermically. The biscycloaliphatic ester containing monomer, 3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexane carboxylate (ERL-4221) and the dioxetane monomer, bis(3-ethyloxetanylmethyl) ether (DOX) are condiserably less reactive under the usual conditions of the vapor phase silane polymerization. At the same time, both monomers exhibit fast, exothermic polymerization when TMDS is added as a reducing agent to the neat monomers containing 3.0%. DPS−C_1C_{12} SbF_6 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_1C_{12} SbF_6 with 16 ppm of $Cl_2(COD)Pd^{II}$ as a catalyst. As may be noted, the polymerizations of these two vinyl ether monomers under redox conditions are both rapid and exothermic. They proceed with only a short induction period. The more rapid and exothermic polymerization of DVE-3 is due to the fact

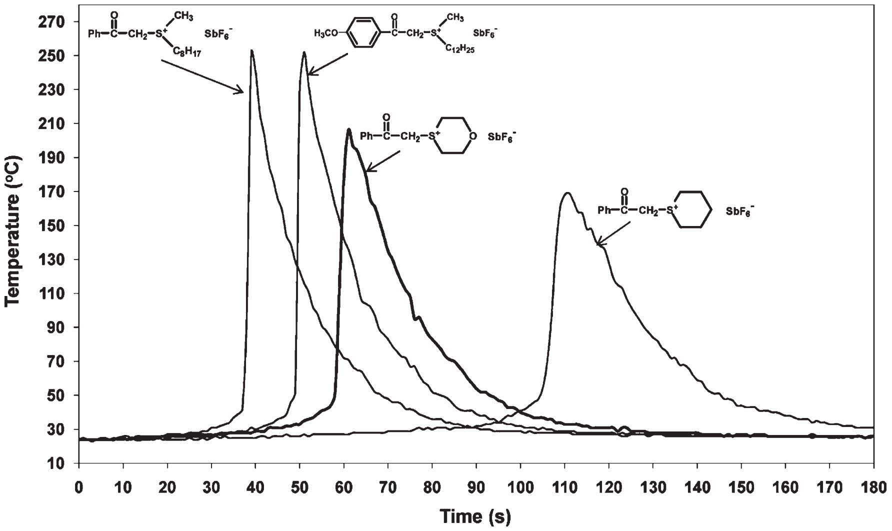


Figure 8. Comparison of the polymerization of VCHDO with 3.0% of various DPS−SbF_6 salts using 8 ppm Karstedt catalyst with TMDS as the reducing agent.

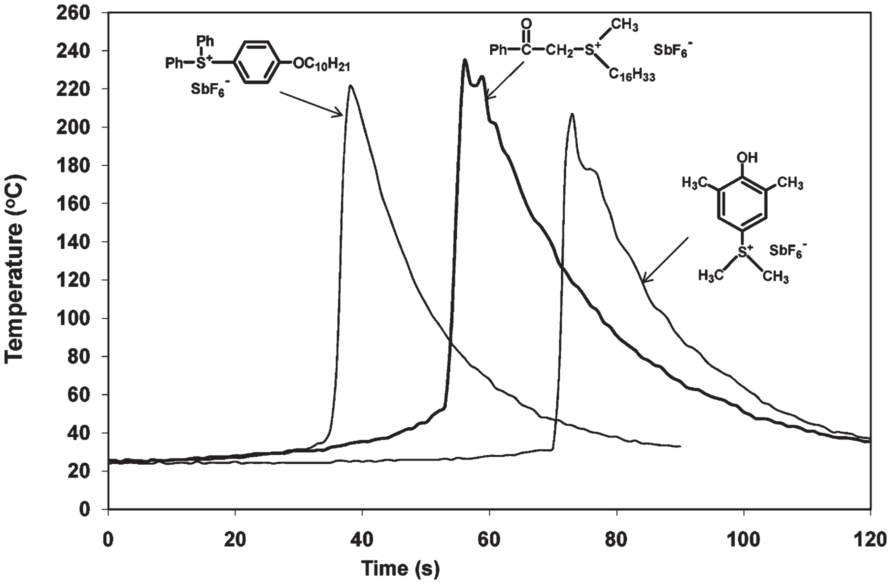


Figure 9. Comparison of the polymerization of VCHDO with 3.0% DPS−C_1C_{12} SbF_6, SOC-10 SbF_6, and HPS−SbF_6, using 8 ppm Karstedt catalyst with TMDS as the reducing agent.

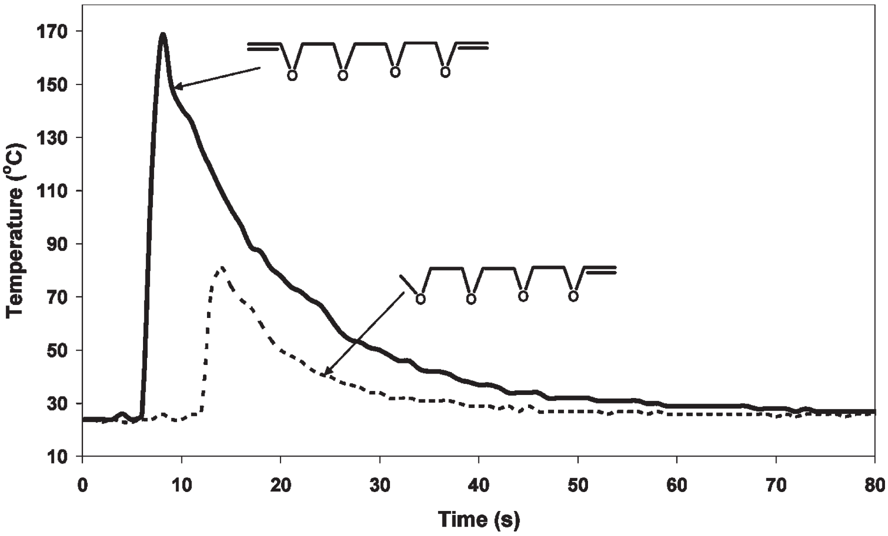


Figure 10. Polymerizations of DVE-3 and triethyleneglycol methyl vinyl ether with 3.0% DPS$-$C$_1$C$_{16}$ SbF$_6$, 16 ppm Cl$_2$(COD)Pd^{II} using TMDS as the reducing agent.

that it is a difunctional vinyl ether monomer. When these polymerizations were carried out with the platinum-containing Karstedt catalyst, rather slow polymerization was observed and the OP curves were not monomodal. The reasons for this catalyst dependent behavior are not fully understood at this time, but presumably they indicate that there is an interaction between the metal center of the catalyst and the monomer that leads in the case of the Karstedt catalyst to retardation of the polymerization. It is worth noting that both DVE-3 and triethyleneglycol methyl vinyl ether are monomers that possess three methylenedioxy groups that can likely coordinate to metals as multidendate ligands.

The observed variation in the induction periods of the monomers is due to the corresponding variations in the stability/reactivity of the intermediates formed by reaction of the strong acid generated by the initiator system and the monomer. We have previously commented on this phenomenon in cationic photopolymerizations carried out on epoxy and oxetane monomers.[40,41]

Potential Applications of Redox Cationic Polymerizations. Apart from the convenience of using redox couples of the type described in this paper for the *in situ* generation of strong Brønsted acids with which to conduct various cationic polymerization reactions, there appears to be several obvious areas of potential practical applications. For example, redox cationic polymerizations can be employed in the traditional applications for epoxy resins such as casting, encapsulation, and composite applications. In addition, the vapor induced redox polymerizations present unique possibilities. These are primarily applications that rely on the deposition and polymerization of thin cross-linked 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. The advantage of vapor induced redox polymerizations over photopolymerizations in many of these applications is that they can be used in situations in which, due to the geometry of the object, it is difficult or impossible to deliver direct light irradiation (i.e., "shadowing effects"). Similarly, redox polymerizations can be carried out on highly pigmented, filled or opaque substrates whereas photopolymerizations are ineffective.

One simple demonstration of the use of the DPS$-$silane redox couple as a cationic initiator is presented here. A 4 cm × 8 cm aluminum panel was knife coated with VCHDO containing 3.0% DPS$-$C$_1$C$_{12}$ SbF$_6$ and 8 ppm of the Karstedt catalyst to give a film with a thickness of 50 μm. The panel was placed in a desiccator containing an open vial of TMDS, the desiccator was closed, a vacuum drawn and sealed and allowed to stand at room temperature for 10 min. After this time, it was opened and the film was found to be dry and tack-free. It was further observed that the hardness of the film continued to increase with time.

Conclusions

The facile noble metal catalyzed reduction of *S*,*S*-dialkyl-*S*-phenacylsulfonium salts (DPS) by silanes provides a novel and convenient means for generating strong Brønsted acids that can be employed for initiating cationic vinyl and ring-opening polymerizations under solution and bulk conditions. The development of this novel redox couple also offers the unique possibility of conducting cationic polymerizations that are triggered by exposure to the silane in the vapor state. Under these conditions, the polymerizations of many of the aforementioned monomers take place rapidly and exothermically. We have employed optical pyrometry to monitor the progress of these fast, silane vapor-induced polymerizations.

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