Redox Intitiated Cationic Polymerization

James V. Crivello

Summary: Two novel redox initiator systems have been developed for carrying out the cationic polymerizations of vinyl and heterocyclic monomers. The initiators are based on various onium salts as the oxidant together with an alkylborane or an organosilane as the reducing agent. Using both redox cationic initiator systems, the polymerizations of a wide variety of monomers can be carried out at or below room temperature in the presence or absence of unreactive solvents. Also described in this communication is the novel use of a two-component redox system in which the reducing agent, a silane, is delivered to the monomer sample in the vapor state. Optical pyrometry (infrared thermography) was employed as a convenient method with which to monitor the polymerizations in real-time. A study of the effects of variations in the structures of the onium salt, the silane and the type of noble metal catalyst were carried out. The use of these initiator systems for carrying out commercially attractive crosslinking polymerizations for coatings, composites and electronic encapsulations is discussed.

Keywords: cationic polymerization; epoxides; initiators; redox initiators

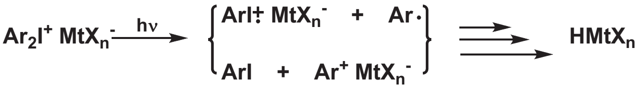
Introduction

Free radical redox initiators have found use in a wide range of commercial applications including the emulsion and suspension polymerizations of vinyl monomers. Due to the low activation energy[1] of these initiator systems, they are often employed under ambient temperature conditions in production of thermosetting polymers for use in fiber reinforced composites, coatings, adhesives, electrical and electronic potting and encapsulating resins, as well as many other applications. Free radical redox systems are also notable in that they are generally inexpensive, stable and are easily handled as two-component initiators in the above applications. These advantages make such initiator systems increasingly attractive for use where considerations of worker safety and ecological impact are of particular importance.

It is notable, that while free radical generating redox initiator systems are well known and widely implemented in many commercial applications, there has been little attention given in the literature to the development of analogous redox initiator systems that generate either reactive anions or cations. Work in this laboratory has specifically focused on redox initiated cationic polymerizations and this is for very practical reasons. Since cationic polymerizations are not subject to oxygen inhibition, they can be carried out in air. This is not generally true for either free radical or anionic polymerizations. From a broader perspective, cationic polymerizations are actually more versatile than free radical polymerizations in terms of the types of monomers that can be used. Thus, one can carry out the cationic polymerizations of vinyl monomers as well as the ring-opening polymerizations of a broad range of heterocyclic monomers. This implies that a correspondingly broad range of chemical and mechanical properties can be potentially afforded by the cationic redox polymerization of such monomers.

Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, 110 8th Street, Troy, New York, 12180, USA
Fax: 518-276-6825; E-mail: crivej@rpi.edu

We have reported that diaryliodonium salts, **I**, in which MtX_n^- represents an anion of low nucleophilic character are highly potent and efficient photoinitiators for cationic polymerization. The photolysis of **I** shown in equation 1, results in the formation of a strong Brønsted acid, $HMtX_n$, that serves as an initiator of cationic polymerization.



$$Ar_2I^+ MtX_n^- \xrightarrow{h\nu} \left\{\begin{matrix} ArI^{+\cdot}\ MtX_n^- + Ar\cdot \\ ArI + Ar^+\ MtX_n^- \end{matrix}\right\} \longrightarrow HMtX_n \qquad (1)$$

I

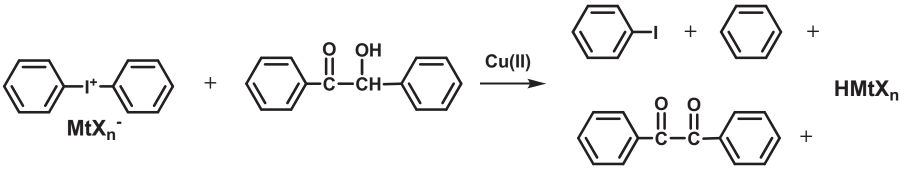
Diaryliodonium salts are members of the class of hypervalent compounds in which the formal oxidation state of iodine is assigned a +3. For this reason, these compounds can be considered oxidizing agents. Recognizing this fact, in 1983 we[2] showed that diphenyliodonium salts undergo copper catalyzed reduction in the presence of benzoin and its analogs to yield the products depicted in equation 2 among which is the Brønsted acid, $HMtX_n$. In subsequent studies,[3] we demonstrated that the active catalyst is a copper(I) species formed by the reduction of the copper(II) compound by benzoin. This diaryliodonium salt-benzoin redox couple can be used for the cationic ring-opening polymerizations of epoxides and oxetanes. However, due to the presence of the hydroxyl groups in benzoin, it is of limited use for other monomers such as styrene and vinyl ethers. Further, the poor solubility of benzoin and its analogs in many nonpolar monomers and the need to carry out the polymerization at elevated temperatures are additional limitations to the use of this redox initiator system.

Similarly, several cationic redox systems based on reducible free radicals generated by the thermolysis of benzopinacole and the photolysis of compounds containing arylketone groups together with diaryliodonium salts as oxidants were described by Morgan and Kyle[4] and by Ledwith et al..[5] Despite several drawbacks inherent in these systems, the concept of cationic redox initiators was successfully demonstrated. From these results we concluded that such systems could be markedly improved if better reducing agents could be found for diaryliodonium and other onium salts. To achieve this goal, the reducing agent must be stable in air at room temperature and it must also be either neutral or even, slightly acidic so that it does not inhibit or retard the subsequent cationic polymerization. A number of candidate reducing agents were evaluated for use in cationic redox couples. Two novel redox systems based on different classes of reducing agents were subsequently discovered and are discussed in this communication.

Results and Discussion

The Diaryliodonium Salt-9-BBN Redox Couple

Boranes, such as diborane and alkylboranes, are Lewis acidic compounds that are excellent reducing agents for many types of organic functional groups. However, they react rapidly with oxygen and, in some



(2)

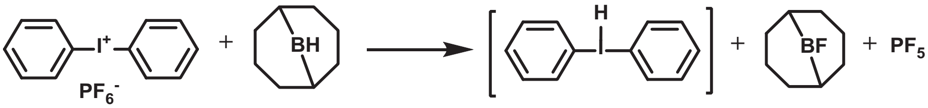
cases, are even pyrophoric. A notable exception is 9-borabicyclo[3.3.1]nonane (9-BBN). Knights and Brown[6] showed that 9-BBN can be readily prepared as depicted in equation 3 by the reaction of 1,5-cyclooctadiene with diborane. 9-BBN is a colorless crystalline compound with a melting point of 140–142 °C that is stable in the presence of air. Brown[7,8] reported that 9-BBN is a highly versatile reducing agent for many organic functional groups including: esters, amides, carboxylic acids, carboxylic acid chlorides, ketones, aldehydes, nitro compounds and nitriles.

(3)

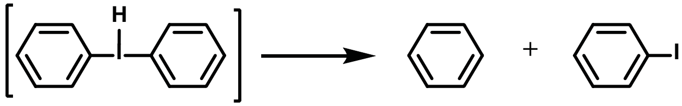
9-BBN

Diaryliodonium salts have reduction potentials of approximately -5 kcal/mol.[9] We have found that a wide variety of substituted and unsubstituted diaryliodonium salts containing a variety of aromatic and heterocyclic groups are spontaneously and rapidly reduced at 25 °C by 9-BBN.[10] For example, the reduction of diphenyliodonium hexafluoridophosphate is proposed to proceed by a two step mechanism (equations 4 and 5) that gives benzene, iodobenzene, 9-fluoro-9-borabicyclo[3.3.1]nonane and phosphorous pentafluoride. The products were identified using GC/MS.

Mechanism of the Reduction of Diaryliodonium Salts by 9-BBN



(4)



(5)

When the reduction is performed in the presence of a cationically polymerizable monomer such as an epoxide, the phosphorous pentafluoride that is generated in combination with traces of water or other protonic impurities catalyzes a spontaneous exothermic ring-opening polymerization. We have employed optical pyrometry (OP) as a convenient method to monitor the redox initiated cationic polymerizations described in this communication. General descriptions of the apparatus construction, sampling and analytical techniques used in the optical pyrometric analysis for photopolymerization reactions were given in previous publications from this laboratory.[11–13] Essentially, the progress of an exothermic polymerization is monitored in real-time by remotely following the sample temperature using an infrared camera (optical pyrometer). An Omega Corp. Model OS 552-V1-6 infrared camera was mounted in an acrylic cabinet with the sample stage placed at a fixed distance of 13.5 cm from the camera lens. The basic apparatus was slightly modified to adapt it for studying cationic redox polymerizations. A magnetic stirrer was mounted just below and in contact with the sample stage. Polymerizations were carried out in standard 44 mm dia. 20 mL Fischer Scientific aluminum weighing dishes. These containers were very regular both in size and in weight (1.0–1.1 g). To the weighing dish was added 1.0 g of the monomer followed by a predetermined amount of the diaryliodonium salt. An acetone washed and dried 22 mm long #1 steel paper clip was added to the weighing dish to serve as a stirrer. The mixture was stirred until all the diaryliodonium salt had dissolved. Assuming a density of approximately 1.0 g/mL, the thickness of the liquid layer in the weighing dish was 0.33 mm. The weighing dish was positioned on the sample stage of the OP apparatus with focal point of the infrared camera located at the surface of the monomer film. This was achieved with the aid of a laser sighting device. After an equilibration period of 20 seconds, a predetermined amount of a 0.5 M THF solution of 9-BBN was added to the pan using a syringe while the monomer-diaryliodonium salt solution was rapidly stirred. All polymerizations were carried out in ambient air and humidity at an initial temperature of 23–25 °C. During kinetic runs, the sample was monitored at a rate of one temperature measurement per second.

Optical pyrometry does not provide direct conversion versus time information. However, in previous studies we have been able to show that the initial rate of temperature increase is directly related to the rate of conversion.[14] Further, integration of the temperature versus time optical pyrometry curve produces a curve that is superimposable on the conversion versus time curve obtained by real-time infrared spectroscopy. This confirms the relationship between the two analytical techniques.

In Figure 1, is shown the redox initiated cationic crosslinking polymerization of 4-vinylcyclohexene dioxide (VCHDO) carried out using (4-*n*-undecyloxyphenyl)-phenyliodonium hexafluoridoantimonate (IOC-11 SbF_6) and 9-BBN. There is approximately a 30 second induction period after the addition of the 9-BBN that is followed by exceedingly rapid, exothermic autoaccelerated polymerization with the temperature rising to an impressive 335 °C. Within 2–3 seconds, virtually all the epoxide groups are consumed and the temperature of the thin film sample rapidly begins to fall. A similar study is given in Figure 2 in which the cationic crosslinking polymerization of triethylene glycol divinyl ether was carried out using di(4-*tert*-butylphenyl)iodonium perchlorate as the oxidant and 9-BBN as the reducing agent. In this instance, a diaryliodonium salt was used that liberates perchloric acid on reduction with 9-BBN. This acid is sufficiently strong enough to rapidly polymerize the highly reactive divinyl ether monomer.

The sharpness of the OP curves in Figures 1 and 2 also suggests a very high conversion of monomer functional groups. Usually, when monomer conversion is low, the polymerization proceeds over a prolonged

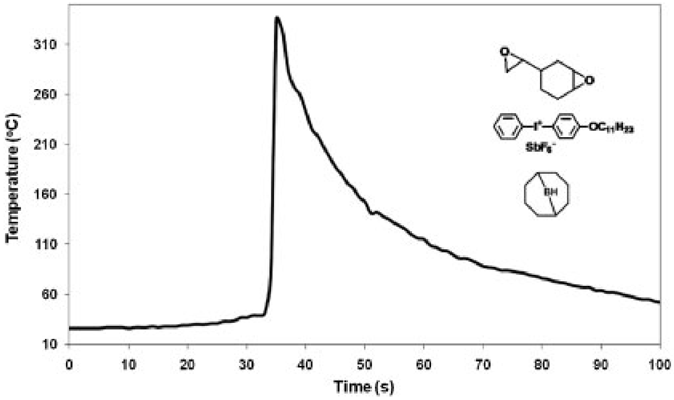


Figure 1.
Redox polymerization of 1.0 g 4-vinylcyclohexene dioxide, 4×10^{-5} mol. 9-BBN, 7.6×10^{-5} mol IOC-11 SbF_6.

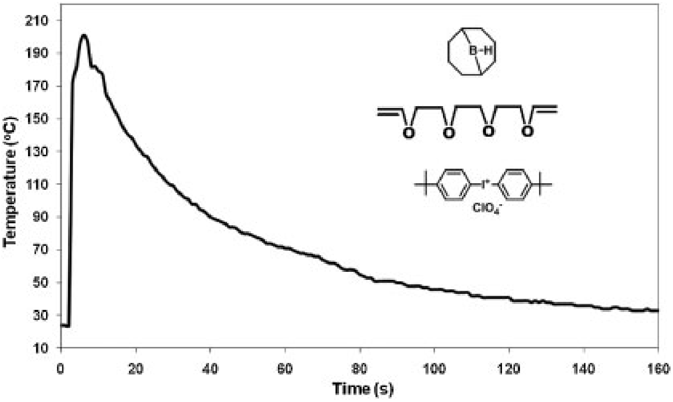


Figure 2.
Redox cationic polymerization of triethyleneglycol divinyl ether with di(4-*t*-butylphenyl)-iodonium perchlorate (4.0×10^{-5} mol) using 3.5×10^{-5} mol 9-BBN as the reducing agent.

period of time with consequent broadening of the temperature versus time curves.

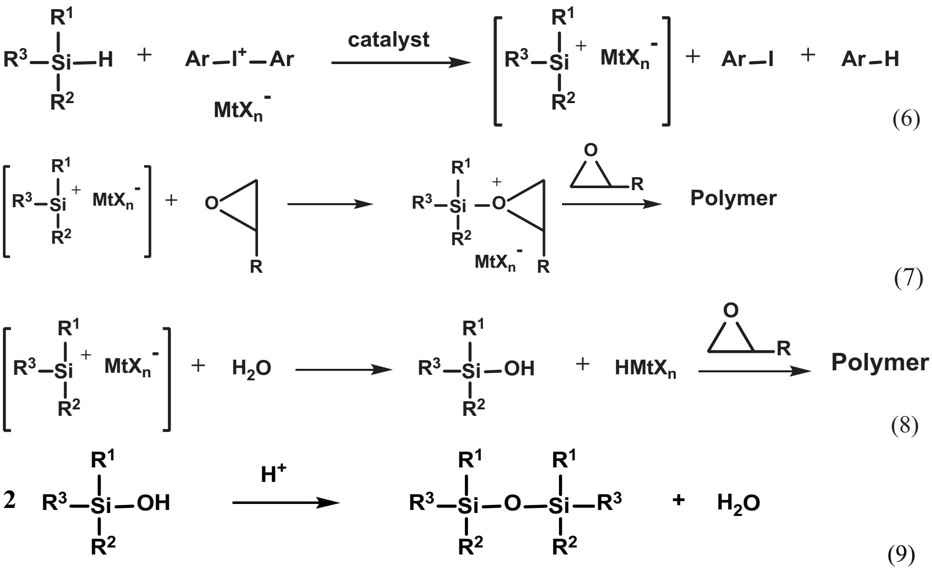
Although only two examples are given above, this new diaryliodonium salt-9-BBN redox initiator system is widely applicable to many other types of cationically polymerizable monomers. Among those which have been investigated are included: oxetanes, 1,3,5-trioxane, tetrahydrofuran, 1,3-dioxolane, ketene acetals, N-vinylcarbazole, and styrene. Attempts to extend the general concept of the reduction by 9-BBN to other classes of onium salts was unsuccessful. This was attributed to the higher reduction potentials of those onium salts. For example, triarylsulfonium salts ($E_{red} = -28\,\text{kcal mol}^{-1}$)[15] and S,S-dialkyl-S-phenacylsulfonium salts ($E_{red} = -14.5\,\text{kcal mol}^{-1}$)[16] were not reduced by 9-BBN.

Onium Salt-Silane Redox Couples

Organosilanes containing the Si-H bond are effective reducing agents for a wide assortment of functional groups including aldehydes, ketones, esters, amides, olefins and metal halides.[17] Moreover, silanes are neutral compounds which would not significantly interfere with either cationic vinyl or ring-opening polymerizations. Additionally, they are non-toxic, non-corrosive and possess considerable hydrolytic and oxidative stability. Lastly, the reducing character of these compounds can be readily "tuned" by appropriate substitution of the groups on the silicon atom.

It was observed that organosilanes containing the Si−H bond do not spontaneously reduce diaryliodonium salts. However, this reaction does proceed smoothly at room temperature when catalyzed by a number of noble metal catalysts.[18] Prominent among these catalysts are complexes of platinum, rhodium and palladium. Dicobalt octacarbonyl also functions as a catalyst for the reduction of diaryliodonium salts by organosilanes. Only parts per million amounts of these catalysts are required for the reduction to proceed. We have observed that the most active catalysts are the same ones that catalyze the hydrosilation reaction. A large number of organosilanes were examined and found suitable for use in the construction of onium salt-silane redox couples. This includes both low molar mass compounds as well as poly(silanes) and poly(siloxanes) bearing terminal and/or pendant Si−H groups. In equations 6–9 is presented the proposed mechanism for the reduction of diaryliodonium salts and their subsequent use in the initiation of the cationic ring-opening polymerization of epoxides.

Proposed Mechanism for the Reduction of Diaryliodonium Salts by Silanes



The first step (eq. 6) involves the catalyst-mediated reduction of a diaryliodonium salt by the silane. At this time, the precise means by which the catalyst functions in this reaction is not understood. It is, however, worth noting that silanes are known to coordinate to noble metal catalysts.[19] We suggest that the reduction of a diaryliodonium salt by a silane results in the formation of a highly reactive silicenium ion as a transient species. Following its formation, the silicenium cation can directly attack a monomer such as an epoxide to form the corresponding oxonium species (eq. 7) that is capable of undergoing further polymerization by a conventional cationic propagation process. However, only a small proportion of polymers isolated from this reaction was observed to bear the expected alkoxysilane chain ends was detected by NMR spectroscopy. Therefore, instead, we suggest that rapid reaction of silicenium cations with traces of water or other protonic impurities results in the formation of the silanol and a strong Brønsted acid that ultimately initiates polymerization (eq. 8). In the presence of the acid, the silanol undergoes condensation to form the siloxane (eq. 9) which was detected in the reaction mixture by GC/MS analysis.

The positively charged sulfur atom present in sulfonium salts has a formal +4 oxidation state. Triarylsulfonium salts display reduction potentials that are nearly five times higher than for diaryliodonium salts; nonetheless, they still undergo facile reduction in the presence of Si–H containing organosilanes.[20] As with diaryliodonium salts, reduction of triarylsulfonium salts does not proceed in the absence of a noble metal catalyst. Triarylsulfonium salts are of great interest since these compounds are widely employed as photoinitiators in numerous applications such as coatings, adhesives, printing inks and in many imaging uses including photoresists, digital imaging and stereolithography. In the course of this investigation, we have shown that a wide range of structurally diverse triarylsulfonium salts with an equally broad range of anions are readily reduced by Si–H containing silanes in the presence of noble metal catalysts. Similarly, S,S-dialkyl-S-phenacylsulfonium salts with reduction potentials considerably lower than triarylsulfonium salts are also smoothly reduced under the same conditions.[21] We have

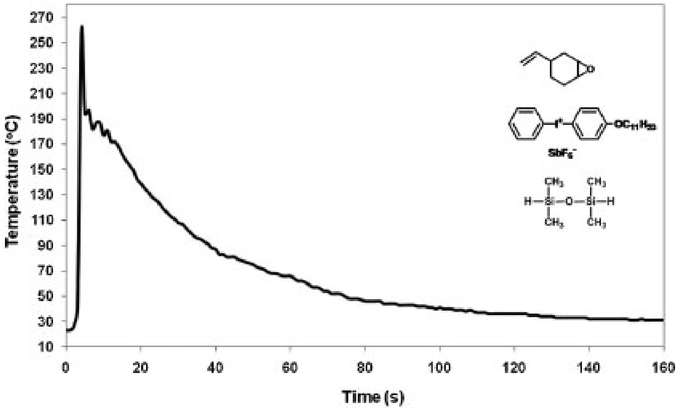


Figure 3.

OP study of the polymerization of 4-vinylcyclohexene oxide with 3.8×10^{-5} mol (4-*n*-undecyloxyphenyl)phenyliodonium hexafluoridoantimonate (IOC-11 SbF_6), 40 ppm Lamoreaux catalyst using 2.2×10^{-5} mol 1,1,3,3-tetramethyldisiloxane (TMDS) as the reducing agent.

proposed mechanisms analogous to that given above in equations 6–9 for the reduction of these latter sulfonium salts. Although a large number of platinum, palladium and rhodium complexes for this reaction were screened and found to be active as catalysts, we have most often employed commercially available platinum hydrosilation catalysts such as the Lamoreaux[22] or Karstedt[23] catalysts or chloroplatinic acid since they are commercially available as solutions and can be conveniently and reproducibly added to the reaction mixtures by syringe. Similarly, we have also used $Cl_2(COD)Pd(II)$ as a 50% solution in nitromethane.

The diaryliodonium, triarylsulfonium and S,S-dialkyl-S-phenacylsulfonium salt-silane redox couples are applicable to a broad range of cationically polymerizable monomers. These include vinyl and heterocyclic monomers. Two typical examples are shown in Figures 3 and 4. In these cases, the onium salt and the noble metal catalyst

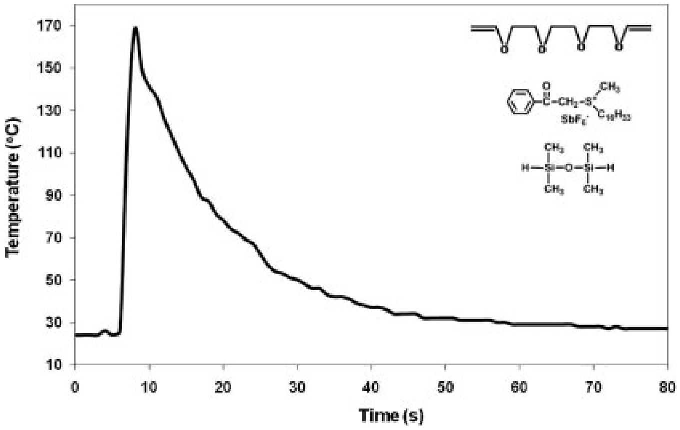


Figure 4.

Polymerization of triethylene glycol divinyl ether (DVE-3) with 3.0% S-methyl-S-*n*-hexadcecyl-S-phenacylsulfonium hexafluoridoantimonate (DPS-C_1C_{16} SbF_6), 16 ppm $Cl_2(COD)Pd$, with 80 μL TMDS as the reducing agent.

were added to the monomer and thoroughly mixed together. As may be noted in the polymerization studies of the respective epoxide and vinyl ether monomers, platinium (Lamoreaux catalyst) and palladium (Cl_2(COD)Pd) catalysts were used. OP monitoring of the polymerization was begun when the organosilane was added to the rapidly stirred mixture by means of a syringe. Both iodonium and sulfonium salt-based redox initiator systems were quite reactive and polymerization starts spontaneously after a very short induction period with the temperature rising abruptly accompanied by the very rapid consumption of the monomer. The polymerizations were carried out under ambient air conditions and are insensitive to the presence of free radical inhibitors. The polymerizations are strongly inhibited in the presence of 2,6-di-*tert*-butylpyridine as well as by other bases.

Among the many organosilanes that can be used together with onium salts for cationic redox couples, low molar mass organosilanes are particularly interesting due to their low boiling points and high vapor pressures. This observation led to the speculation that it might be possible to conduct cationic polymerizations in which the organosilane reducing agent was delivered to the reaction mixture in the vapor state. A simple experiment confirmed the viability of this concept. A thin layer of a difunctional epoxy monomer (3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexanecarboxylate) containing 3% by weight of (4-*n*-octyloxyphenyl)phenyliodonium hexafluoridoantimonate (OPPI SbF_6) and 80 ppm Lamoreaux catalyst were coated onto a steel panel. The panel was placed in a vacuum desiccator containing an open small vial of 1,1,3,3-tetramethyldisiloxane (TMDS, b.p. 70–71 °C) and then the desiccator was closed and briefly evacuated. After 10 minutes, the desiccator was opened and the liquid epoxide coating was found to have polymerized to produce a dry, solid film. The results of this experiment suggest that it may be possible to conduct low energy, solventless, environmentally attractive coating processes on objects with complex geometries without the input of heat or light energy.

To further pursue the development of this concept, it was desired to have a more quantitative method for the evaluation of these new vapor induced cationic redox polymerizations. Accordingly, we modified the basic optical pyrometry instrument to achieve this goal. The liquid monomer sample was absorbed into a thin (0.2 mm) 15 mm × 15 mm sheet of nonwoven polyester fabric (veil) placed on a thin 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 dia. × 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 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. To initiate polymerization, a small amount (~0.3 ml) of the designated organosilane reducing agent was injected into a cell filled with glass wool to enhance vaporization. Vapors of the silane were carried into the sample cell by a slow stream of dry air 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. Using this modified OP apparatus, a number of cationic redox polymerization studies were conducted. Figure 5 shows two redox polymerizations of cyclohexene oxide carried out using the iodonium salt, OPPI SbF_6, in the presence of the Lamoreaux catalyst with TMDS as the volatile reducing agent. Very good run-to-run reproducibility was obtained with this system. The polymerization begins rapidly after an induction period of approximately 15 seconds with the sample temperature briefly reaching 175 °C. In

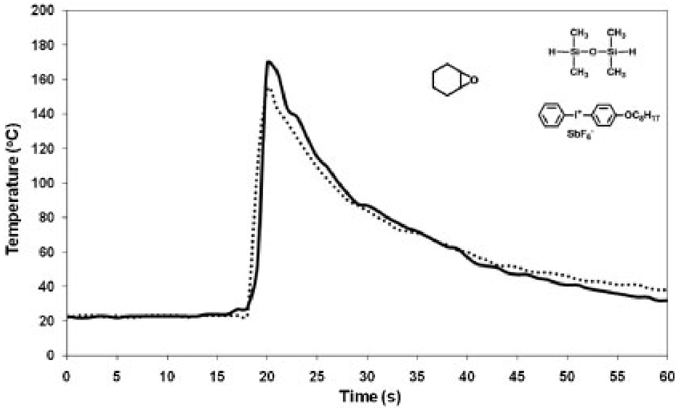


Figure 5.
OP study of the polymerization of cyclohexene oxide with 2.0% (4-*n*-octyloxyphenyl)-phenyliodonium hexafluoridoantimonate (OPPI SbF_6), 4 ppm Lamoreaux catalyst using TMDS as the reducing agent.

Figure 6, is shown the results of a study in which redox couples incorporating various iodonium salts bearing the $(C_6F_5)_4B^-$, AsF_6^- and PF_6^- anions were used with TMDS as the volatile reducing agent. The superiority of Rhodorsil 2074 (4-isopropylphenyl-4-methylphenyliodonium tetrakis-(pentafluorophenyl)borate, Rhone-Poulenc) in this study is clearly evident. We have also used the modified OP apparatus to evaluate the efficiency of various silanes as reducing agents. An example is shown in Figure 7. In this instance, the sulfonium salt S-4-*n*-decyloxyphenyl-S,S-diphenylsulfonium hexafluoridoantimonate (SOC-10 SbF_6) was used as the onium salt oxidant with the commercially available platinum-containing Karstedt catalyst. 4-Vinylhexene-1,2-dioxide (VCHDO) was employed as the monomer. Among the various silanes, TMDS was observed to exhibit the highest reactivity. This was ascribed to its low boiling point and the fact that it possesses two reducing Si–H groups in the same molecule.

Another example of the use of a cationic redox system in which the reducing agent is delivered to the sample in the vapor state is shown in Figure 8. The difunctional oxetane monomer, bis(3-ethyl-3-methyoxetanyl) ether (DOX) was polymerized using OPPI

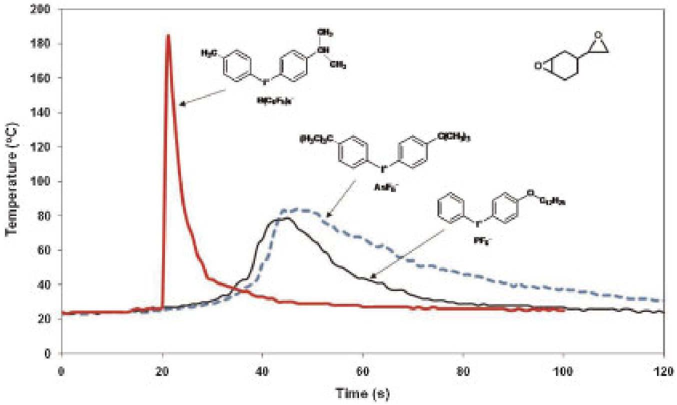


Figure 6.
Comparison the effects of the use of three different diaryliodonium salts in the polymerization of VCHDO (2.5% diaryliodonium salt, 4 ppm Lamoreaux catalyst with TMDS as the reducing agent).

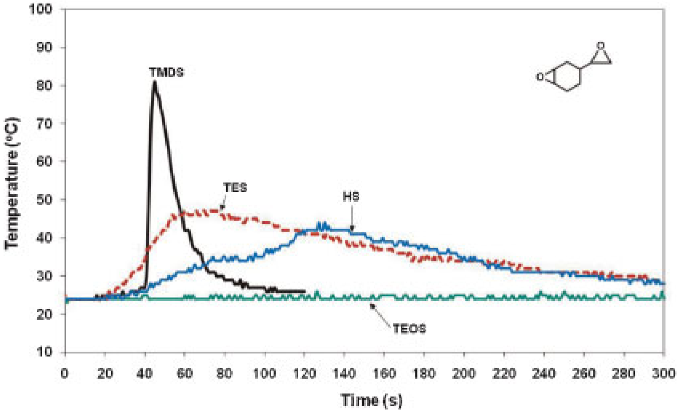


Figure 7.
Polymerization of VCHDO with 2.5% SOC-10 SbF_6, 4 ppm Karstedt catalyst using triethoxysilane (TEOS), *n*-hexylsilane (HS), triethylsilane (TES) and 1,1,3,3-tetramethyldisiloxane (TMDS) as reducing agents.

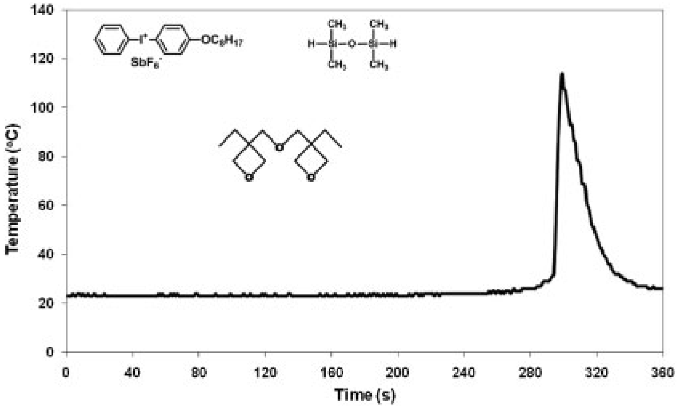


Figure 8.
OP study of the polymerization of DOX with 2.5% OPPI SbF_6 and 4 ppm Lamoreaux catalyst using TMDS as the reducing agent.

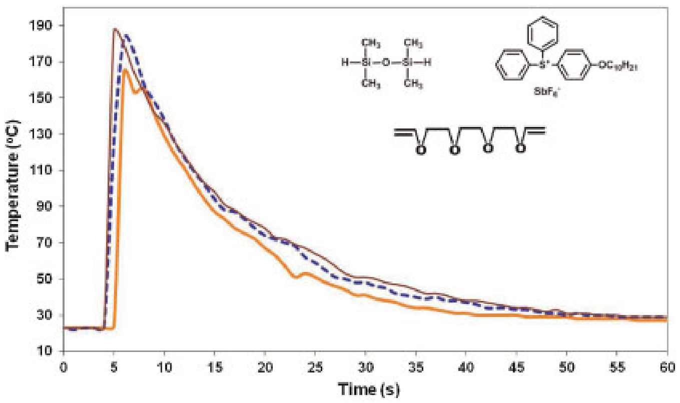


Figure 9.
Polymerization of DVE-3 with 1.0% SOC-10 SbF_6 8 ppm Cl_2(COD)Pd(II) with TMDS as the reducing agent (three runs are shown).

SbF_6 together with 4 ppm of the Lamoreaux catalyst using TMDS as the volatile reducing agent. Highly exothermic ring-opening polymerization is observed after a lengthy (300 s) induction period. In Figure 9 are displayed the OP plots of three polymerization runs conducted for the cationic polymerization of triethylene glycol divinyl ether (DVE-3). The high reactivity of both the redox initiator and this monomer produce a highly exothermic polymerization that takes place after a very short exposure to the vapor of TMDS.

Conclusion

In this communication, the development of several new and practical redox systems for cationic vinyl and ring-opening polymerizations has been described. Although we have provided only a few representative examples in this communication, it is anticipated that these redox cationic initiator systems can be extended to include the polymerizations of virtually all types of cationically polymerizable monomers. We are optimistic that these cationic redox polymerizations will find special use in a wide variety of thermoset applications among which include coatings, adhesives, composites, potting and encapsulations. The main attractive feature of these redox initiator systems is that they are easy to implement since they use readily available and reasonably inexpensive starting materials. Of special interest are the newly developed redox initiator systems that employ a volatile silane reducing agent. Such redox systems can be employed in many novel ways. For example, they can be used to conduct the room-temperature crosslinking polymerization of opaque, filled epoxy based coatings that can be applied to substrates with complex geometries.

[1] G. Moad, D. H. Solomon, *The Chemistry of Radical Polymerization*, Elsevier, New York **2006**, pp. 85–106.

[2] J. V. Crivello, J. L. Lee, *J. Polym. Sci. Part A: Polym. Chem.* **1983**, *21*(4), 1097.

[3] J. V. Crivello, J. L. Lee, *Polymer J.* **1985**, *17*(1), 73; J. V. Crivello, *Thermally or Photochemically Induced Cationic Polymerization*, ACS Symp. Series No. 286, J. E. McGrath, editor, American Chemical Soc. Pub, **1985**, pp. 195–1204.

[4] C. R. Morgan, D. R. Kyle, U.S. Patent 3,474,963, Feb. 22, **1983**.

[5] F. A. M. Abjul-Rasoul, A. Ledwith, Y. Yagci, *Polymer* **1978**, *19*, 1220.

[6] E. F. Knights, H. C. Brown, *J. Am. Chem. Soc.* **1968**, *90*, 5280.

[7] H. C. Brown, *Organic Synthesis via Boranes*, John Wiley, New York **1975**, pp. 32, 40.

[8] H. C. Brown, U.S. Patent 4,078,002, Mar. 7, **1978**.

[9] J. V. Crivello, BT Ring-Opening Polymerization, D. J. Brunelle, (Ed., Hanser, Munich **1993**.

[10] J. V. Crivello, *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*(21), 5639.

[11] B. Falk, S. M. Vallinas, J. V. Crivello, *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *41*(4), 579.

[12] J. V. Crivello, B. Falk, S. M. Vallinas, *Polym. Mater. Sci. Eng. Prepr.* **2003**, *88*, 209.

[13] J. V. Crivello, B. Falk, M. Jang, M. R. Zonca, Jr, S. M. Vallinas, *RadTech Report*, May/June, 36–43, **2004**.

[14] J. V. Crivello, In: *Photochemistry and UV Curing: New Trends*, In: J. P. Fouassier, Ed., Research Signpost, Triverandrum **2006**, pp. 277–266.

[15] J. V. Crivello, J. L. Lee, *Polym. J.* **1985**, *17*(1), 73.

[16] J. M. Saveant, *C. R. Hebd. Seances Acad. Sci Ser. C* **1964**, *258*, 585.

[17] *Silicon-Based Reducing Agents*, Supplement to the Gelest Catalog, G. L. Larson, editor, available on-line at: www.gelest.com **2008**, 1–132.

[18] J. V. Crivello, *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*(7), 1825.

[19] B. Marciniec, *Comprehensive Handbook on Hydrosilation*, Pergamon Press, Oxford **1992**.

[20] J. V. Crivello, *Silicon* **2009**, *1*(2), 111.

[21] J. V. Crivello, M. Molleo, *Macromolecules* **2009**, *42*(12), 3982.

[22] H. F. Lamoreaux, U.S. Patent 3,220,972, Nov. 30, **1965**, to General Electric Corp.

[23] B. D. Karstedt, U.S. Patent 3,715,334, Feb. 6, **1973**, to General Electric Corp.