(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
8 July 2010 (08.07.2010)

PCT

(10) International Publication Number
WO 2010/077606 A1

(51) International Patent Classification:
C08F 4/26 (2006.01) ***C08F 2/01*** (2006.01)
C08F 4/40 (2006.01) ***B01J 19/00*** (2006.01)

(21) International Application Number:
PCT/US2009/066985

(22) International Filing Date:
7 December 2009 (07.12.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/201,255 8 December 2008 (08.12.2008) US
61/185,737 10 June 2009 (10.06.2009) US

(71) Applicant *(for all designated States except US)*: **RENSSELAER POLYTECHNIC INSTITUTE** [US/US]; 110 8th Street, Troy, New York 12180 (US).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **CRIVELLO, James, V.** [US/US]; 756 Carlton Road, Clifton Park, New York 12065 (US).

(74) Agent: **FREDERICKS, Kellie, S.**; Heslin Rothenberg Farley & Mesiti P.C., 5 Columbia Circle, Albany, New York 12203 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

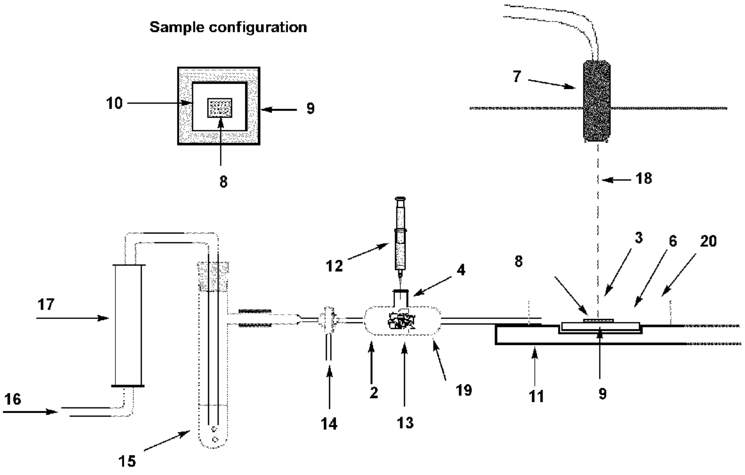
(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

(54) Title: REDOX-INITIATED CATIONIC POLYMERIZATION USING VAPOR-STATE REDUCING AGENTS

FIGURE 2:



(57) Abstract: The novel use of a two-component redox system for cationic photopolymerization reactions is presented in which the reducing agent is delivered as a vapor to a thin film monomer sample containing the oxidizing agent. Diaryliodonium, triarylsulfonium and 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.

WO 2010/077606 A1

Redox-Initiated Cationic Polymerization Using Vapor-State Reducing Agents

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority of US provisional application 61/201,255, filed December 8, 2008, and US provisional application 61/185,737, filed June 10, 2009, the entire disclosures of which are incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The invention relates to a two-component redox system for cationic polymerization of epoxide, oxetane and alkyl vinyl ether resins and to compositions, methods and apparatus for carrying out the polymerization.

BACKGROUND OF THE INVENTION

[0003] Redox systems that generate free radicals are well known and in wide spread use for a number of commercial applications. 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.

[0004] In contrast to their free radical counterparts, redox systems capable of initiating cationic polymerization are relatively unknown, although it has been found that diaryliodonium salts can be employed as with ascorbic acid, benzoin, or stannous octoate to initiate cationic polymerizations.

[0005] Free radicals generated either by thermolytic or by photolytic methods can be used as reducing agents for diaryliodonium salts, and these combination systems can be 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, as the reactions do not take place spontaneously and require an external stimulus (heat or light).

This can be attributed to the considerably greater difficulty of reducing triarylsulfonium salts ($E_{red} = -28$ k-cal mol^{-1}) as compared to diaryliodonium salts ($E_{red} = -5$ k-cal mol^{-1}).

[0006] The development of a low temperature, controllable and convenient means of conducting the crosslinking polymerization of epoxy monomers and epoxy functional oligomers that meets the requirements of minimal energy usage, eliminates the use of solvents and is economically viable remains an elusive goal.

SUMMARY OF THE INVENTION

[0007] New cationic redox systems that are capable of initiating cationic polymerizations of epoxide, oxetane or alkyl vinyl ether resins spontaneously at room temperature are provided. These redox systems consist of a diaryliodonium or a triarylsulfonium salt as the oxidant with a volatile 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. The reducing agent is delivered as a vapor to a thin film monomer sample containing the oxidizing agent.

[0008] A mixture of onium salt, catalyst, and monomer or oligomer or mixture thereof is presented in accordance with the present invention. This mixture is referred to as the "MOC mixture" to represent **M**er (monomer, oligomer or mixture thereof), **O**nium salt, and **C**atalyst.

[0009] An aspect of the present invention relates to a method for forming a polymer comprising exposing to a reducing agent in the vapor state a mixture of onium salt, catalyst, and vinyl or heterocyclic monomer or oligomer or mixture thereof capable of cationic polymerization ("MOC mixture").

[0010] A second aspect of the present invention relates to a composition for cationic polymerization comprising: an onium salt; a vinyl or heterocyclic monomer or oligomer or mixture thereof capable of cationic polymerization; a metal-containing catalyst; and a reducing agent in the vapor state.

[0011] A third aspect of the present invention relates to a composition for cationic polymerization comprising an onium salt, a catalyst, a vinyl or heterocyclic monomer or oligomer or mixture thereof capable of cationic polymerization, and a reducing agent selected from a silane and a siloxane containing at least one Si-H functional group.

[0012] A fourth aspect of the present invention relates to a composition for cationic polymerization comprising: a) an onium salt selected from an iodonium salt and a sulfonium salt; b) vinyl or heterocyclic monomer or oligomer or mixture thereof capable of non-radical cationic polymerization selected from 1,3-bis(3,4-epoxycyclohexyl-2-ethyl) -1,1,3,3-tetramethyldisiloxane; cyclohexene oxide; 4- vinylcyclohexene-1,2-oxide; 4-vinylcyclohexene dioxide; limonene dioxide; 1,2-epoxydecane; 1,2,7,8-diepoxyoctane; 3,4-epoxycyclohexylmethyl-3',4'epoxycyclohexane carboxylate; bisphenol-A diglycidyl ether; trimethylolpropane triglycidyl ether; novolac epoxides; epoxidized vegetable oils; bis(3-ethyloxyetanylmethyl) ether; triethyleneglycol divinyl ether; and triethyleneglycol methyl vinyl ether; c) a metal-containing catalyst; and d) a reducing agent selected from a silane and a siloxane containing at least one Si-H functional group.

[0013] A fifth aspect of the present invention relates to an apparatus comprising a) a container having an inlet for receiving pressurized gas, an outlet, a port in said inlet for receiving a vaporizable liquid and a zone in said inlet for vaporizing said liquid, said zone in fluid communication with said container; b) a target vessel enclosed by said container and operatively connected to said inlet and said outlet; and c) a material characterization device positioned to detect a characteristic of a chemical reaction occurring in the target vessel.

[0014] A sixth aspect of the invention relates to a method for forming a polymer using an apparatus comprising a) a container having an inlet for receiving pressurized gas, an outlet, a port in said inlet for receiving a vaporizable liquid and a zone in said inlet for vaporizing said liquid, said zone in fluid communication with said container; b) a target vessel enclosed by said container and operatively connected to said inlet and said outlet; and c) a material characterization device positioned to detect a characteristic of a chemical reaction occurring in the target vessel; wherein said vaporizable liquid is injected into the port of said inlet and wherein pressurized gas passes through the container to deliver the vapor to the target vessel.

[0015] A seventh aspect of the invention relates to a method for delivering a vaporized reducing agent to a target vessel comprising: a) injecting a vaporizable reducing agent into a port of a container having an inlet and an outlet; b) delivering pressurized gas to said reducing agent through said inlet; c) delivering vaporized reducing agent to a target vessel in fluid communication with the outlet; and d) detecting a characteristic of a chemical reaction using a characterization device.

[0016] A eighth aspect of the present invention relates to a method of polymerization comprising delivering a vaporized reducing agent to a target vessel containing a MOC mixture using an apparatus comprising: a) a container having an inlet for receiving pressurized gas, an outlet, and a port for receiving a vaporizable reducing agent to said container; b) a target vessel operatively connected to the outlet; and c) a material characterization device positioned to detect a characteristic of a chemical reaction.

[0017] A ninth aspect of the present invention relates to a method of polymerization comprising: a) forming a vaporized reducing agent; b) introducing said vaporized reducing agent to a MOC mixture; and c) detecting the temperature of the resulting polymerization reaction to determine the state of polymerization.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1.	Apparatus for delivery of vaporizable reducing agent.
Figure 2.	Modified apparatus for delivery of vaporizable reducing agent used in studies.
Figure 3.	Optical pyrometry (OP) study of the polymerization of cyclohexene oxide with 3.0% DPS-C_1C_{16} SbF_6 and 8 ppm Karstedt catalyst using 1,1,3,3-tetramethyldisiloxane (TMDS) as the reducing agent.
Figure 4.	OP study of the polymerization of VCHDO with 3.0% DPS-C_1C_{16} SbF_6 and 8 ppm Karstedt catalyst using TMDS as the reducing agent.
Figure 5.	OP study of the polymerization of VCHDO with 3.0% DPS-C_1C_{16} SbF_6 and 8 ppm Cl_2(COD)Pd(II) using TMDS as the reducing agent.
Figure 6.	Effect of the Karstedt catalyst concentration on the polymerization of VCHDO using 3.0% DPS-C_1C_{16} SbF_6 and TMDS as the reducing agent.
Figure 7.	Polymerization of VCHDO with 3.0% DPS-C_1C_{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
Figure 8.	Comparison of the polymerization of VCHDO with 3.0% DPS-C_1C_{12} SbF_6, DPS-C_1C_{12} AsF_6, and DPS-C_1C_{12} PF_6, 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_6 salts using 8 ppm Karstedt catalyst with TMDS as the reducing agent.
Figure 10.	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 11.	Polymerizations of DVE-3 and triethyleneglycol methyl vinyl ether with 3.0 % DPS-C1C16 SbF6, 16 ppm Cl2(COD)Pd(II) using TMDS as the reducing agent.
Figure 12.	OP study of the polymerization of cyclohexene oxide with 2.0% (4-n-octyloxyphenyl)phenyliodonium hexafluoroantimonate (OPPI SbF_6), 4 ppm Lamoreaux catalyst using 1,1,3,3-tetramethyldisiloxane (TMDS) as the reducing agent.
Figure 13.	OP study of the polymerization of 4-vinylcyclohexene dioxide (VCHDO) with 2.5% OPPI SbF_6, 4 ppm Lamoreaux catalyst using TMDS as the reducing agent.
Figure 14.	Polymerization of VCHDO with 2.5% OPPI SbF_6, 4 ppm Lamoreaux catalyst using triethoxysilane (TEOS) as the reducing agent.
Figure 15.	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 16.	OP study of the polymerization of limonene dioxide (LDO) with 2.5% OPPI SbF_6, 4 ppm Lamoreaux catalyst using TMDS as the reducing agent.
Figure 17.	Polymerization of PC-1000 with 2.5% OPPI SbF_6, 4 ppm Lamoreaux catalyst using TMDS as the reducing agent.
Figure 18.	OP study of the cationic photopolymerizations of 1,2-epoxydecane and 1,2,7,8-diepoxyoctane in the presence of 2.5%, OPPI SbF_6, 4 ppm Lamoreaux catalyst using TMDS as the reducing agent.
Figure 19.	Polymerization of styrene oxide with 1.0% OPPI SbF_6, 0.5-1 ppm $[Cl(CO)_2Rh(I)]_2$ using TMDS as the reducing agent.
Figure 20.	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 21.	Polymerization of DVE-3 with 1.0% OPPI SbF_6, 0.5-1 ppm $[Cl(CO)_2Rh(I)]_2$ with TMDS as the reducing agent

DETAILED DESCRIPTION OF THE INVENTION

[0018] In one embodiment, the invention relates to a method for forming a polymer comprising exposing to a reducing agent in the vapor state a mixture of onium salt, catalyst, and vinyl or heterocyclic monomer or oligomer or mixture thereof capable of cationic polymerization ("MOC mixture"). In a further embodiment, the polymer is formed at ambient temperature without the addition of actinic radiation. In still another embodiment, the polymer is formed at ambient temperature without the addition of actinic radiation or heat.

[0019] In one embodiment, the invention relates to a composition for cationic polymerization comprising: an onium salt; a vinyl or heterocyclic monomer or oligomer or mixture thereof capable of non-radical cationic polymerization; a metal-containing catalyst; and a reducing agent in the vapor state.

[0020] In one embodiment, the invention relates to a composition for cationic polymerization comprising an onium salt, a catalyst, a vinyl or heterocyclic monomer or oligomer or mixture thereof capable of cationic polymerization, and a reducing agent selected from a silane and a siloxane containing at least one Si-H functional group.

[0021] In one embodiment, the invention relates to a composition for cationic polymerization comprising: an onium salt selected from an iodonium salt and a sulfonium salt; a vinyl or heterocyclic monomer or oligomer or mixture thereof capable of non-radical cationic polymerization selected from selected from 1,3-bis(3,4-epoxycyclohexyl-2-ethyl) -1,1,3,3-tetramethyldisiloxane; cyclohexene oxide; 4- vinylcyclohexene-1,2-oxide; 4-vinylcyclohexene dioxide; limonene dioxide; 1,2-epoxydecane; 1,2,7,8-diepoxyoctane; 3,4-epoxycyclohexylmethyl-3',4'epoxycyclohexane carboxylate; bisphenol-A diglycidyl ether; trimethylolpropane triglycidyl ether; novolac epoxides; epoxidized vegetable oils; bis(3-ethyloxyetanylmethyl) ether; triethyleneglycol divinyl ether; and triethyleneglycol methyl vinyl ether; a metal-containing catalyst; and a reducing agent selected from a silane and a siloxane containing at least one Si-H functional group.

[0022] In an embodiment of the methods and compositions described above, the reducing agent is a silane or siloxane containing at least one Si-H functional group. In yet another embodiment, the reducing agent is selected from silane; 1,1,3,3-tetramethyldisiloxane; triethylsilane; triethoxysilane; n-hexylsilane; dimethylphenylsilane; diphenylmethylsilane; 1,3,5,7-tetramethylcyclotetrasiloxane; and 1,3,5,7,9-pentamethylcyclopentasiloxane. In a further embodiment, the reducing agent is selected from 1,1,3,3-tetramethyldisiloxane, triethylsilane and triethoxysilane.

[0023] In some embodiments of the invention in which the reducing agent is not necessarily in the vapor state, the reducing agent may be an oligomeric siloxane. In further embodiments, the reducing agent is selected from poly(methylhydrogensiloxane) and oligo-poly(methylhydrogensiloxane-co-dimethylsiloxane)).

[0024] In an embodiment of the methods and compositions described above, the onium salt is selected from an iodonium salt and a sulfonium salt. In another embodiment, the onium salt is selected from a diaryliodonium salt, a dialkylphenacylsulfonium salt, a 2,6-dialkyl-4-hydroxyphenylsulfonium salt and a triphenylsulfonium salt. In yet another embodiment, the onium salt is selected from diaryliodonium SbF_6, diaryliodonium PF_6, dialkylphenacylsulfonium SbF_6, dialkylphenacylsulfonium AsF_6, dialkylphenacylsulfonium PF_6 or triphenylsulfonium SbF_6. In still another embodiment, the onium salt is selected from (4-n-octyloxyphenyl)phenyliodonium SbF_6, (4-n-octyloxyphenyl)phenyliodonium PF_6, S-methyl-S-n-octyl-S-phenacylsulfonium SbF_6, S-methyl-S-n-hexadecyl-S-phenacylsulfonium SbF_6, (4-n-pentadecyloxyphenyl)phenyliodonium SbF_6, S-methyl-S-n-dodecyl-S-phenacylsulfonium SbF_6, S-methyl-S-n-dodecyl-S-phenacylsulfonium PF_6, S-methyl-S-n-dodecyl-S-phenacylsulfonium AsF_6, S-pentamethylene-S-phenacylsulfonium SbF_6 and triphenylsulfonium SbF_6.

[0025] In an embodiment of the methods and compositions described above, the monomer is selected from an alkyl vinyl ether, an oxetane and an epoxide. In a further embodiment, the monomer is selected from 1,3-bis(3,4-epoxycyclohexyl-2-ethyl) -1,1,3,3-tetramethyldisiloxane; cyclohexene oxide; 4- vinylcyclohexene-1,2-oxide; 4-vinylcyclohexene dioxide; limonene dioxide; 1,2-epoxydecane; 1,2,7,8-diepoxyoctane; 3,4-epoxycyclohexylmethyl-3',4'epoxycyclohexane carboxylate; bisphenol-A diglycidyl ether; trimethylolpropane triglycidyl ether; novolac epoxides; epoxidized vegetable oils; bis(3-ethyloxyetanylmethyl) ether; triethyleneglycol divinyl ether; and triethyleneglycol methyl vinyl ether.

[0026] In an embodiment of the methods and compositions described above, the catalyst is a noble metal-containing catalyst. In a further embodiment, the catalyst contains a noble metal selected from rhodium, palladium, iridium and platinum. In still another embodiment, the catalyst is selected from the Karstedt catalyst, Lamoreaux catalyst, Speier's catalyst, Ashby's catalyst, chloroplatinic acid, $[Cl(COD)Pt(I)]_2$, $Cl_2(C_6H_5CN)_2Pt(II)$, $Cl_2[(C_2H_5)_2S]_2Pt(II)$, $[Cl(COD)Rh(I)]_2$, $[Cl(CO)_2Rh(I)]_2$, $[Cl(COD)Rh(I)]$ and $Cl_2(COD)Pd(II)$, H_2PtCl_6, and $Cl(COD)Pt(II)_2$.

[0027] In one embodiment, the invention relates to an apparatus comprising: a container having an inlet for receiving pressurized gas, an outlet, a port in said inlet for receiving a vaporizable liquid and a zone in said inlet for vaporizing said liquid, said zone in fluid communication with said container; a target vessel enclosed by said container and operatively connected to said inlet and said outlet; and a material characterization device positioned to detect a characteristic of a chemical reaction occurring in the target vessel.

[0028] In another embodiment, the characterization device comprises a detector capable of quantifying temperature. In a further embodiment, the characterization device comprises an infrared detector. In still another embodiment, the apparatus further comprises a data acquisition system linked to the characterization device.

[0029] In yet another embodiment, the apparatus additionally comprises a means for heating said zone in said inlet. In another embodiment, the invention relates to a method for forming a polymer comprising using the apparatus described above, wherein said vaporizable liquid is injected into the port of said inlet and wherein pressurized gas passes through the container to deliver the vapor to the target vessel.

[0030] In one embodiment, the invention relates to a method for delivering a vaporized reducing agent to a target vessel comprising: injecting a vaporizable reducing agent into a port of a container having an inlet and an outlet; delivering pressurized gas to said reducing agent through said inlet; delivering vaporized reducing agent to a target vessel in fluid communication with the outlet; and detecting a characteristic of a chemical reaction using a characterization device.

[0031] In one embodiment, the invention relates to a method of polymerization comprising delivering a vaporized reducing agent to a target vessel containing a MOC mixture using an apparatus comprising: a container having an inlet for receiving pressurized gas, an outlet, and a port for receiving a vaporizable reducing agent to said container; a target vessel operatively connected to the outlet; and a material characterization device positioned to detect a characteristic of a chemical reaction.

[0032] In one embodiment, the invention relates to a method of polymerization comprising: forming a vaporized reducing agent; introducing said vaporized reducing agent to a MOC mixture; and detecting the temperature of the resulting polymerization reaction to determine state of polymerization.

DEFINITIONS

[0033] Throughout this specification the terms and substituents are defined when first introduced and retain their definitions.

[0034] Unless otherwise specified, alkyl is intended to include linear, branched, or cyclic hydrocarbon structures and combinations thereof. A combination would be, for example, cyclopropylmethyl. Lower alkyl refers to alkyl groups of from 1 to 6 carbon atoms. Examples of lower alkyl groups include methyl, ethyl, propyl, isopropyl, butyl, s-and t-butyl and the like. Preferred alkyl groups are those of C_{20} or below. A cycloalkyl is a subset of alkyl and includes cyclic hydrocarbon groups having from about 3 to about 8 carbon atoms. Examples of cycloalkyl groups include but are not limited to cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, norbornyl, and the like.

[0035] Heterocycle means a cycloalkyl or aryl carbocycle residue in which from one to three carbons is replaced by a heteroatom selected from the group consisting of N, O and S. The nitrogen and sulfur heteroatoms may optionally be oxidized, and the nitrogen heteroatom may optionally be quaternized. Unless otherwise specified, a heterocycle may be non-aromatic or aromatic.

[0036] Aryl and heteroaryl mean (i) a phenyl group (or benzene) or a monocyclic 5- or 6-membered heteroaromatic ring containing 1-4 heteroatoms selected from O, N, or S; (ii) a bicyclic 9- or 10-membered aromatic or heteroaromatic ring system containing 0-4 heteroatoms selected from O, N, or S; or (iii) a tricyclic 13- or 14-membered aromatic or heteroaromatic ring system containing 0-5 heteroatoms selected from O, N, or S. The aromatic 6- to 14-membered carbocyclic rings include, e.g., benzene, naphthalene, indane, tetralin, and fluorene and the 5- to 10-membered aromatic heterocyclic rings include, e.g., imidazole, pyridine, indole, thiophene, benzopyranone, thiazole, furan, benzimidazole, quinoline, isoquinoline, quinoxaline, pyrimidine, pyrazine, tetrazole and pyrazole.

[0037] Actinic radiation is understood in the art as electromagnetic radiation in the wavelengths that initiate photochemical reactions. (See Academic Press Dictionary of Science and Technology, 1992 p. 31.) This functional definition is intended for the term as it is used in the present application. In the absence of a photosensitizer, radiation in the wavelengths between 4 and 400 nm is actinic radiation. If a photosensitizer is added, longer wavelength radiation can function to initiate photochemical reactions and would in that case be considered equivalent to actinic radiation as defined for this application.

[0038] Ambient temperature is the temperature of the surroundings in which a reaction is carried out. For most normal human activities carried out in an enclosed space, unless the temperature of the space is regulated for a purpose not related to human activity, ambient temperature will be close to 23°C.

[0039] **MOC mixture:** A mixture of onium salt, catalyst, and monomer or oligomer or mixture thereof is presented in accordance with the present invention. This mixture is referred to as the "MOC mixture" to represent **M**er (monomer, oligomer or mixture thereof), **O**nium salt, and **C**atalyst. The MOC mixture comprises a vinyl or heterocyclic monomer or oligomer or mixture thereof capable of cationic polymerization, a catalyst and an onium salt. The catalyst may contain a noble metal.

[0040] The monomer component may comprise one or more of a monomer chosen from oxetane monomers, epoxide monomers, and alkyl vinyl ether monomers. Examples of an oxetane monomer component that may be used in an embodiment of the present invention include, but are not limited to, oxetane, 3-ethyl-3-phenoxymethyloxetane, 3-ethyl-3-allyloxymethyloxetane, 3-methyl-3-phenoxymethyloxetane, 3-ethyl-3-[(2-ethylhexyloxy)methyl]oxetane, bis{[(1-ethyl(3-oxetanyl)]methyl} ether, 1,4-bis[(3-ethyl-3-oxetanylmethoxy)methyl]benzene, bis[(3-ethyl-3-oxetanylmethoxy)methyl] terephthalate, bis[(3-ethyl-3-oxetanylmethoxy)methyl]phenyl ether, 2-phenyloxetane, 3,3-bischloromethyloxetane, 3,3-dimethyloxetane, 3,3-bisbromomethyloxetane, other like 3,3-substituted oxetanes. Examples of epoxides that may be used in an embodiment of the present invention include, but are not limited to, an allyl glycidyl ether, a benzyl glycidyl ether, an α,α-1,4-xylyldiglycidyl ether, a bisphenol-A diglycidyl ether, cresyl glycidyl ether, an ethyleneglycol diglycidyl ether, a diethyleneglycol diglycidyl ether, a neopentylglycol diglycidyl ether, a 1,4-butanediol diglycidyl ether, a 1,4-cyclohexanedimethanol diglycidyl ether, a trimethylopropanetriol triglycidyl ether, a glycerol triglycidyl ether, a cresyl glycidyl ether, a diglycidyl phthalate, a cresol novolac epoxide, a phenol novolac epoxide, a bisphenol-A novolac epoxide, 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane, bis(3,4-epoxycyclohexylmethyl) adipate, 4-vinylcyclohexene-1,2 oxide, limonene dioxide, limonene monoxide, 1,2-epoxydecane, 1,2-epoxydodecane, 1,2-7,8-diepoxyoctane, epoxidized soybean oil, epoxidized linseed oil, epoxidized castor oil, epoxidized natural rubber, epoxidized poly(1,2-butadiene), epoxy functional silicone resins, and the like. Examples of alkyl vinyl ethers that may be used in an embodiment of the present invention include, but are not limited to, methyl vinyl ether, ethyl vinyl ether, propyl vinyl ether, isopropyl vinyl ether, butyl vinyl ether, triethyleneglycol divinyl ether, trimethylolpropane trivinyl ether and the like.

[0041] Monomers that contain two or more polymerizable functional groups are classified, *i.e.* named, based on the predominant functional group present. For example, a monomer having 70 units of an epoxide functionality and 30 units of an acrylate functionality would be named an epoxide monomer in accordance with the present invention. Another example is a monomer containing 98 units of an oxetane functionality and 2 units of an ethylenic functionality. The monomer would be referred to as an oxetane monomer and not an olefin monomer in accordance with the present invention. The aforementioned examples are meant to clarify how to classify or name monomers that contain two or more polymerizable functional groups. The examples are not meant to describe the actual ratio or ranges of functional groups in a monomer that may be used in accordance with the present invention. One ordinarily skilled in the art would be able to distinguish between monomers having multiple polymerizable functionalities capable for use in the present invention and monomers having multiple functionalities that would be excluded from use in the present invention. In some embodiments, the monomer will comprise only a single class of polymerizable group such as an epoxide or an oxetane or a vinyl ether.

[0042] The MOC mixture additionally contains an onium salt. The onium salt is chosen from the group consisting of a triarylsulfonium salt; a diaryliodonium salt; a dialkylphenacylsulfonium salt; and the like. These salts have counterions chosen from SbF_6^-, $[(C_6F_5)_4B]^-$, AsF_6^-, PF_6^-, $C_4F_9SO_3^-$, FSO_3^-, GaF_6^-, $(CF_3SO_2)_2CH^-$, $(CF_3SO_2)_3C^-$, BF_4^- and $CF_3SO_3^-$. Preferred strong acid anions are SbF_6^- and $[(C_6F_5)_4B]^-$. These onium salts are commercially available and are described in journal publications to Crivello, J.V.; Lee, J.L. Alkoxy-Substituted Diaryliodonium Salt Cationic Photoinitiators. *J. Polym. Sci. Part A: Polym. Chem. Ed.* 1989, 27, 3951; S.R. Akhtar, J.V. Crivello, J.L. Lee, *J. Org. Chem.* 55 (1990) 4222; Akhtar *et al.*, *Chem. Mater.* 2, 732-737 (1990); J.V. Crivello, S. Kong, *Macromolecules* 33 (2000) 833, and in US patents 4,882,201; 4,941,941; 5,073,643; 5,274,148; 6,031,014; 6,632,960; and 6,863, 701, all of which are incorporated herein by reference.

[0043] The examples of diaryliodonium salts described above are not meant to limit the kinds of diaryliodonium salts that may be used in accordance with the present invention. Diaryliodonium salts that may be used in an embodiment of the MOC mixture and method (described *infra*) of the present invention include salts of the following formula:

$$\text{Ar-I}^{+}\text{-Ar'}\ \ \text{MtX}_n^{-}$$

[0044] In the above structure, Ar and Ar' are the same or different aryl groups that may bear from 0 to 5 substitutents. Those substituents may be aliphatic, aromatic, halo, haloalkyl, nitro, keto, alkoxy, or may contain hydroxyl groups, carboxylic acid groups, unsaturated groups or alkylaryl groups. Further, Ar and Ar'may also represent heterocyclic groups such as furan, thiophene, thioxanthene, thioxanthone or thianthrene groups. In the above structure, MtX_n^{-} represents an anion of low nucleophilicity.

[0045] The MOC mixture additionally contains a catalyst. The catalyst may be a metal containing catalyst and, in some embodiments, may contain a noble metal. In some embodiments, the noble metal is selected from rhodium, palladium, iridium and platinum. The catalyst may be selected in some embodiments from the Karstedt catalyst ($Pt_2\{[(CH_2{=}CH)Me_2Si]_2O\}_3$), Lamoreaux catalyst ($H_2PtCl_6$ in octyl alcohol), Speier's catalyst (H_2PtCl_6 in ethyl alcohol), chloroplatinic acid, $[Cl(COD)Pt(I)]_2$, $Cl_2(C_6H_5CN)_2Pt(II)$, Ashby catalyst Pt complexed with tetramethyl, tetravinylcyclotetrasiloxane), $Cl_2[(C_2H_5)_2S]_2Pt(II)$, $[Cl(COD)Rh(I)]_2$, $[Cl(CO)_2Rh(I)]_2$, $[Cl(COD)Rh(I)]$ and $Cl_2(COD)Pd(II)$, H_2PtCl_6, and $Cl(COD)Pt(II)_2$.

[0046] The MOC mixture can be prepared by independently combining a catalyst component, an onium salt, and a monomer listed above to form a homogeneous solution containing the aforementioned.

[0047] The MOC mixtures of the present invention may additionally comprise one or more of a filler, a colorant, a surface active agent, or a leveling agent.

[0048] Examples of a filler that may be used in an embodiment of the present invention include but are not limited to inorganic particulate fillers such as silica, talc or clays. Examples of reinforcing fibers include glass, poly(ethylene), carbon, and polyimide fibers, as well as impact modifiers, such as core-shell type elastomers, and the like. Examples of a colorant or dye that may be used include but are not limited to copper phthalocyanine, carbon black, dayglow pigments, iron oxide, titanium dioxide, zinc oxide, copper oxide, cadmium sulfide, and the like.

[0049] Examples of a surface active agent that may be used in embodiment of the present invention include but are not limited to polyethylene glycol-silicone copolymers, fluorinated silicones, fluorinated alkyl ethers, and the like. Examples of leveling and matting agents that may be used include but are not limited to silicones, stearyl alcohol, oleic acid, poly(ethylene) wax, carnauba wax, zein wax, poly(tetrafluoroethylene), and the like.

[0050] The MOC mixture is a liquid. Viscosity is an inherent property of liquids, and for the purposes of the present invention, materials having a viscosity below 500,000 centipoises (cP) are considered useful liquids. The terminology “functionally unchanged” referring to viscosity means that the viscosity is changed immeasurably or that it is changed measurably but not sufficiently that the change in viscosity alters the function of the mixture. Changes that result in less than 50% increase in absolute viscosity (η) are to be considered “functionally unchanged”.

[0051] Examples of techniques for applying the MOC mixture to a substrate include, but are not limited to, dip, roll, brush, pad or spray coating, screen printing, needle dispensing, casting and other like application techniques. Examples of a substrate that may be used in an embodiment of the present invention include but are not limited to a polymer material, a glass material, a wood material, a metal material, a textile material, a ceramic material, and combinations thereof.

[0052] Although this invention is susceptible to embodiment in many different forms, preferred embodiments of the invention are shown. It should be understood, however, that the present disclosure is to be considered as an exemplification of the principles of this invention and is not intended to limit the invention to the embodiments illustrated. It may be found upon examination that certain members of the claimed genus are not patentable to the inventors in this application. In this event, subsequent exclusions of species from the compass of applicants' claims are to be considered artifacts of patent prosecution and not reflective of the inventors' concept or description of their invention; the invention encompasses all of the members of the genus that are not already in the possession of the public.

EXPERIMENTAL AND EXAMPLES

[0053] **Materials.** Limonene dioxide (1-methyl-4-(2-methyloxiranyl)-oxabicyclo[4.1.0]-heptane), and 1,2-epoxydecane was obtained from the Viking Chemical Co., Minneapolis, MN. 1,3-Bis (3,4-epoxycyclohexyl-2-ethyl),1,1,3,3-tetramethyldisiloxane (PC-1000) was prepared according to an established procedure (Crivello, J.V.; Lee, J.L. The UV Cure of Epoxy-Silicone Monomers, ACS Symp Series No. 417, Hoyle C.E., Kinstle, J.F. editors American Chemical Society, Washington, DC, 1989, p. 398-411). Bis(3-ethyloxetanylmethyl) ether (DOX) was obtained from the Toagosei Chemical Company, Ltd. Nagoya, Japan. 3,4-Epoxycyclohexylmethyl 3’,4’-epoxycyclohexane carboxylane (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 obtained from 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 obtained from Gelest, Inc., Morrisville, PA. All other metal complexes used as catalysts in this work were obtained from Strem Chemicals, Inc., Newburyport, MA. All other monomers, reagents and chemicals were used as obtained from the Aldrich Chemical Co., Milwaukee, WI. Cyclohexene oxide was purified prior to use by distillation over CaH_2.

[0054] The S,S-dialkyl-S-phenacylsulfonium salts (DPS) and S(4-n-decyloxyphenyl)-S,S-diphenylsulfonium hexafluoroantimonate (SOC-10 SbF_6), were synthesized and purified by a previously described method (J.V. Crivello and S. Kong "Synthesis and Characterization of Second Generation Dialkylphenacylsulfonium Salt Photoinitiators" Macromolecules, 33(3), 825-832 (2000). Triphenylsulfonium SbF_6 was prepared according to the method of Potratz et al. (Wildi, D.S.; Taylor, S.W.; Potratz, H.A. *J. Am. Chem. Soc.* **1951**, *73* 1965). The diaryliodonium salts, (4-n-octyloxyphenyl)phenyliodonium hexafluoroantimonate (OPPI SbF_6), (4-n-decyloxyphenyl)phenyliodonium hexafluorophosphate (DOPI PF_6) and di(t-butylphenyl)iodonium hexafluoroarsenate (DTBPI AsF_6) were synthesized and purified by previously described methods (Crivello, J.V.; Lee, J.L. J Polym Sci Part A: Polym Chem 1989, 27, 3951-3968). Rhodrosil 2746 was obtained from the Ciba-Geigy Corporation of Basel, Switzerland.

[0055] **Optical Pyrometry (OP).** Using optical pyrometry (OP), the temperature of a liquid film of a monomer, mixture of monomers or a prepolymer undergoing polymerization is monitored as a function of time. We have shown that the increase of temperature of such a sample can be directly related to a corresponding increase in the conversion of the monomer undergoing polymerization. OP is a highly sensitive, reproducible and rapid analytical method.

[0056] The instant invention includes a method of polymerization by using a modified optical pyrometry apparatus to deliver a vaporized reducing agent to a MOC mixture. Figure 1 shows a schematic diagram of the apparatus with the modifications made for conducting polymerization studies using a volatile silane reducing agent. The apparatus comprises a container (1). The container (1) comprises an inlet (2), an outlet (3), a port in the inlet (4), a zone for vaporization (5), a target vessel (6) and a characterization device (7). Briefly, the target vessel (6) may contain a MOC mixture. A volatile reducing agent is injected into the port (4). Pressurized gas is blown through the inlet (2), causing vaporization of the reducing agent in the zone (5). The vaporized reducing agent is delivered by the pressurized gas to the target vessel (6) and out the outlet (3). The characterization device (7) measures a characteristic of a chemical reaction which takes place in the target vessel (6).

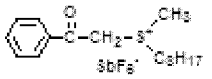
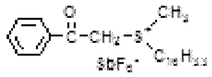
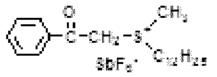
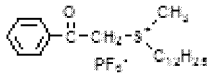
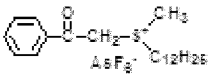
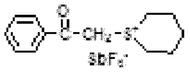
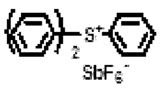
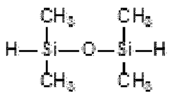
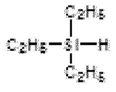
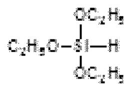
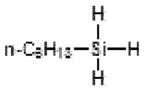
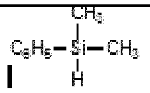
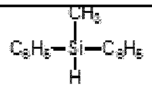
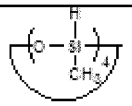
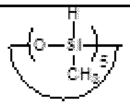
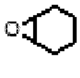
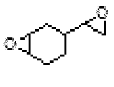
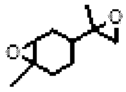
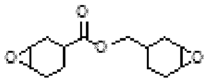
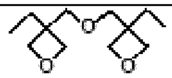
[0057] Figure 2 shows a schematic diagram of the apparatus used in the current application. The liquid sample (8) was absorbed into a thin (0.2 mm) 15 mm x 15 mm sheet of nonwoven polyester fabric (veil) placed on a thin (0.25 mm) fluorinated polyethylene film (10) mounted in a plastic 2 cm x 2 cm slide frame (9). The slide frame (9) was placed into a recessed sample holder (11) and an 8.5 cm diameter x 1.0 cm circular glass housing (20) was used to cover the target vessel (6) and was placed over the sample (8). A 1 cm diameter aperture was cut into the top of the housing (20) as the outlet (3) to permit direct line-of-sight access to the sample (8) for the infrared radiation (18) and the characterization device (7, in this case, an infrared camera) and to function as a vent. The sample (8) was positioned at the center of the outlet (3) and at such a distance that it lies at the focal point of the characterization device (7). 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 by syringe (12) through a port (4) into a chamber (19) filled with glass wool (13) that provides a zone for vaporization (5, in Figure 1). Dry air was produced by blowing air (16) through a drying tube (17) and a mineral oil bubbler (15). A three-way valve (14) was present to control the air flow. A slow stream of this dry air passing through the chamber (19) carried the vapors of the silane into the target vessel (6) via a glass tube that was positioned with the end at a distance of 2.5 cm from the sample (8). The housing (20) served to confine the silane vapor to the area about the sample (8). 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.

[0058] 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 obtained 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_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.

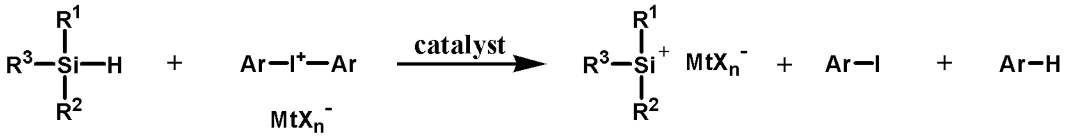
[0059] In these experiments, an Omega Corp. Model OS 552-V1-6 infrared camera with a sensitivity of ± 0.5 °C over the range of -18-538 °C was employed. Reactions that produce a sample temperature change of at least 1 °C/min can be monitored with this instrument.

[0060] The structures, names and abbreviations of many of the onium salts, silanes and monomers described in this communication are given in Table 1:

Table 1
Structures of Sulfonium Salts, Silanes and Monomers

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_{14} PF_6** S-methyl-S-n-dodecyl-S-phenacylsulfonium PF_6
 **DPS-C_1C_{14} 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** Triphenylsulfonium 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	 limonene dioxide
 **ERL-4221** 3,4-epoxycyclohexylmethyl 3',4' epoxycyclohexane carboxylate	 **DOX** bis(3-ethyloxetanylmethyl) ether	 **DVE-3®** triethylene glycol divinyl ether	 **LDO** Triethyleneglycol methyl vinyl ether

[0061] A large variety of structurally diverse organosilane compounds are available as potential reducing agents. In the structure shown below, the only basic requirement is that the compound must contain at least one Si-H group to function as a reducing agent. The other three groups about silicon can be any combination of, hydrogen, alkyl, aryl, silicon, siloxy, alkoxy or halogen. Although the applicant does not wish to be constrained by any hypothesis as to how the invention works, the reactions involved may proceed as depicted in Scheme 2, which involves the ionic reduction of the diaryliodonium salt by the silane.



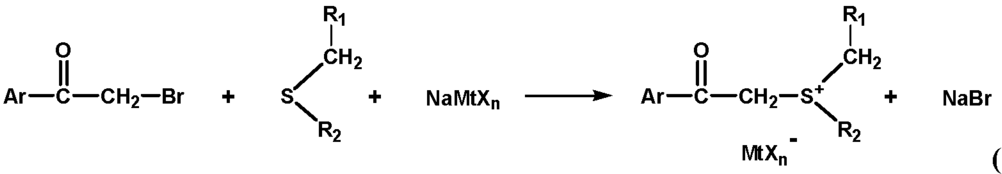
Scheme 2. Mechanism of the redox cationic initiation of epoxide polymerization by silanes

[0062] The reduction of diaryliodonium salts in dichloromethane with triethylsilane leads to the production of very acidic solutions. When these solutions are added to cyclohexene oxide, instantaneous exothermic polymerization occurs. It was found that the polymerization of epoxide monomers could be carried out in nitrobenzene solution using the new redox catalyst system.

[0063] 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 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. 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.

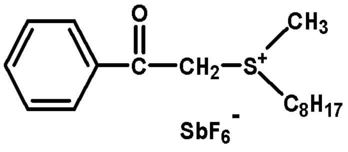
[0064] **Solution Redox Cationic Polymerization of Cyclohexene Oxide.** Into a clean dry 4 dram amber screw cap vial equipped with a Teflon microstirbar and fitted with a with a polyethylene liner were placed 1.96 g (0.02 mol) distilled cyclohexene oxide, 0.0284 g (5×10^{-5} mol) DPS-C_1C_8 SbF_6 and 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 icewater 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 THF gave a M_n = 11000 g/mol based on polystyrene standards. 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.

[0065] **S,S-Dialkyl-S-phenacylsulfonium salts.** S,S-dialkyl-S-phenacylsulfonium salts (DPS) bearing anions, MtX_n^-, of low nucleophilic character were first reported in a publication from this laboratory. A new synthetic pathway was developed, shown in equation 2. 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.



(2)

[0066] 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_aC_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_1C_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_1C_8 SbF_6

[0067] **Preliminary Evaluation of the DPS-Silane Redox Couple.** 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 moles 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_1C_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. 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. 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 inhibitor/retarder for free radical reactions and this observation lends support to the rationale that the redox reaction likely takes place by an ionic rather than a free radical reaction. Additional evidence is provided by the 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.

[0068] **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. The poly(cyclohexene oxide) that was obtained had a M_n of 11,000 g/mol.

[0069] 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. 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.

[0070] This apparatus was further modified to allow the reducing agent to be delivered to the sample in the vapor state. Figures 1 and 2 (described in detail earlier) show schematic drawings of the modified OP apparatus. When the reducing agent vapor contacts the MOC sample, reduction of the onium salt takes place resulting in the release of a Brønsted acid with consequent polymerization of the monomer.

[0071] 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 3 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.

[0072] 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 were 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 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 was an excellent catalyst at the 2-8 ppm Pt level for redox cationic polymerizations involving DPS. Figure 4 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 second induction period and then takes place by a vigorous autoacceleration process that drives the temperature of the thin film sample to 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 5, 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.

[0073] Figure 6 shows the results of a study of the effects of varying the concentration of the Karstedt catalyst on the TMDS vapor-induced polymerization of VCHDO with DPS-C_1C_{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.

[0074] A series of vapor-induced polymerizations of VCHDO with DPS-C_1C_{16} SbF_6 was carried out at room temperature using four different volatile silane reducing agents. The results obtained are depicted in Figure 7. 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 (b.p. 70-71 ^oC), 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 (b.p. 114-115 ^oC). This polymerization proceeds with a very short induction period but does not proceed to completion. Triethoxysilane (TEOS, 134-135 ^oC) gives similar results while triethylsilane (TES, b.p. 107-108 ^oC) generally shows a low order of reactivity. 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.

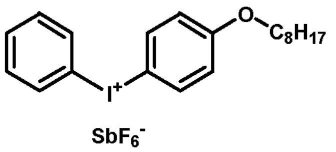
[0075] In Figures 8 and 9 we show the results of our OP investigations into the structure of the DPS. In all cases, VCHDO was used as the monomer along with TMDS and the Karstedt catalyst. A study of the effect of DPS-C_1C_{12} salts bearing different anions is presented in Figure 8. A complimentary study is given in Figure 9 in which the structure of the cation of the DPS is modified maintaining the same SbF_6^- anion. Shown in Figure 10 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. Also included in Figure 10 is an OP curve in which S(4-hydroxy-3,5-dimethyl)-S,S-dimethylsulfonium SbF_6 was employed as the oxidant.

[0076] 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 considerably 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 11 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.

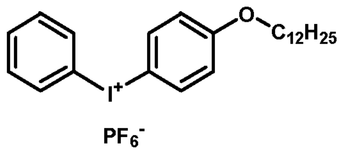
[0077] In Figure 12 is shown an OP study of the ring-opening polymerization of cyclohexene oxide carried out using (4-n-octyloxyphenyl)phenyliodonium hexafluoroantimonate (OPPI SbF_6) with 1,1,3,3-tetramethyldisiloxane (TMDS) as the reducing agent. The commercially available Lamoreaux catalyst was used. In addition, mixtures of this catalyst together with diaryliodonium salts in mono- and difunctional epoxy monomers were stable for long periods (weeks) of time provided that they were stored in the dark. The Lamoreaux catalyst is prepared by heating chloroplatinic acid together with an excess of n-octanol. The catalyst is stable at room temperature and was added to the monomer-diaryliodonium salt solution by means of a syringe. Two runs are shown in Figure 12 and the similarity of the curves demonstrates the reproducibility of the OP method. As can be seen in Figure 12, the polymerization proceeds exothermically after approximately a 20 second induction period with the temperature rising to a maximum of 154-169 °C. The polymerization of this monomer displays classical autoacceleration behavior in which the heat of polymerization drives the reaction to a high conversion within a very short time.

[0078] Very similar polymerization behavior is observed for 4-vinylcyclohexene dioxide (VCHDO) and the results are depicted in Figure 13. When the amount of the platinum catalyst was reduced to 2 ppm, the induction period was unchanged; however the overall OP curve was broadened and the maximum temperature attained by the sample was lowered to 136 °C. Figure 14 shows the results obtained when TMDS was replaced by triethoxysilane (TEOS). Duplicate runs are given in this figure. Analogous studies were conducted using triethylsilane ($(C_2H_5)_3SiH$; b.p. 107-108 °C) and n-hexylsilane (n-$C_6H_{13}SiH_3$; b.p. 114-115 °C) as volatile reducing agents with substantially the same results.

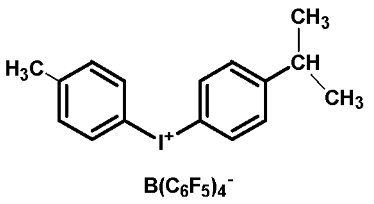
[0079] Figure 15 shows OP curves that were obtained for the three diaryliodonium salts whose structures are depicted below. As can be noted, the diaryliodonium salts differ with respect to both their cations and anions. The results obtained show that the reactivity of Rhodorsil 2074 bearing the highly non-nucleophilic tetrakis(pentafluorophenyl)borate anion is comparable to the previously used OPPI SbF_6, (Figure 13).



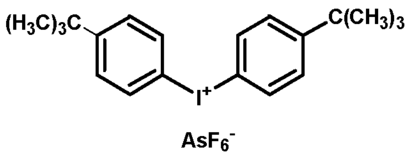
OPPI SbF_6



DOPI PF_6

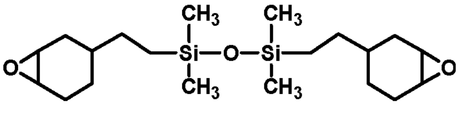


Rhodorsil 2074



DTBPI AsF_6

[0080] As depicted in Figure 16, the polymerization of LDO takes place rapidly and exothermically after a short (8 second) induction period when the sample is exposed to TMDS in the vapor state. The very high exotherm encountered in this reaction distorts the sample and gives rise to the artifact of the multiple peaks that are observed. Figure 17 shows the response of the PC-1000 monomer (image below) to the redox cationic initiator system using TMDS as the volatile reducing agent. The OP curve obtained shows that the cationic ring-opening polymerization is quite exothermic, but that the curve is quite broadened. Some monomers may undergo crosslinking during the course of the polymerization. In these cases, the top layer of the sample that was directly exposed to the TMDS vapor may be crosslinked and hardened, but the underlying portion of the sample may remain in the liquid state. With such monomers, a longer exposure to the vapor of the reducing agent than indicated by the OP analysis may be necessary for it to diffuse into the sample and for the polymerization to be completed.



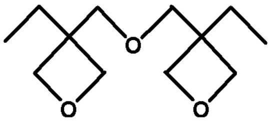
PC-1000

[0081] Terminal epoxy alkanes (α-olefin oxides) also display quite high reactivity in photoinitiated cationic ring-opening polymerizations. Figure 18 shows the polymerizations of two of these monomers; 1,2-epoxydecane and 1,2,7,8-diepoxyoctane. The two monomers display markedly different polymerization behaviors. While the polymerization of 1,2-epoxydecane proceeds smoothly at room temperature under redox initiation conditions, 1,2,7,8-diepoxyoctane displays an induction period of approximately 1 minute that is followed by a rapid, thermally autoaccelerated polymerization.

[0082] Styrene oxide is an exceedingly reactive monomer. It was found that the rhodium dimer complex, $[Cl(CO)_2Rh(I)]_2$, formed room temperature stable solutions of styrene oxide in the presence of OPPI SbF_6. Since the rhodium catalyst was not completely soluble in the monomer, its concentration could only be estimated at 0.5-1.0 ppm. As shown in Figure 19, these monomer solutions are unusually reactive when they are exposed to TMDS in the vapor state.

[0083] Some reactions, for instance with phenyl glycidyl ether, n-butylglycidyl ether, bisphenol-A diglycidyl ether and bisphenol-F diglycidyl ether, may progress too slowly for accurate measurement by the OP method. Nevertheless, it will still be possible to observe physical changes such as an increase in viscosity, film formation and hardening that accompany polymerization in the aforementioned monomers using the same redox cationic initiator system that was employed for the more reactive monomers described here.

[0084] 3,3-Disubstituted oxetanes are strained cyclic ethers that undergo facile cationic ring-opening polymerizations. Bis(3-ethyl-3-oxetanylmethyl) ether (DOX) is a reactive monomer that contains two polymerizable oxetane groups in the same molecule. The redox initiated cationic polymerization of DOX is shown in Figure 20.



DOX

[0085] The use of the rhodium dimer complex, $[Cl(CO)_2Rh(I)]_2$, gave stable solutions with several different mono- and difunctional vinyl ether monomers. Figure 21 depicts a study consisting of three OP runs of the cationic redox polymerization of triethyleneglycol divinyl ether (DVE-3) induced by TMDS in the vapor state. DVE-3 displays very high reactivity as indicated by a short induction period that is followed by the very rapid and high temperature polymerization of the monomer.

[0086] On the basis of the results of this preliminary work, it is anticipated that the redox cationic initiator described in this communication can be extended to include the polymerizations of virtually all types of cationically polymerizable monomers. Moreover, the application of this technology to accomplish crosslinking polymerization in typical coating, adhesive, encapsulation and composites technology is self-evident. As a demonstration, a two-ply laminate was fashioned by impregnating glass cloth with PC-1000 containing 2.5% OPPI SbF_6 with 4 ppm Lamoreaux platinum catalyst. The laminate was suspended in a vacuum desiccator and a small reservoir of TMDS was placed in the bottom of the desiccator. The vessel was closed, a vacuum drawn and the desiccator was sealed and allowed to stand at room temperature. After one hour, the desiccator was opened and the laminate examined and found to be dry and fully rigidified.

[0087] **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 appear to be several obvious areas of potential practical applications. For example, redox cationic polymerizations can be used in the traditional areas 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 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 herein in which the reducing agent is delivered in the vapor state to the monomer containing an onium 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.

[0088] One simple demonstration of the use of the DPS-silane redox couple as a cationic initiator is presented here. A 4 cm x 8 cm aluminum panel was knife coated with VCHDO containing 3.0 % DPS-C_1C_{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 minutes. 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.

CLAIMS

What is claimed is:

1. A method for forming a polymer comprising exposing to a reducing agent in the vapor state a mixture of onium salt, catalyst, and vinyl or heterocyclic monomer or oligomer or mixture thereof capable of cationic polymerization.
2. A method of claim 1 wherein said polymer is formed at ambient temperature without the addition of actinic radiation.
3. A method of claim 1 wherein said polymer is formed at ambient temperature without the addition of actinic radiation or heat.
4. A method of claim 1 wherein the reducing agent is a silane or siloxane containing at least one Si-H functional group.
5. A method of claim 4 wherein the reducing agent is selected from silane; 1,1,3,3-tetramethyldisiloxane; triethylsilane; triethoxysilane; n-hexylsilane; dimethylphenylsilane; diphenylmethylsilane; 1,3,5,7-tetramethylcyclotetrasiloxane; and 1,3,5,7,9-pentamethylcyclopentasiloxane.
6. A method of claim 5 wherein the reducing agent is selected from 1,1,3,3-tetramethyldisiloxane, triethylsilane and triethoxysilane.
7. A method of claim 1 wherein the onium salt is selected from an iodonium salt and a sulfonium salt.
8. A method of claim 7 wherein the onium salt is selected from a diaryliodonium salt, a dialkylphenacylsulfonium salt, a 2,6-dialkyl-4-hydroxyphenylsulfonium salt and a triphenylsulfonium salt.
9. A method of claim 8 wherein the onium salt is selected from diaryliodonium SbF_6, diaryliodonium PF_6, dialkylphenacylsulfonium SbF_6, dialkylphenacylsulfonium AsF_6, dialkylphenacylsulfonium PF_6 or triphenylsulfonium SbF_6.
10. A method of claim 9 wherein the onium salt is selected from (4-n-octyloxyphenyl)phenyliodonium SbF_6, (4-n-octyloxyphenyl)phenyliodonium PF_6, S-methyl-S-n-octyl-S-phenacylsulfonium SbF_6, S-methyl-S-n-hexadecyl-S-phenacylsulfonium SbF_6, (4-n-pentadecyloxyphenyl)phenyliodonium SbF_6, S-methyl-S-n-dodecyl-S-phenacylsulfonium SbF_6, S-methyl-S-n-dodecyl-S-phenacylsulfonium PF_6, S-methyl-S-n-dodecyl-S-phenacylsulfonium AsF_6, S-pentamethylene-S-phenacylsulfonium SbF_6 and triphenylsulfonium SbF_6.

11. A method of claim 1 wherein the monomer is selected from an alkyl vinyl ether, an oxetane and an epoxide.
12. A method of claim 1 wherein the monomer is selected from 1,3-bis(3,4-epoxycyclohexyl-2-ethyl)-1,1,3,3-tetramethyldisiloxane; cyclohexene oxide; 4-vinylcyclohexene-1,2-oxide; 4-vinylcyclohexene dioxide; limonene dioxide; 1,2-epoxydecane; 1,2,7,8-diepoxyoctane; 3,4-epoxycyclohexylmethyl-3',4'epoxycyclohexane carboxylate; bis(3-ethyloxyetanylmethyl) ether; triethyleneglycol divinyl ether; bisphenol-A diglycidyl ether; trimethylolpropane triglycidyl ether; novolac epoxides; epoxidized vegetable oils and triethyleneglycol methyl vinyl ether.
13. A method of claim 1 wherein the catalyst is a noble metal-containing catalyst.
14. A method of claim 13 wherein the catalyst contains a noble metal selected from rhodium, palladium, iridium and platinum.
15. A method of claim 14 wherein the catalyst is selected from the Karstedt catalyst, Lamoreaux catalyst, Speier's catalyst, Ashby catalyst, chloroplatinic acid, $[Cl(COD)Pt(I)]_2$, $Cl_2(C_6H_5CN)_2Pt(II)$, $Cl_2[(C_2H_5)_2S]_2Pt(II)$, $[Cl(COD)Rh(I)]_2$, $[Cl(CO)_2Rh(I)]_2$, $[Cl(COD)Rh(I)]$ and $Cl_2(COD)Pd(II)$, H_2PtCl_6, and $Cl(COD)Pt(II)_2$.
16. A composition for cationic polymerization comprising:
    a. an onium salt;
    b. vinyl or heterocyclic monomer or oligomer or mixture thereof capable of non-radical cationic polymerization;
    c. a metal-containing catalyst; and
    d. a reducing agent in the vapor state.
17. A composition of claim 16 wherein the reducing agent is a silane or siloxane containing at least one Si-H functional group.
18. A composition of claim 17 wherein the reducing agent is selected from silane; 1,1,3,3-tetramethyldisiloxane; triethylsilane; triethoxysilane; n-hexylsilane; dimethylphenylsilane; diphenylmethylsilane; 1,3,5,7-tetramethylcyclotetrasiloxane; and 1,3,5,7,9-pentamethylcyclopentasiloxane.
19. A composition of claim 18 wherein the reducing agent is selected from 1,1,3,3-tetramethyldisiloxane and triethoxysilane.
20. A composition of claim 16 wherein the onium salt is selected from an iodonium salt and a sulfonium salt.

21. A composition of claim 20 wherein the onium salt is selected from a diaryliodonium salt, a dialkylphenacylsulfonium salt, a 2,6-dialkyl-4-hydroxyphenylsulfonium salt and a triphenylsulfonium salt.
22. A composition of claim 21 wherein the onium salt is selected from diaryliodonium SbF_6, diaryliodonium PF_6, dialkylphenacylsulfonium SbF_6, dialkylphenacylsulfonium AsF_6, dialkylphenacylsulfonium PF_6 or triarylsulfonium SbF_6.
23. A composition of claim 22 wherein the onium salt is selected from (4-n-octyloxyphenyl)phenyliodonium SbF_6, (4-n-octyloxyphenyl)phenyliodonium PF_6, S-methyl-S-n-octyl-S-phenacylsulfonium SbF_6, S-methyl-S-n-hexadecyl-S-phenacylsulfonium SbF_6, (4-n-pentadecyloxyphenyl)phenyliodonium SbF_6, S-methyl-S-n-dodecyl-S-phenacylsulfonium SbF_6, S-methyl-S-n-dodecyl-S-phenacylsulfonium PF_6, S-methyl-S-n-dodecyl-S-phenacylsulfonium AsF_6, S-pentamethylene-S-phenacylsulfonium SbF_6 and triphenylsulfonium SbF_6.
24. A composition of claim 16 wherein the monomer is selected from an alkyl vinyl ether, an oxetane and an epoxide.
25. A composition of claim 16 wherein the monomer is selected from 1,3-bis(3,4-epoxycyclohexyl-2-ethyl) -1,1,3,3-tetramethyldisiloxane; cyclohexene oxide; 4-vinylcyclohexene-1,2-oxide; 4-vinylcyclohexene dioxide; limonene dioxide; 1,2-epoxydecane; 1,2,7,8-diepoxyoctane; 3,4-epoxycyclohexylmethyl-3',4'epoxycyclohexane carboxylate; bisphenol-A diglycidyl ether; trimethylolpropane triglycidyl ether; novolac epoxides; epoxidized vegetable oils; bis(3-ethyloxyetanylmethyl) ether; triethyleneglycol divinyl ether; and triethyleneglycol methyl vinyl ether.
26. A composition of claim 16 wherein the catalyst is a noble metal-containing catalyst.
27. A composition of claim 26 wherein the catalyst contains a noble metal selected from rhodium, palladium, iridium and platinum.
28. A composition of claim 27 wherein the catalyst is selected from the Karstedt catalyst, Lamoreaux catalyst, Speier's catalyst, Ashby catalyst, chloroplatinic acid, $[Cl(COD)Pt(I)]_2$, $Cl_2(C_6H_5CN)_2Pt(II)$, $Cl_2[(C_2H_5)_2S]_2Pt(II)$, $[Cl(COD)Rh(I)]_2$, $[Cl(CO)_2Rh(I)]_2$, $[Cl(COD)Rh(I)]$ and $Cl_2(COD)Pd(II)$, H_2PtCl_6, and $Cl(COD)Pt(II)_2$.
29. A composition for cationic polymerization comprising:
    a. an onium salt;
    b. vinyl or heterocyclic monomer or oligomer or mixture thereof capable of non-radical cationic polymerization;

   c. a catalyst; and
   d. a reducing agent selected from a silane and a siloxane containing at least one Si-H functional group.

30. A composition according to claim 29 wherein:
    a. the onium salt is selected from an iodonium salt and a sulfonium salt;
    b. the monomer or oligomer or mixture thereof is selected from 1,3-bis(3,4-epoxycyclohexyl-2-ethyl) -1,1,3,3-tetramethyldisiloxane; cyclohexene oxide; 4- vinylcyclohexene-1,2-oxide; 4-vinylcyclohexene dioxide; limonene dioxide; 1,2-epoxydecane; 1,2,7,8-diepoxyoctane; 3,4-epoxycyclohexylmethyl-3',4'epoxycyclohexane carboxylate; bisphenol-A diglycidyl ether; trimethylolpropane triglycidyl ether; novolac epoxides; epoxidized vegetable oils; bis(3-ethyloxyetanylmethyl) ether; triethyleneglycol divinyl ether; and triethyleneglycol methyl vinyl ether; and
    c. the catalyst is a metal-containing catalyst.
31. A composition of claim 30 wherein the reducing agent is selected from silane; 1,1,3,3-tetramethyldisiloxane; triethylsilane; triethoxysilane; n-hexylsilane; dimethylphenylsilane; diphenylmethylsilane; 1,3,5,7-tetramethylcyclotetrasiloxane; and 1,3,5,7,9-pentamethylcyclopentasiloxane.
32. A composition of claim 31 wherein the reducing agent is selected from 1,1,3,3-tetramethyldisiloxane, triethylsilane and triethoxysilane.
33. A composition of claim 30 wherein the reducing agent is an oligomeric siloxane.
34. A composition of claim 33 wherein the reducing agent is selected from poly(methylhydrogensiloxane) and oligopoly(methylhydrogensiloxane-co-dimethylsiloxane).
35. A composition of claim 30 wherein the onium salt is selected from a diaryliodonium salt, a dialkylphenacylsulfonium salt, a 2,6-dialkyl-4-hydroxyphenylsulfonium salt and a triphenylsulfonium salt.
36. A composition of claim 35 wherein the onium salt is selected from diaryliodonium SbF_6, diaryliodonium PF_6, dialkylphenacylsulfonium SbF_6, dialkylphenacylsulfonium AsF_6, dialkylphenacylsulfonium PF_6 or triarylsulfonium SbF_6.
37. A composition of claim 36 wherein the onium salt is selected from (4-n-octyloxyphenyl)phenyliodonium SbF_6, (4-n-octyloxyphenyl)phenyliodonium PF_6, S-methyl-S-n-octyl-S-phenacylsulfonium SbF_6, S-methyl-S-n-hexadecyl-S-phenacylsulfonium SbF_6, (4-n-pentadecyloxyphenyl)phenyliodonium SbF_6, S-methyl-

S-n-dodecyl-S-phenacylsulfonium SbF_6, S-methyl-S-n-dodecyl-S-phenacylsulfonium PF_6, S-methyl-S-n-dodecyl-S-phenacylsulfonium AsF_6, S-pentamethylene-S-phenacylsulfonium SbF_6 and triphenylsulfonium SbF_6.

38. A composition of claim 30 wherein the catalyst is a noble metal-containing catalyst.
39. A composition of claim 38 wherein the catalyst contains a noble metal selected from rhodium, palladium, iridium and platinum.
40. A composition of claim 39 wherein the catalyst is selected from the Karstedt catalyst, Lamoreaux catalyst, Speier's catalyst, Ashby catalyst, chloroplatinic acid, $[Cl(COD)Pt(I)]_2$, $Cl_2(C_6H_5CN)_2Pt(II)$, $Cl_2[(C_2H_5)_2S]_2Pt(II)$, $[Cl(COD)Rh(I)]_2$, $[Cl(CO)_2Rh(I)]_2$, $[Cl(COD)Rh(I)]$ and $Cl_2(COD)Pd(II)$, H_2PtCl_6, and $Cl(COD)Pt(II)_2$.
41. An apparatus comprising:
    a. a container having an inlet for receiving pressurized gas, an outlet, a port in said inlet for receiving a vaporizable liquid and a zone in said inlet for vaporizing said liquid, said zone in fluid communication with said container;
    b. a target vessel enclosed by said container and operatively connected to said inlet and said outlet; and
    c. a material characterization device positioned to detect a characteristic of a chemical reaction occurring in the target vessel.
42. The apparatus according to claim 41 wherein said characterization device comprises a detector capable of quantifying temperature.
43. The apparatus according to claim 41 wherein said characterization device comprises an infrared detector.
44. The apparatus according to claim 41 further comprising a data acquisition system linked to the characterization device.
45. The apparatus according to claim 41 additionally comprising means for heating said zone in said inlet.
46. A method for forming a polymer comprising using the apparatus according to claim 41, wherein said vaporizable liquid is injected into the port of said inlet and wherein pressurized gas passes through the container to deliver the vapor to the target vessel.
47. A method for delivering a vaporized reducing agent to a target vessel comprising:
    a. Injecting a vaporizable reducing agent into a port of a container having an inlet and an outlet;
    b. Delivering pressurized gas to said reducing agent through said inlet;

   c. Delivering vaporized reducing agent to a target vessel in fluid communication with the outlet; and
   d. Detecting a characteristic of a chemical reaction using a characterization device.

48. A method of polymerization comprising delivering a vaporized reducing agent to a target vessel containing a MOC mixture using an apparatus comprising:
   a. a container having an inlet for receiving pressurized gas, an outlet, and a port for receiving a vaporizable reducing agent to said container;
   b. a target vessel operatively connected to the outlet; and
   c. a material characterization device positioned to detect a characteristic of a chemical reaction.

49. A method of polymerization comprising:
   a. forming a vaporized reducing agent;
   b. introducing said vaporized reducing agent to a MOC mixture; and
   c. detecting the temperature of the resulting polymerization reaction to determine state of polymerization.

FIGURE 1:

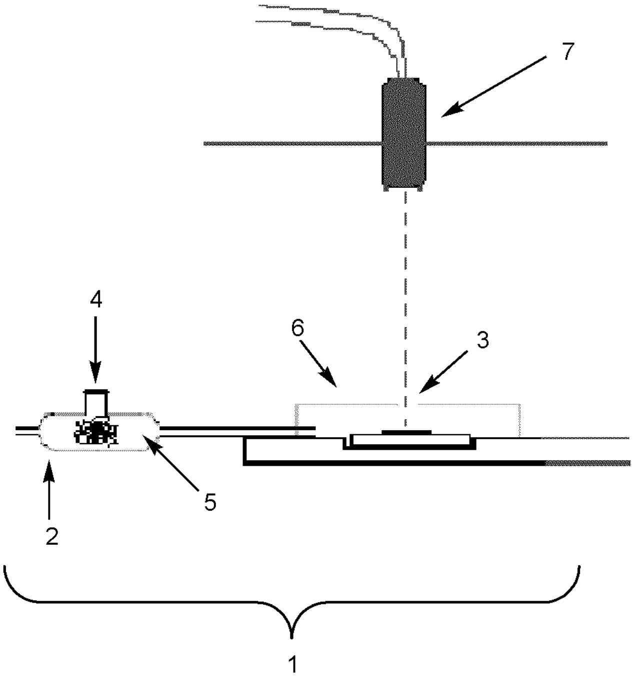


FIGURE 2:

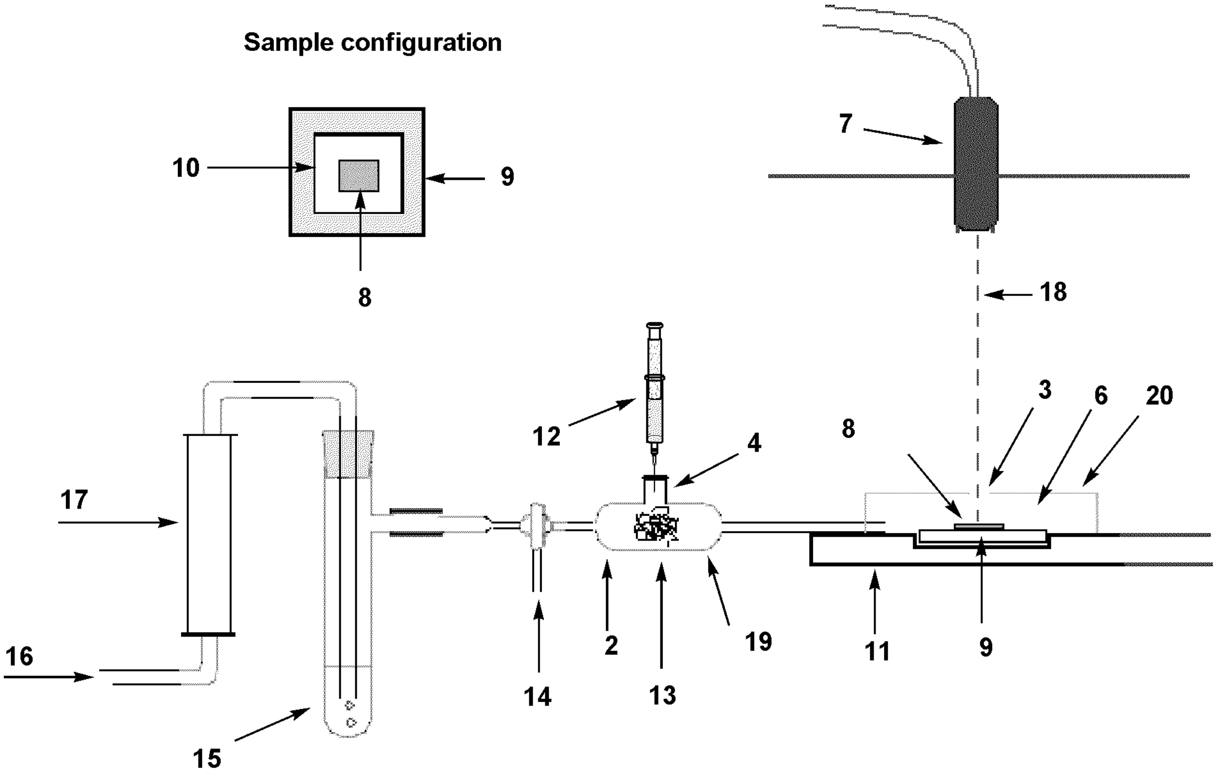


FIGURE 3:

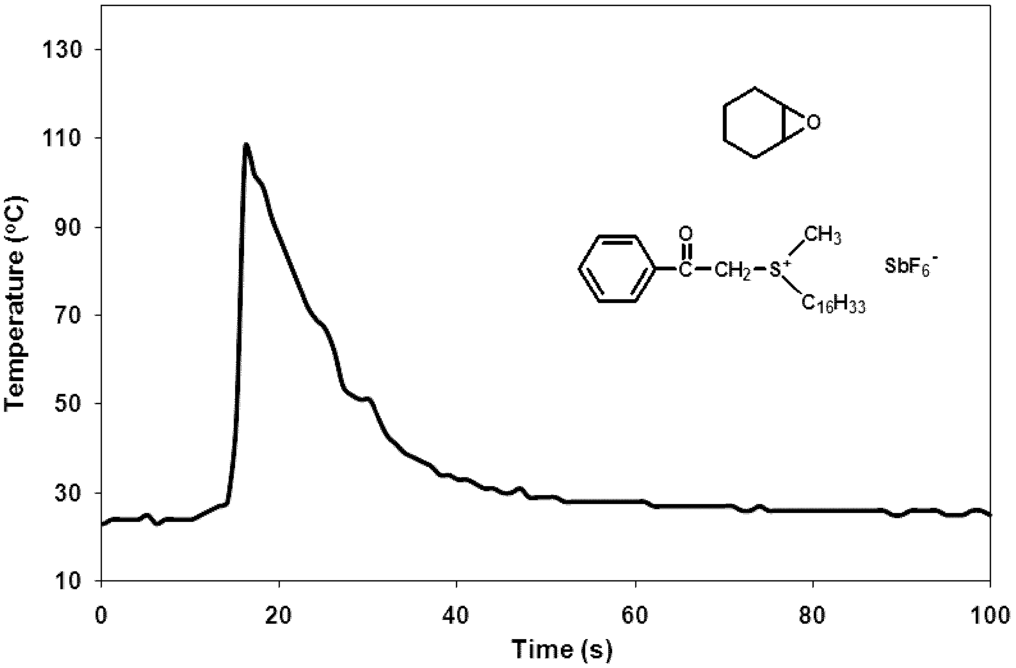


FIGURE 4:

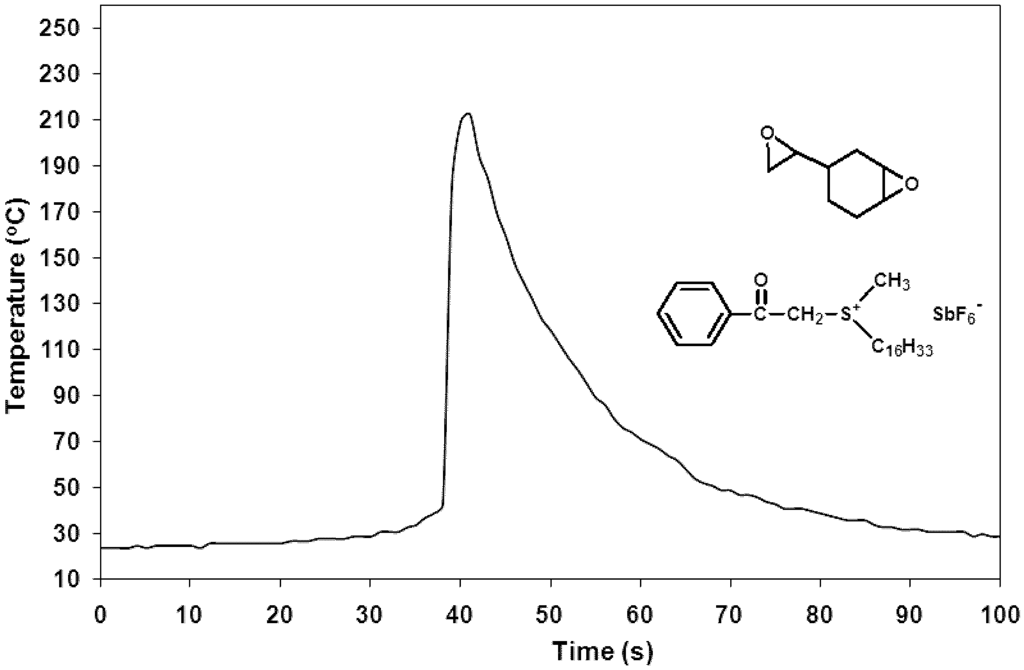


FIGURE 5:

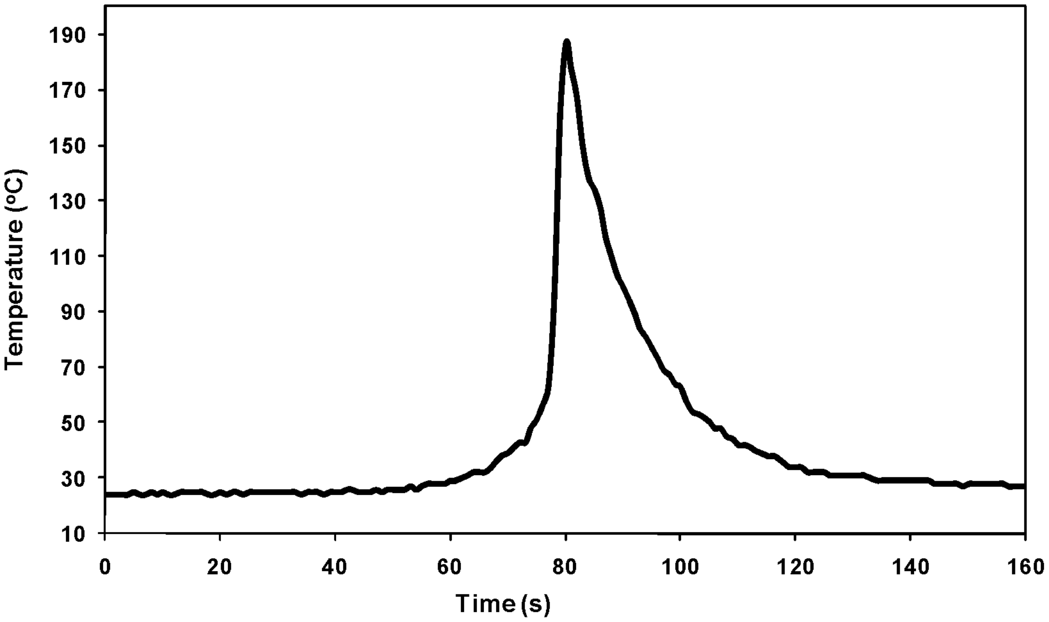


FIGURE 6:

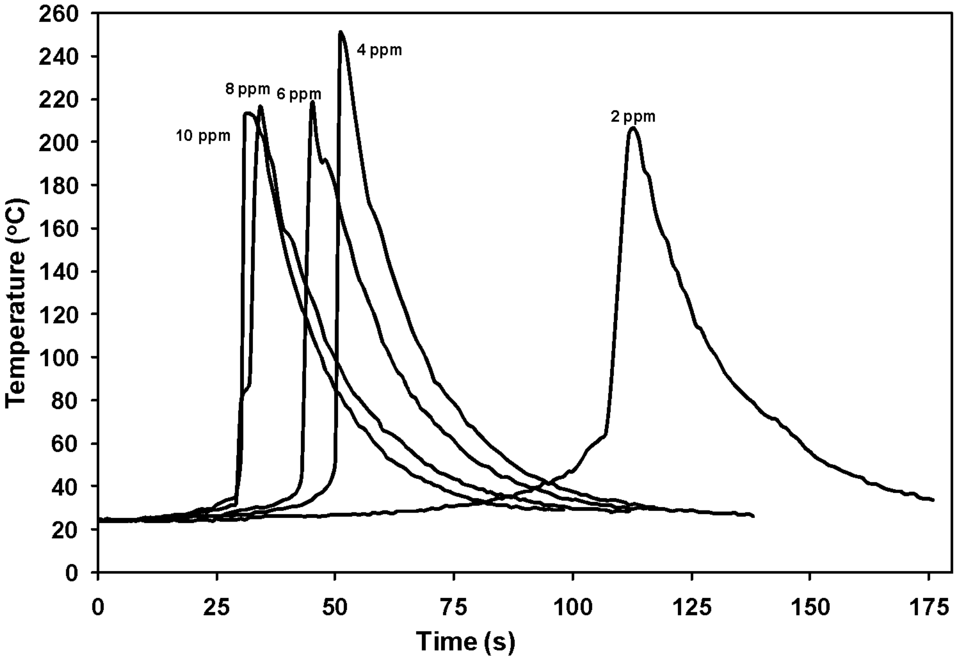


FIGURE 7:

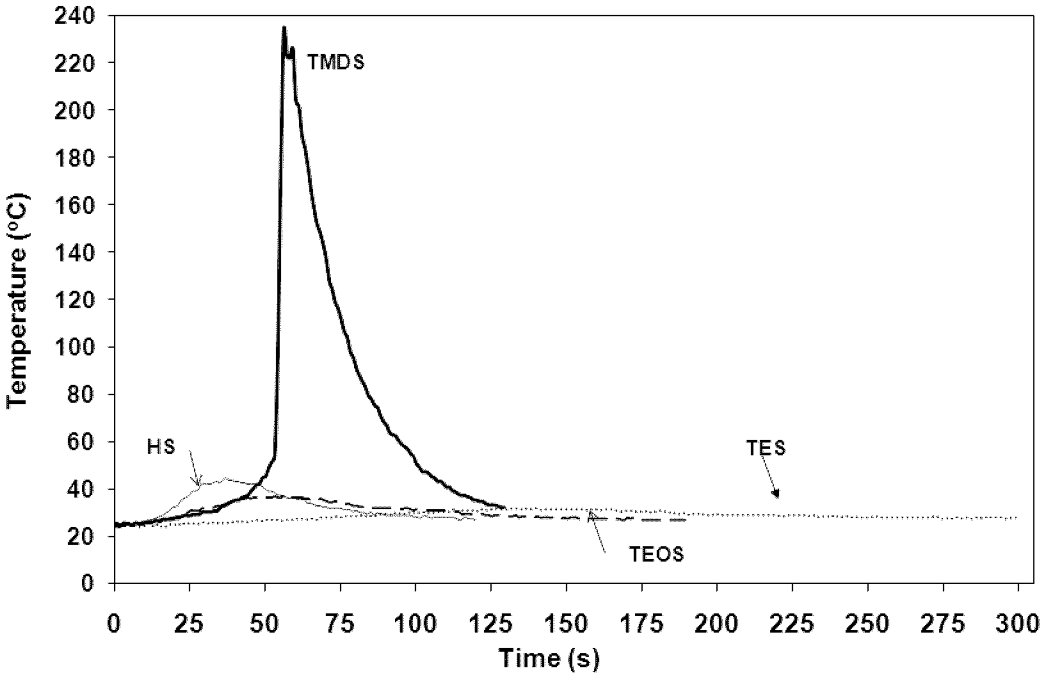


FIGURE 8:

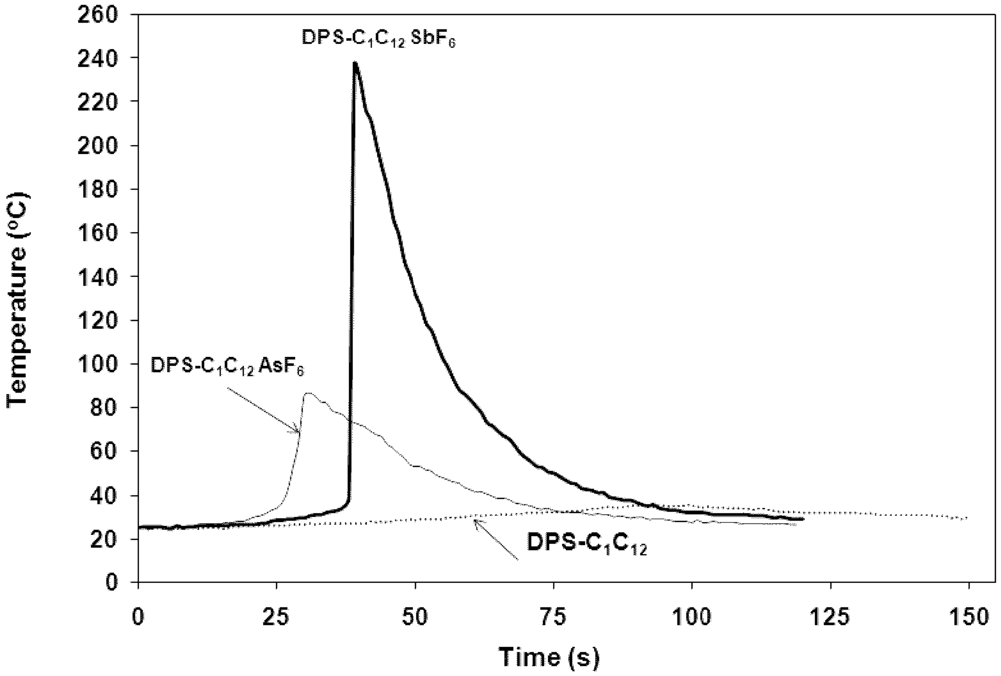


FIGURE 9:

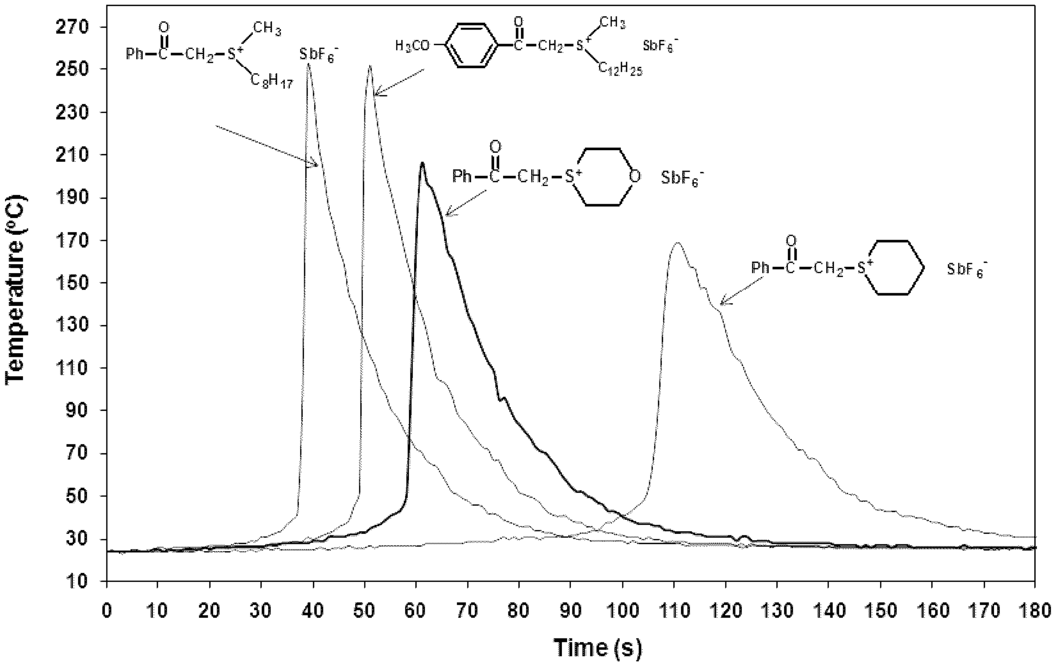


FIGURE 10:

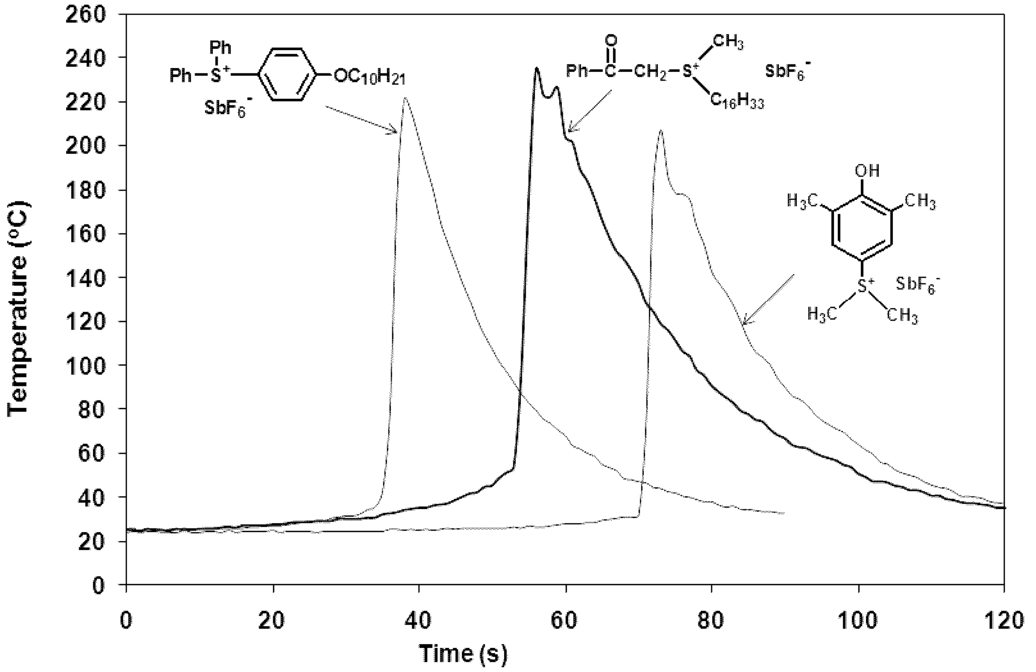


FIGURE 11:

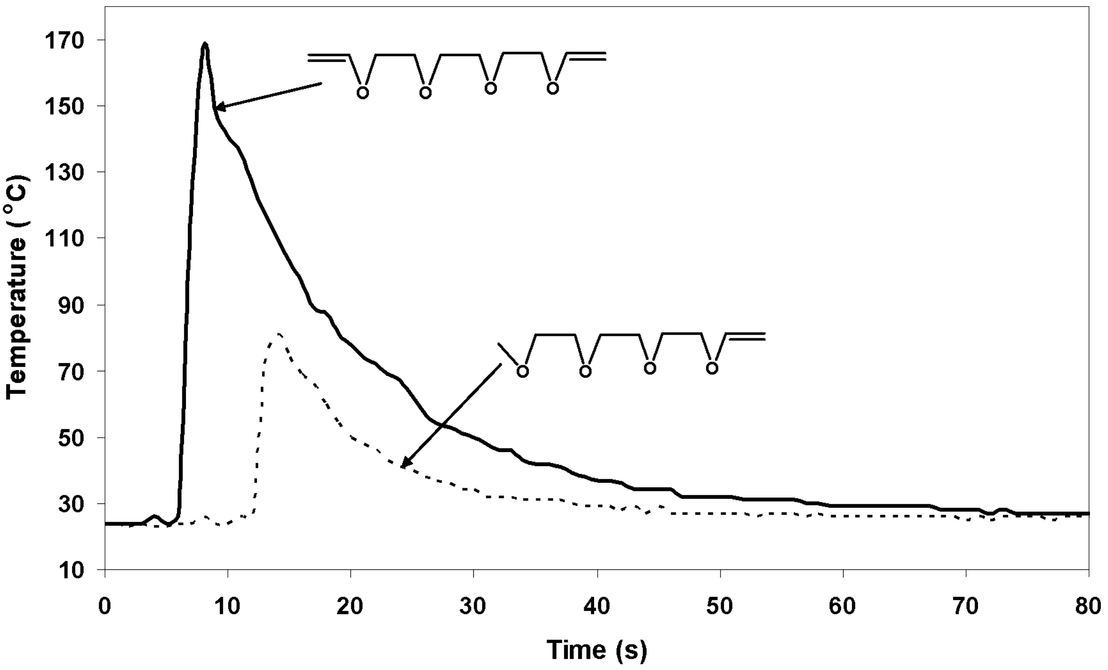


FIGURE 12:

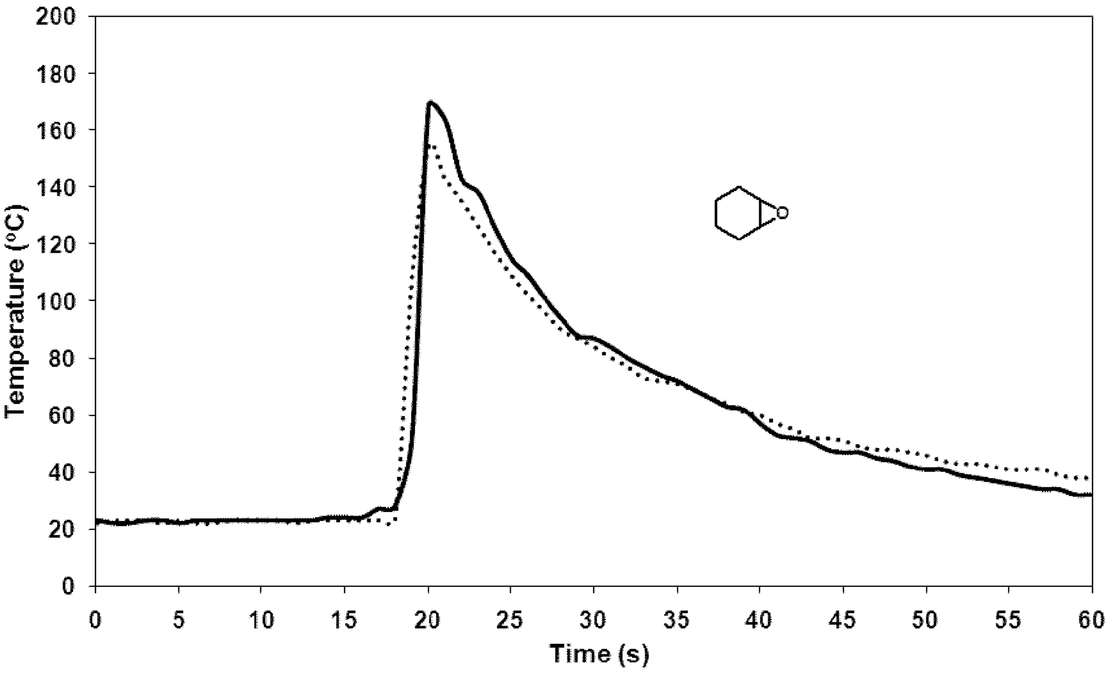


FIGURE 13:

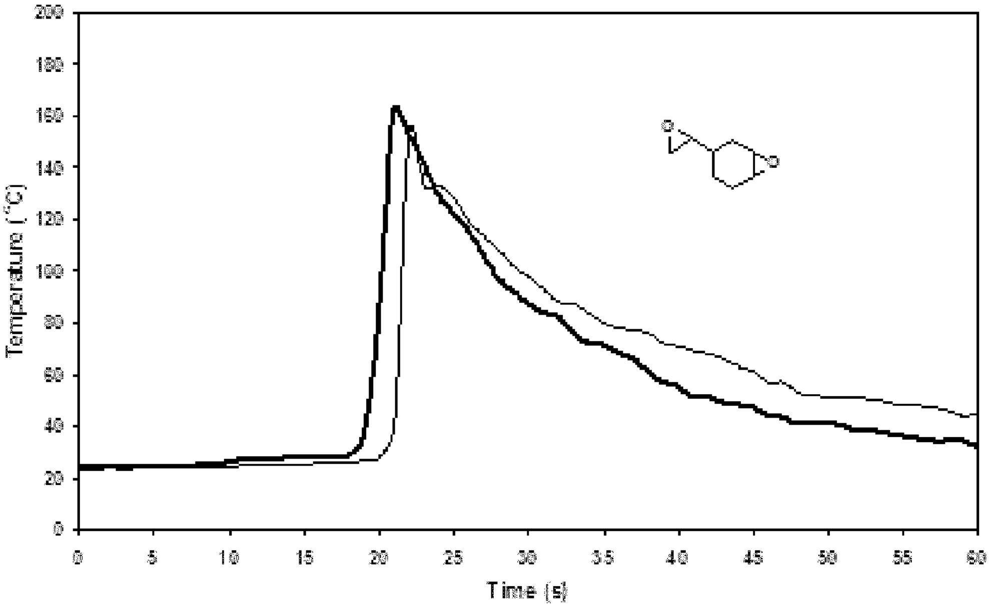


FIGURE 14:

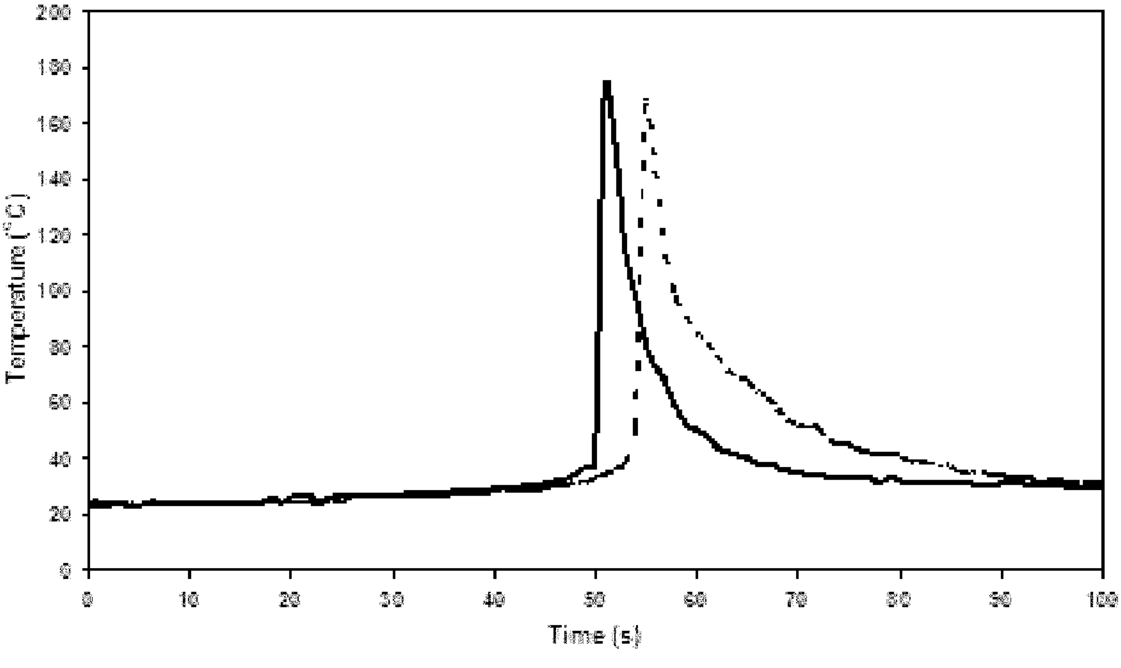


FIGURE 15:

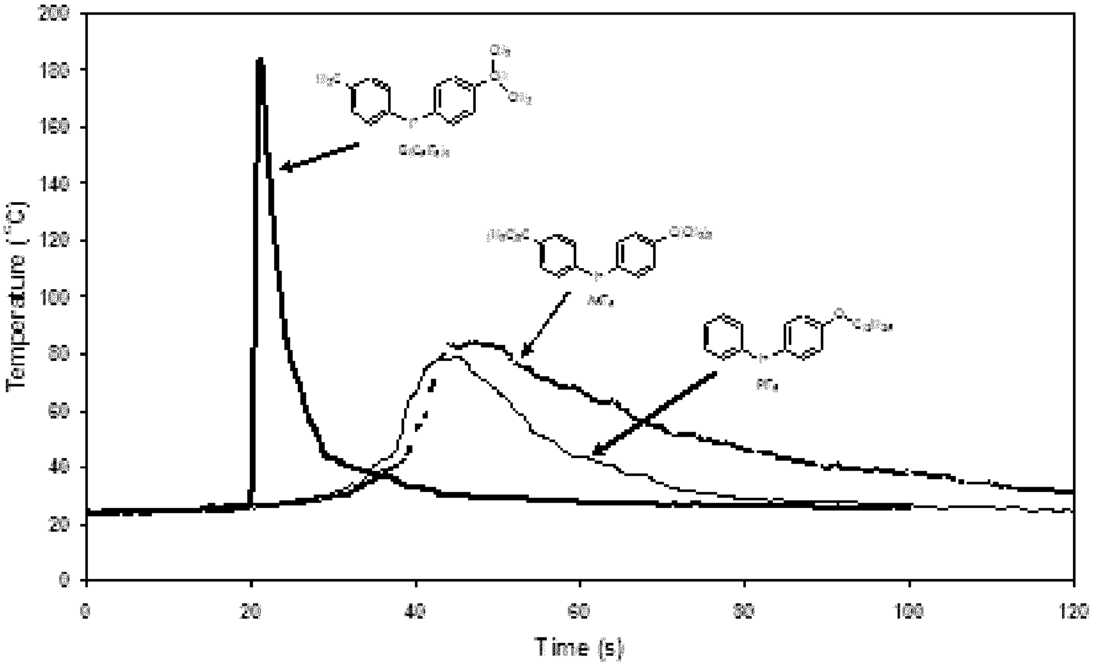


FIGURE 16:

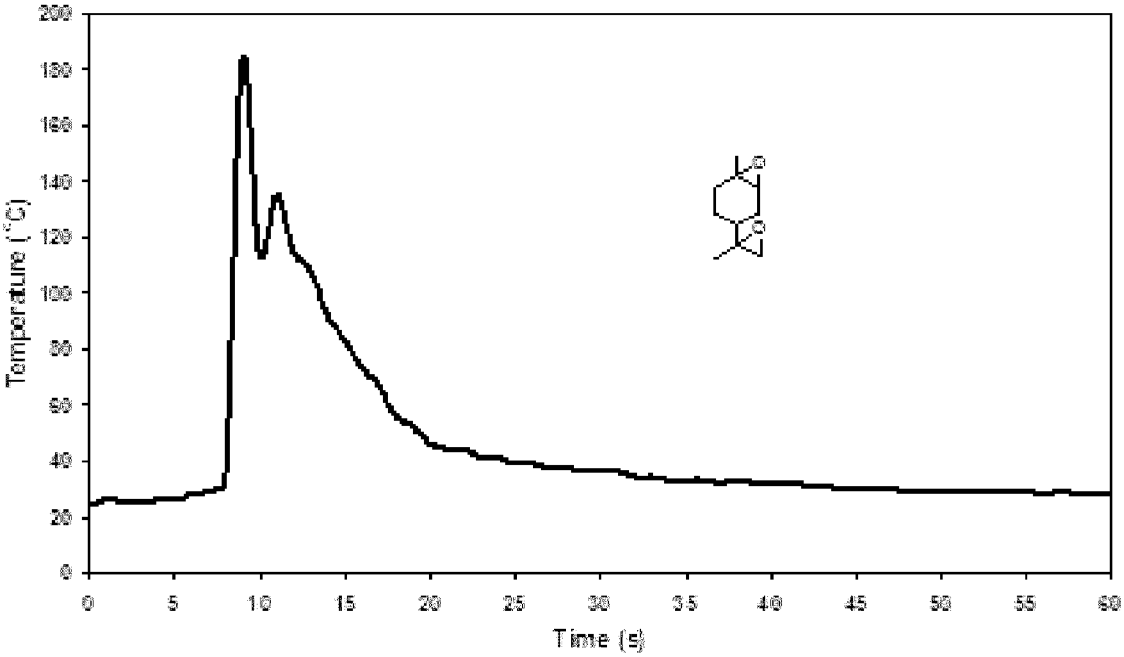


FIGURE 17:

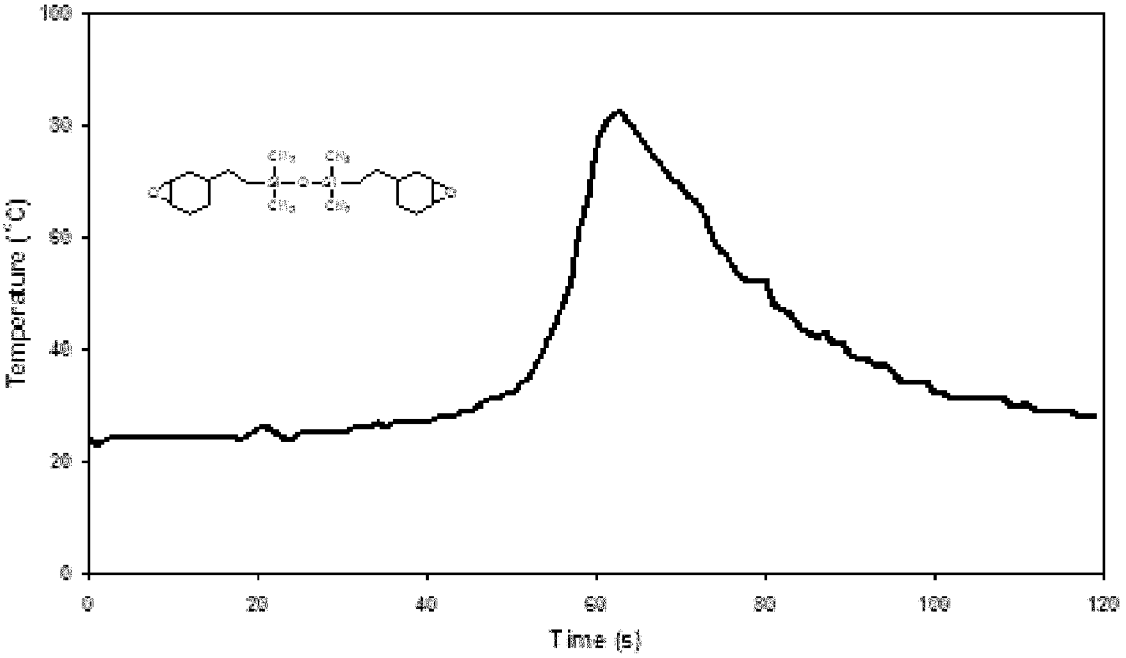


FIGURE 18:

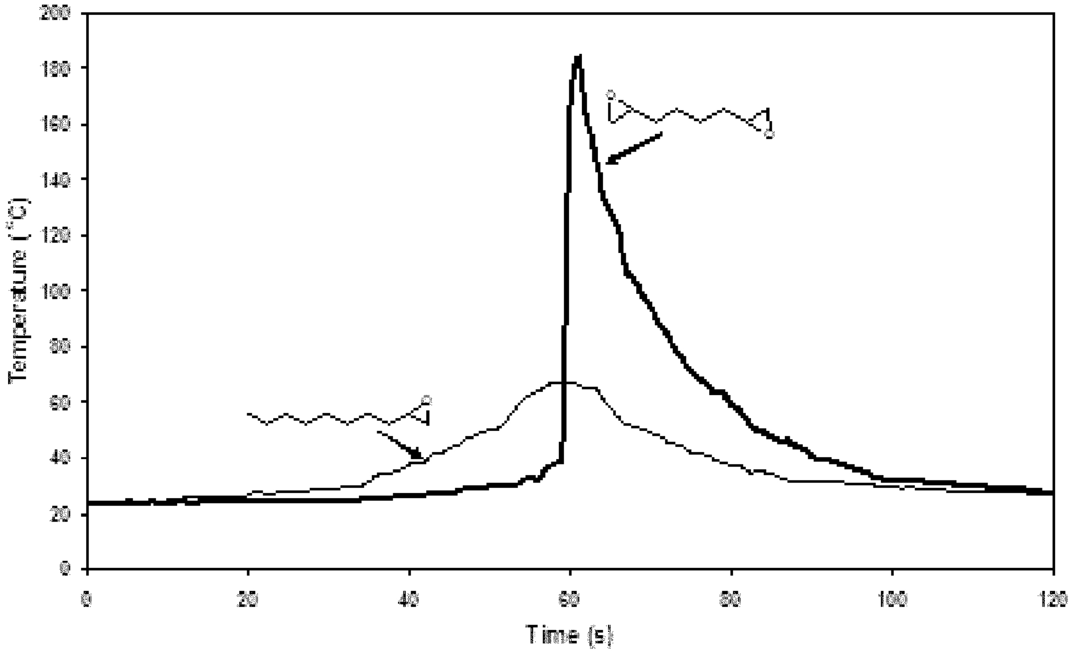


FIGURE 19:

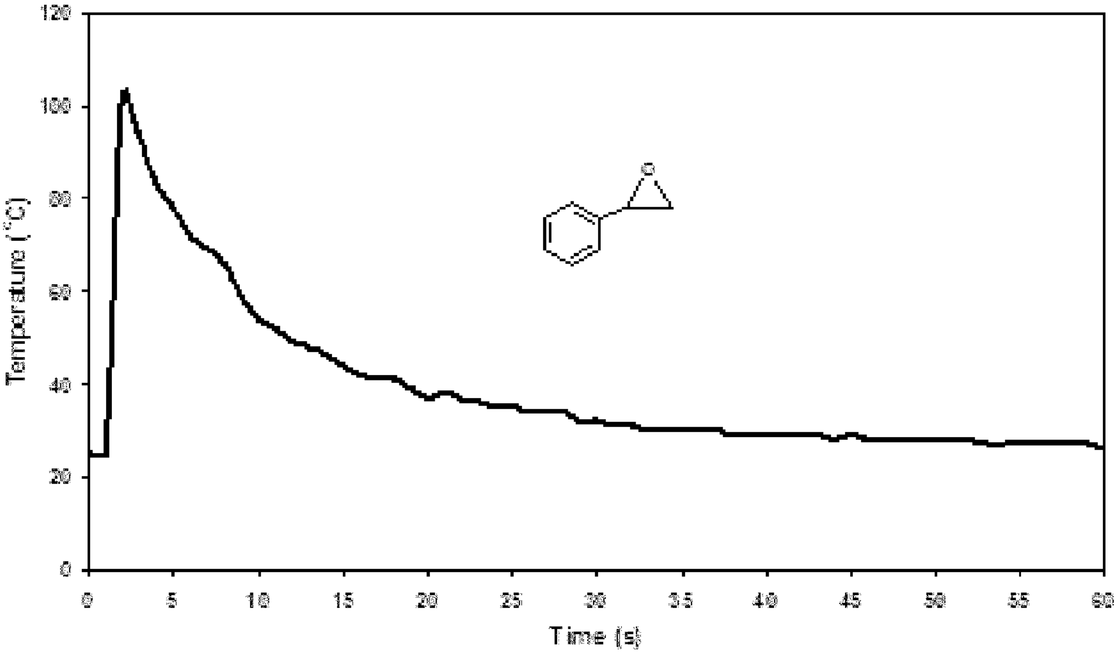


FIGURE 20:

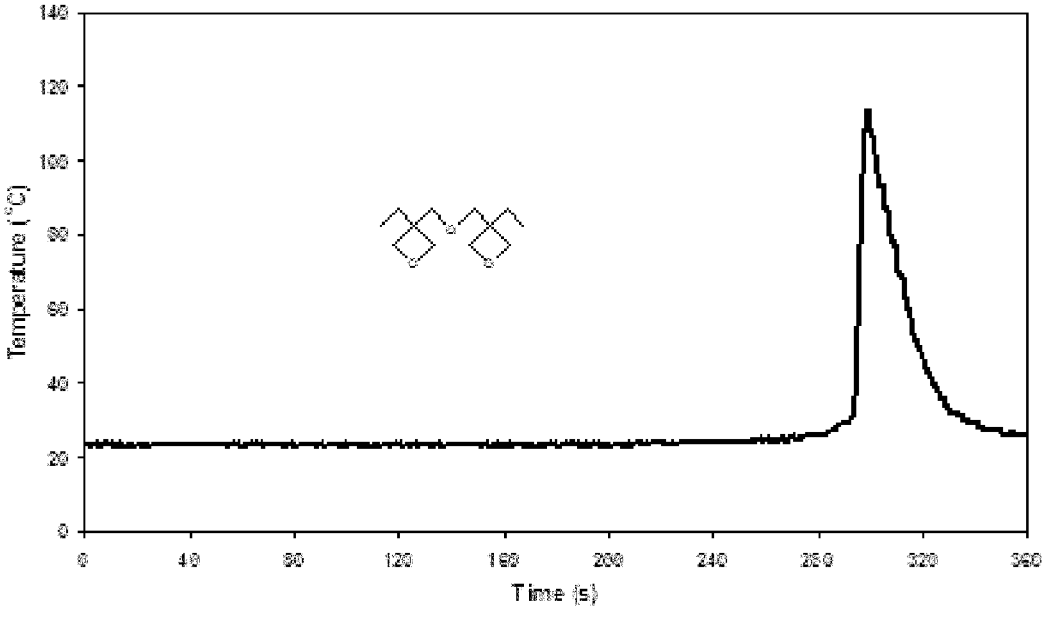
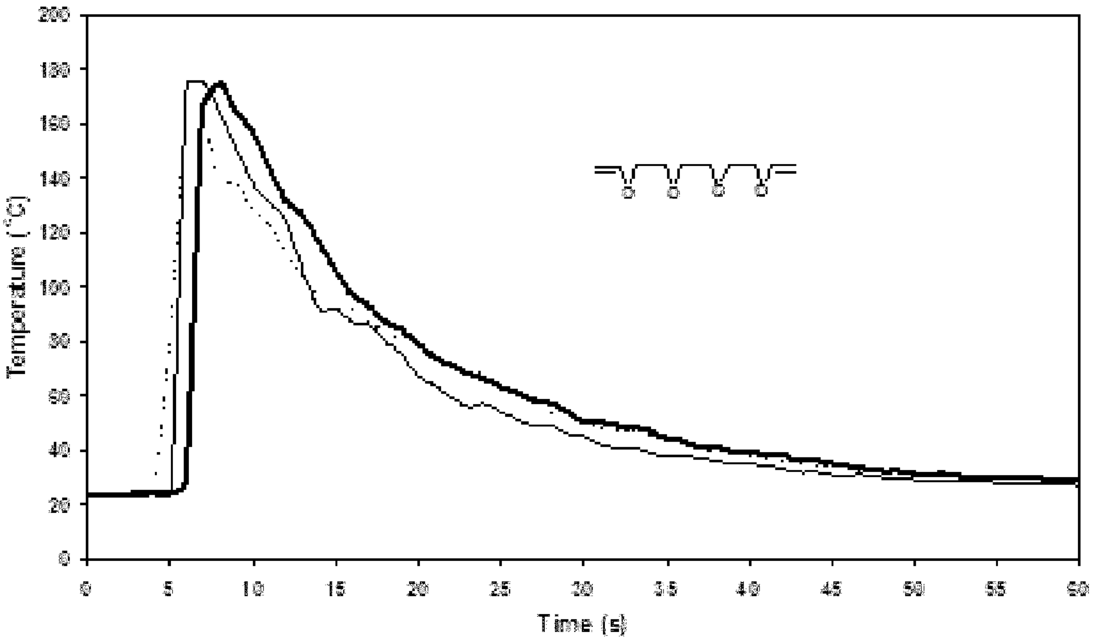


FIGURE 21:


Temperature (°C)
0
20
40
60
80
100
120
140
160
180
200
Time (s)
0
5
10
15
20
25
30
35
40
45
50
55
60

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/066985

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F4/26 C08F4/40 C08F2/01 B01J19/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 591 097 A1 (3M ESPE AG [DE]) 2 November 2005 (2005-11-02) paragraph [0048] - paragraph [0060]; claims; examples	1-40,48, 49
X	WO 2005/016989 A1 (RENSSELAER POLYTECH INST [US]; CRIVELLO JAMES V [US]) 24 February 2005 (2005-02-24) the whole document	1-40,48, 49
X	DE 28 54 011 A1 (GEN ELECTRIC) 3 July 1980 (1980-07-03) page 15 - page 16; claims	1-40,48, 49
X	WO 00/34348 A1 (CRIVELLO JAMES V [US]) 15 June 2000 (2000-06-15) claims	1-40,48, 49
	-/--	

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 1 April 2010	Date of mailing of the international search report 09/04/2010
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Kaumann, Edgar

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/066985

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 274 148 A (DOUGHERTY JAMES A [US] ET AL) 28 December 1993 (1993-12-28) claims	1-40,48, 49
A,P	WO 2009/141444 A1 (LOCTITE R & D LTD [IE]; HENKEL AG & CO KGAA [DE]; FARRELL DAVID [IE];) 26 November 2009 (2009-11-26) the whole document	1-40
X	EP 0 803 519 A1 (BP CHEMICALS SNC [FR]) 29 October 1997 (1997-10-29)	41,42, 45-47
Y	column 9, line 44 - line 48 column 10, line 39 - line 42 column 12, line 7 - column 15, line 24; claims	41-47
Y	WO 2005/040226 A2 (UNIVATION TECH LLC [US]; SANDELL DAVID J [US]; MCBRIDE MARJORIE E [US]) 6 May 2005 (2005-05-06) paragraph [0067]; claims	41-47
X	WO 97/18888 A1 (BP CHEM INT LTD [GB]; NEWTON DAVID [GB]; CHINH JEAN CLAUDE [FR]) 29 May 1997 (1997-05-29) page 15, line 32 - line 35 claims	41,45-47
X	WO 98/18548 A1 (BP CHEM INT LTD [GB]; NEWTON DAVID [GB]; POWER MICHAEL BERNARD [GB]) 7 May 1998 (1998-05-07) page 18, line 24 - line 26 claims	41,45-47
X	US 5 492 724 A (KLINEDINST KEITH A [US] ET AL) 20 February 1996 (1996-02-20) claims abstract	41
X	US 2003/226505 A1 (SIVARAMAKRISHNAN VISWESWAREN [US] ET AL) 11 December 2003 (2003-12-11) claims	41

International application No.
PCT/US2009/066985

INTERNATIONAL SEARCH REPORT

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-40, 48, 49

   methods and polymerizable composition

   ---

2. claims: 41-47

   apparatus not related to the other subject-matter

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1591097 A1	02-11-2005	JP 2005314423 A	10-11-2005
		US 2006116445 A1	01-06-2006
WO 2005016989 A1	24-02-2005	CA 2534635 A1	24-02-2005
		EP 1651700 A1	03-05-2006
		JP 2007501312 T	25-01-2007
		US 2005092428 A1	05-05-2005
DE 2854011 A1	03-07-1980	NONE	
WO 0034348 A1	15-06-2000	AU 2035300 A	26-06-2000
		EP 1151021 A1	07-11-2001
		JP 2002531580 T	24-09-2002
		US 6031014 A	29-02-2000
US 5274148 A	28-12-1993	AU 4541593 A	03-03-1994
		CA 2138411 A1	17-02-1994
		EP 0656041 A1	07-06-1995
		JP 8500100 T	09-01-1996
		WO 9403551 A1	17-02-1994
WO 2009141444 A1	26-11-2009	NONE	
EP 0803519 A1	29-10-1997	NONE	
WO 2005040226 A2	06-05-2005	BR PI0415451 A	19-12-2006
		BR PI0415515 A	12-12-2006
		CA 2542378 A1	06-05-2005
		CA 2542736 A1	06-05-2005
		CN 1863821 A	15-11-2006
		CN 1972964 A	30-05-2007
		EP 1675877 A2	05-07-2006
		EP 1732954 A2	20-12-2006
		JP 2007509205 T	12-04-2007
		JP 2007508444 T	05-04-2007
		RU 2361883 C2	20-07-2009
		RU 2342402 C2	27-12-2008
		US 2005085598 A1	21-04-2005
		US 2005267267 A1	01-12-2005
		WO 2005040227 A2	06-05-2005
WO 9718888 A1	29-05-1997	AU 706078 B2	10-06-1999
		AU 7580896 A	11-06-1997
		BG 102568 A	26-02-1999
		BR 9611561 A	02-03-1999
		CA 2237014 A1	29-05-1997
WO 9718888 A1		CN 1207689 A	10-02-1999
		CZ 9801530 A3	11-11-1998
		EP 0876202 A1	11-11-1998
		HU 9903859 A2	28-03-2000
		JP 2000500393 T	18-01-2000
		NO 982313 A	07-07-1998
		NZ 322136 A	29-04-1999
		PL 326761 A1	26-10-1998
		SK 66398 A3	07-10-1998
		TR 9800905 T2	21-08-1998
		US 6096839 A	01-08-2000

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/066985

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		ZA 9609648 A	18-05-1998
WO 9818548 A1	07-05-1998	AT 222799 T	15-09-2002
		AU 715615 B2	03-02-2000
		AU 4717397 A	22-05-1998
		BG 64078 B1	31-12-2003
		BG 103431 A	31-01-2000
		BR 9712612 A	26-10-1999
		CA 2270049 A1	07-05-1998
		CN 1242716 A	26-01-2000
		DE 69715027 D1	02-10-2002
		DE 69715027 T2	19-12-2002
		DZ 2342 A1	20-06-2004
		EG 21518 A	28-11-2001
		EP 0938372 A1	01-09-1999
		ES 2183143 T3	16-03-2003
		HU 224477 B1	28-09-2005
		ID 21359 A	27-05-1999
		JP 2001503318 T	13-03-2001
		KR 20000052958 A	25-08-2000
		NO 992078 A	30-06-1999
		NZ 335267 A	27-10-2000
		PL 333020 A1	08-11-1999
		PT 938372 E	31-12-2002
		SK 53799 A3	14-02-2000
		TR 9900937 T2	23-08-1999
		TW 413684 B	01-12-2000
		US 6214943 B1	10-04-2001
		ZA 9709619 A	21-05-1998
US 5492724 A	20-02-1996	CA 2143071 A1	23-08-1995
		US 5595603 A	21-01-1997
US 2003226505 A1	11-12-2003	US 2002014207 A1	07-02-2002