Synthesis and Electron-Beam Polymerization of 1-Propenyl Ether Functional Siloxanes

James V. Crivello[a]; BO Yang[a]; Whan-Gi Kim[ab]

[a] Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York [b] Sam Yang R&D Center 63-2 Hwaam-Dong, Yusung-ku, Taejeon, Korea

PLEASE SCROLL DOWN FOR ARTICLE

SYNTHESIS AND ELECTRON-BEAM POLYMERIZATION OF 1-PROPENYL ETHER FUNCTIONAL SILOXANES

JAMES V. CRIVELLO,* BO YANG, and WHAN-GI KIM†

Department of Chemistry
Rensselaer Polytechnic Institute
Troy, New York 12180-3590

Key Words: Electron-beam initiated cationic polymerization; 1-Propenyl ethers; Siloxanes; 1-Propenyl ether functionalized siloxanes

ABSTRACT

A novel synthesis of 1-propenyl ether functionalized siloxanes has been achieved by the controlled, rhodium-catalyzed, chemoselective hydrosilation of 1-allyloxy-4(1-propenoxy)butane (APB) with various H-functional siloxanes. Chemoselective hydrosilation using a variety of Si—H functional siloxanes proceeds exclusively at the allyl ether group of the APB without participation at the 1-propenyl ether group. The electron-beam-induced cationic polymerization of these monomers in the presence of a diaryliodonium salt was studied and found to take place very rapidly and at very low radiation doses.

†Present address: Sam Yang R&D Center 63-2 Hwaam-Dong, Yusung-ku, Taejeon, Korea.

INTRODUCTION

Functionalized siloxane monomers and oligomers which undergo thermally and hydrolytically induced crosslinking reactions are important materials which find uses in such diverse areas as elastomers, caulks and sealing agents, adhesives, and as release agents [1]. More recently, there has been much interest in the development of radiation curable siloxanes which undergo crosslinking at very high rates for specific use in high-speed coating applications. A great deal of the current effort has centered about the design of photocurable siloxanes, although electron-beam-induced crosslinking has also been explored as a means of curing these materials.

The most widely applied approach employed to provide siloxanes which can undergo electron-beam-induced polymerization is to functionalize those materials by the attachment of acrylate or methacrylate functional groups which can undergo free radical polymerization [2–4]. While this approach is workable, it is not entirely satisfactory since such acrylated or methacrylated siloxanes are subject to serious oxygen inhibition effects during polymerization. Consequently, they require blanketing with nitrogen to give optimal polymerization rates. Work in this laboratory has centered about the preparation of epoxy-modified silanes and siloxanes and their UV-induced cure using cationic photoinitiators [5–8]. Similar efforts have also been proceeding at the General Electric [9, 10] and the Rhone-Poulenc [11] companies. We have recently reported that in addition to photopolymerization, epoxy functionalized siloxanes also undergo facile electron-beam-induced polymerization [12].

It had been shown earlier that one class of monomers which exhibits even higher reactivity toward photoinduced cationic polymerization in the presence of onium salt photoinitiators is vinyl ethers [13]. In addition, Hult and his coworkers reported that these monomers undergo facile electron-beam-induced polymerization at very high rates [14]. The electron beam dose required to initiate the polymerization of vinyl ether monomers in the presence of onium salts is very low and of the order of 0.2–0.4 Mrad (2–4 kGy) [15]. Based on these observations, it appeared attractive to design vinyl ether functionalized siloxanes. This has already been attempted by workers at Wacker Chemie [16] using the route depicted schematically in Eq. (1).

eq. 1
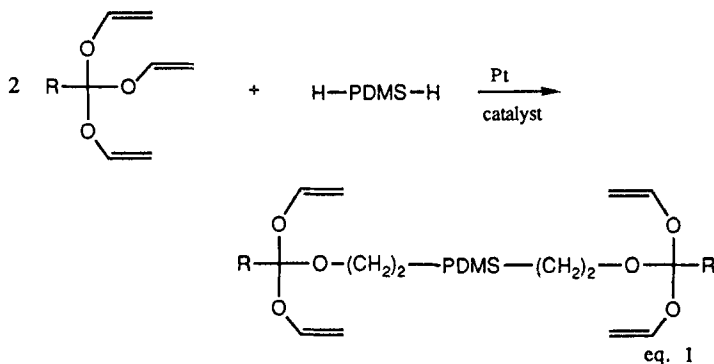
This method depends on the hydrosilation of a trivinyl ether with an α,ω-Si—H functional polydimethylsiloxane. However, since this reaction occurs without

selectivity at all the vinyl ether groups, it is difficult to control the synthesis of the vinyl ether-functional silicone in a manner that will avoid gelation during synthesis. For the same reason, it is very difficult to design resins which possess a high degree of vinyl ether functionality. The first objective of this investigation was to develop novel chemistry which will allow the attachment of highly reactive vinyl ether-type groups without complicating side reactions. Second, we wished to examine the sensitivity of such monomers and oligomers in electron-beam-induced polymerizations.

EXPERIMENTAL

General Methods and Materials

1,1,1,3,3-Pentamethydisiloxane, 1,1,3,3,5,5-hexamethyltrisiloxane, methyltris(dimethylsiloxy)silane, tetrakis(dimethylsiloxy)silane, 1,3,5,7-tetramethylcyclotetrasiloxane, and poly(dimethylsiloxane-co-methylhydrosiloxane) copolymer (50–55% methylhydro, 45–50% dimethyl, MW_n = 900–1000 g/mol) were purchased from Hüls America Inc. 1,4-Butanediol, allyl bromide, tetra-n-butylammonium bromide, tris(triphenylphosphine)ruthenium (II) dichloride, and tris(triphenylphosphine)rhodium(I) chloride were purchased from Aldrich Chemical Co. and used without further purification. The cationic photoinitiator, (4-n-decyloxyphenyl)phenyliodonium hexafluoroantimonate, was prepared as described previously [17].

^{1}H- and ^{13}C-NMR spectra were obtained in dichloromethane solution on a Varian XL-200 MHz Spectrometer, and the chemical shifts are given in parts per million down field from tetramethysilane as internal standard. Gas chromatographic analyses were performed on a Hewlett-Packard HP-5890A Gas Chromatograph equipped with 6 ft × 1/8 in. OV-17 phenylsilicone columns and a flame ionization detector. Thermogravimetric analyses were performed using a Perkin-Elmer TGA-7 Thermogravimetric Analyzer. Elemental analyses were carried out by Quantitative Analyses, Whitehouse, NJ.
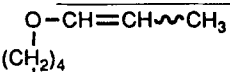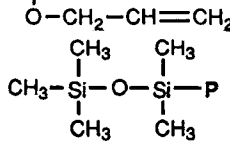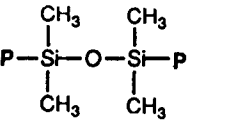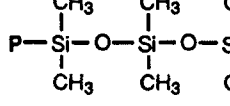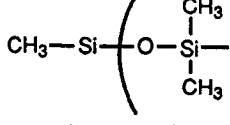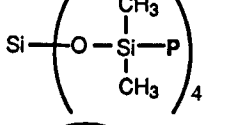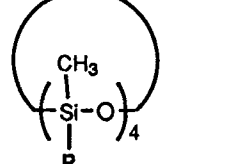
Monomer Synthesis

The following procedures are typical of the preparative methods used for the synthesis of all the 1-propenyl ether functionalized silicone (PFS) monomers and oligomers whose chemical structures are shown in Table 1.

Preparation of 1-Allyloxy-4(1-propenoxy)butane (PAB)

Into a 1-L round-bottomed flask fitted with a magnetic stirrer, reflux condenser, and nitrogen inlet were placed 1,4-butandiol (100 g, 1.11 mol), allyl bromide (134 g, 1.11 mol), tetra-n-butylammonium bromide (7 g, 22 mmol), NaOH (44 g, 1.11 mol), and toluene (300 mL). The mixture was stirred and heated to 70°C and held at that temperature for 10 hours. After cooling to room temperature, the mixture was filtered to remove the inorganic salts. The filtrate was poured into ~500 mL distilled water, and the organic layer was separated by a separatory funnel. The aqueous layer was extracted with toluene and all the toluene solutions combined. The toluene was removed on rotary evaporator giving 101 g (70% yield) of 4-allyloxy-1-butanol.

TABLE 1.   Structure and Elemental Analysis of 1-Propenyl Ether
Functionalized Siloxanes[a]

Monomer	Notation	Yield, %	Elemental analysis	
			% C	% H
PAB	PAB	95	Calcd: 70.58	10.58
			Found: 70.34	10.44
Si1PE	Si1PE	98	Calcd: 56.54	10.75
			Found: 56.46	10.86
SiD2PE	SiD2PE	91	Calcd: 60.71	10.61
			Found: 60.61	10.69
Si2PE	Si2PE	98	Calcd: 56.88	10.28
			Found: 56.38	10.42
Si3PE	Si3PE	93	Calcd: 57.02	10.08
			Found: 56.84	9.98
Si4PE	Si4PE	98	Calcd: 57.10	9.98
			Found: 57.01	10.02
SiD4PE	SiD4PE	99	Calcd: 57.35	9.63
			Found: 56.98	9.82

[a]P = $-(CH_2)_3O-(CH_2)_4-CH=CH\sim CH_3$.

^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 1.63 (m, 4H, $-CH_2-$); 2.69 (t, 1H, $-OH$); 3.42 (t, 2H, $-CH_2O-CH_2$); 3.58 (m, 2H, $HO-CH_2-$); 3.78 (d, 2H, $CH_2-CH=CH_2$); 5.13 (m, 2 H, $-CH=CH_2$); 5.83 (m, 1H, $-CH=CH_2$).

4-Allyloxy-1-butanol (30 g, 0.23 mol), potassium *t*-butoxide (51.7 g, 0.46 mol), and dimethyl sulfoxide (200 mL) were stirred under a nitrogen blanket for 1 hour at 130°C. The reaction was monitored by ^{1}H-NMR and showed complete isomerization of the allyl group to the 1-propenyl group. The resulting 1-propenyl ether product consisted almost exclusively of the *Z* isomer with less than 5% of the *E* isomer present. The mixture was cooled to room temperature and slowly poured

into 500 mL distilled water. The solution was extracted with methylene chloride. The extract was washed several times with distilled water and then dried over anhydrous Na_2SO_4. The solvent was removed using a rotary evaporator, and the residue was distilled at 95°C under a pressure of 1.0 mmHg to afford 4(1-propenoxy)-1-butanol in 83% yield.

^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 1.51 (d, 3H, —CH_3); 1.71 (m, 4H, —CH_2—); 2.62 (t, 1H, OH); 3.58 (m, 2H, HO—CH_2—); 3.68 (t, 2H, CH_2—OCH=CH); 4.32 (m, —CH—CH_3, Z isomer); 4.71 (m, —CH—CH_3, E isomer); 5.89 (m, =CH—O, Z isomer); 6.13 (m, =CH—O, E isomer).

A mixture of 4(1-propenoxy)-1-butanol (20 g, 0.15 mol), allyl bromide (24.2 g, 0.2 mol), tetra-n-butylammonium bromide (1.26 g, 3.9 mmol), NaOH(8 g, 0.2 mol), and toluene (60 mL) was stirred at 60°C for 10 hours. The work-up procedure was the same as in the previous allylation reaction. The yield was 85%.

^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 1.51 (d, 3H, —CH_3); 1.68 (m, 4H, —CH_2—); 3.41 (m, 2H, —CH_2—O—CH_2—); 3.72 (t, 2H, —CH_2—O—CH=CH_2); 3.91 (m, 2H, =CH—CH_2); 4.32 (m, =CH—CH_3, Z isomer); 4.71 (m, =CH—CH_3, E isomer); 5.13 (m, 2H, —CH=CH_2); 5.83 (m, —CH=CH_2); 5.89 (m, =CH—O, Z isomer); 6.13 (m, =CH—O, E isomer).

Chemoselective Hydrosilation of 1-Allyloxy-4(1-propenoxy)butane with 1,1,3,3,5,5-Hexamethyltrisiloxane (Si2PE)

Combined in a 10-mL round-bottomed flask fitted with a magnetic stirrer and a reflux condenser were 1-allyloxy-4(1-propenoxy)butane (2.0 g, 11.75 mmol), 1,1,3,3,5,5-hexamethyltrisiloxane (1.225 g, 5.87 mmol), and $Rh[(C_6H_5)_3P]_3Cl$ (10.87 mg, 1.18 × 10^{-5} mol). The reaction mixture was heated at 65°C for 1 hour. The ^{1}H-NMR of the reaction mixture after this time showed no evidence of bands at 4.3 and 5.5 ppm assigned respectively to the Si—H and vinyl protons of terminal carbon of the allyl groups. At this point the reaction was deemed complete and the reaction mixture was placed under high vacuum to remove all starting materials. The isolated yield of product was 2.97 g or 92% of theory.

Chemoselective Hydrosilation of 1-Allyloxy-4(1-propenoxy)butane with 1,3,5,7-Tetramethylcyclotetrasiloxane (SiD4PE)

A mixture of 1-allyloxy-4(1-propenoxy)butane (2.83 g, 16.63 mmol) and 1,3,5,7-tetramethylcyclotetrasiloxane (1 g, 4.158 mmol) were placed in a 10-mL round-bottomed flask equipped with a magnetic stirrer, reflux condenser, and thermometer. To this solution, $Rh[(C_6H_5)_3P]_3Cl$ (4.935 mg, 5.33 × 10^{-6} mol) was added, and the resulting mixture was heated at 65°C for 1 hour. The ^{1}H-NMR spectrum of the reaction mixture after this time showed no evidence of bands at 4.3 and 5.5 ppm assigned respectively to the Si—H and vinyl protons of terminal carbon of the allyl groups, indicating that the reaction was complete. The yield was quantitative (3.81 g).

Hydrosilation of 1-Allyloxy-4(1-propenoxy)butane with Poly(Dimethylsiloxane-co-Methylhydrosiloxane) Copolymer

1-Allyloxy-4(1-propenoxy)butane (2 g, 11.75 mmol) and methylhydrodimethylsiloxane copolymer (1.57 g, 11.75 mmol of silane functional groups) were placed in a 10-mL round-bottomed flask fitted with a thermometer, magnetic stirrer, and

reflux condenser. To this solution was added $Rh[(C_6H_5)_3P]_3Cl$ (10.87 mg, 5.33 $\times$ 10^{-6} mol), and the resulting mixture was heated to 65°C for 30 minutes. The ^{1}H-NMR spectrum of the reaction mixture after this time showed no evidence of bands at 4.3 and 5.5 ppm assigned respectively to the Si—H of copolymers and vinyl proton of allyl groups, indicating that all the silane and allyl groups had been consumed. The yield of 1-propenyl ether functionalized copolymer was quantitative (3.57 g).

Electron-Beam-Induced Polymerizations

Samples to be irradiated were coated onto 2 mil (50 μm) poly(ethylene terephthalate) carrier films using a 3-mil drawknife. An Energy Sciences Inc. Electrocurtain Model CCB-150 electron beam irradiator, operating at 165 KeV and equipped with a 15-cm linear cathode, was used to irradiate the samples. The samples on the carrier films were attached to a continuous web and passed through the beam. Experiments were run under nitrogen and air at a constant web speed. The dose was varied by changing the amperage applied to the filament or the web speed.

Samples were tested for tackiness immediately on exiting the irradiation chamber. This qualitative test was performed by placing and twisting a thumb under moderate pressure on the irradiated film. If the film was nontacky and did not deform or smudge under these conditions, it was classified as tack-free.

RESULTS AND DISCUSSION

Monomer Synthesis

Since vinyl ether groups undergo hydrosilation in the presence of noble metal catalysts, it is not possible to introduce these groups directly into silanes. Previous synthetic approaches involving the use of the hydrosilation reaction for the condensation of multifunctional silanes with divinyl ethers relies on the presence of a stoichiometric excess of the divinyl ether. While this approach works for some substances, as mentioned earlier, the products are often ill-defined and difficult to control due to intermolecular coupling reactions. In other instances the approach fails altogether due to the formation of crosslinked networks (i.e., gelation). Accordingly, we sought a novel approach for the synthesis of very highly reactive silicon-containing monomers and oligomers.

The method which we successfully employed for the preparation of highly reactive 1-propenyl ether functional siloxanes is shown in Scheme 1 and Eq. (5). This synthetic approach relies on a recent observation made in this laboratory that compounds containing the 1-propenyl ether group undergo extremely sluggish hydrosilation reactions. At the same time, we have also shown that 1-propenyl ether monomers have cationic photopolymerization rates comparable to and in some cases even higher than those of vinyl ethers [18]. With these considerations in mind, it can be concluded that for the synthesis of 1-propenyl ether functionalized siloxanes an intermediate such as 1-allyloxy-4(1-propenoxy)butane (APB) would be required. This compound bears a reactive allyl ether site for the attachment of the siloxane by a hydrosilation reaction together with a 1-propenyl ether group at the other end of the molecule which is unreactive in this same reaction but which undergoes extremely facile cationic polymerization.

The synthesis of APB was accomplished by first monoallylating 1,4-butanediol (Eq. 4) followed by isomerization of the monoallyl ether to the corresponding

$$HO-(CH_2)_4-OH \quad + \quad CH_2{=}CH-CH_2 \cdot Br \xrightarrow[R_4N^+Br^-]{NaOH} CH_2{=}CH-CH_2-O-(CH_2)_4-OH$$

$$+ \quad NaBr$$

eq. 2

$$CH_2{=}CH-CH_2-O-(CH_2)_4-OH \xrightarrow[DMSO]{KO\text{-}t\text{-}Bu} CH_3\sim CH{=}CH-O-(CH_2)_4-OH$$

eq. 3

$$CH_3\sim CH{=}CH-O-(CH_2)_4-OH \quad + \quad CH_2{=}CH-CH_2 \cdot Br \xrightarrow[R_4N^+Br^-]{NaOH}$$

$$CH_3\sim CH{=}CH-O-(CH_2)_4-O-CH_2-CH{=}CH_2$$

APB   eq. 4
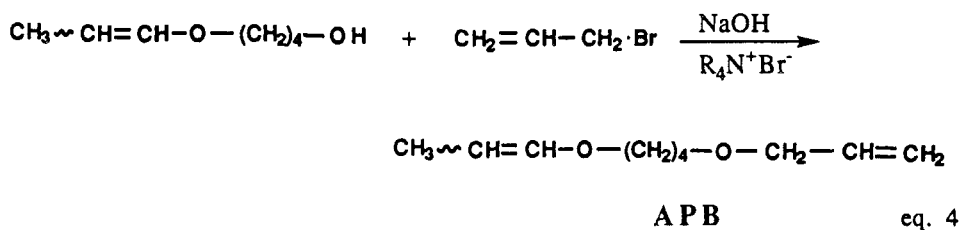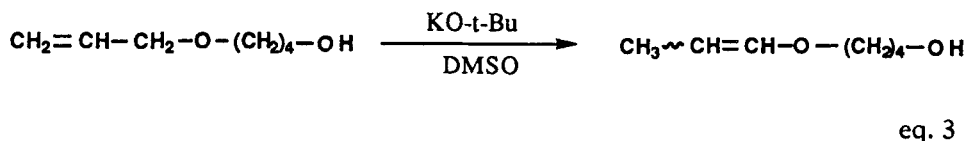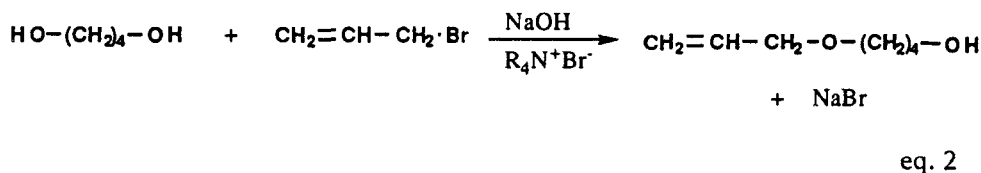
SCHEME 1.

1-propenyl ether in the presence of potassium *t*-butoxide in DMSO (Eq. 3). The synthesis is completed by once again allylating the resulting alcohol (Eq. 4). The product APB consists almost exclusively of the *Z* isomer ($<5\%$ of the *E* isomer).

^{1}H-NMR spectra for 4-allyloxy-1-butanol, 4(1-propenoxy)1-butanol and APB are given in Fig. 1. It has been observed that APB undergoes chemoselective hydrosilation as predicted only at the allyl group, allowing the synthesis of 1-propenyl ether functionalized siloxanes (PFS). As an example, the synthesis of Si2PE is shown in Eq. (5).

$$2 \ CH_3\sim CH{=}CH-O-(CH_2)_4-O-CH_2-CH{=}CH_2 \quad + \quad H-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-H$$

$$\Big\downarrow Rh[(C_6H_5)_3P]_3Cl$$

$$\left[CH_3\sim CH{=}CH-O-(CH_2)_4-O-(CH_2)_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O \right]_2 \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}$$

Si2PE   eq. 5
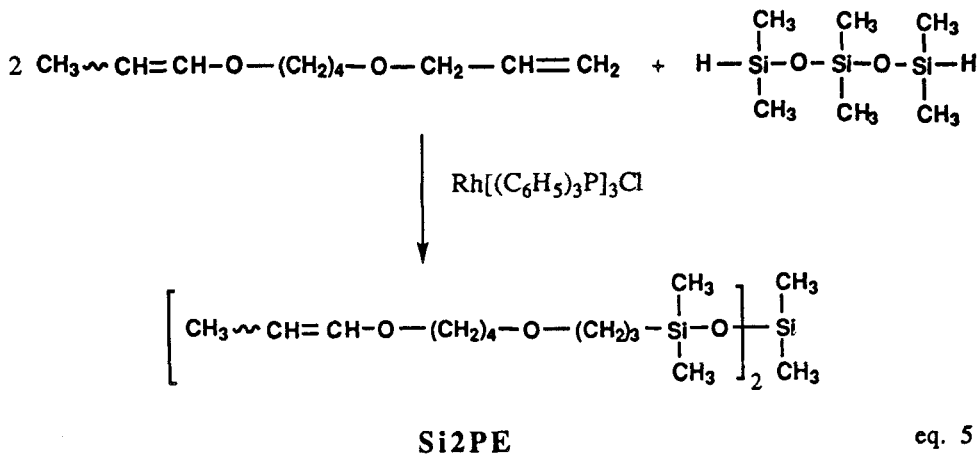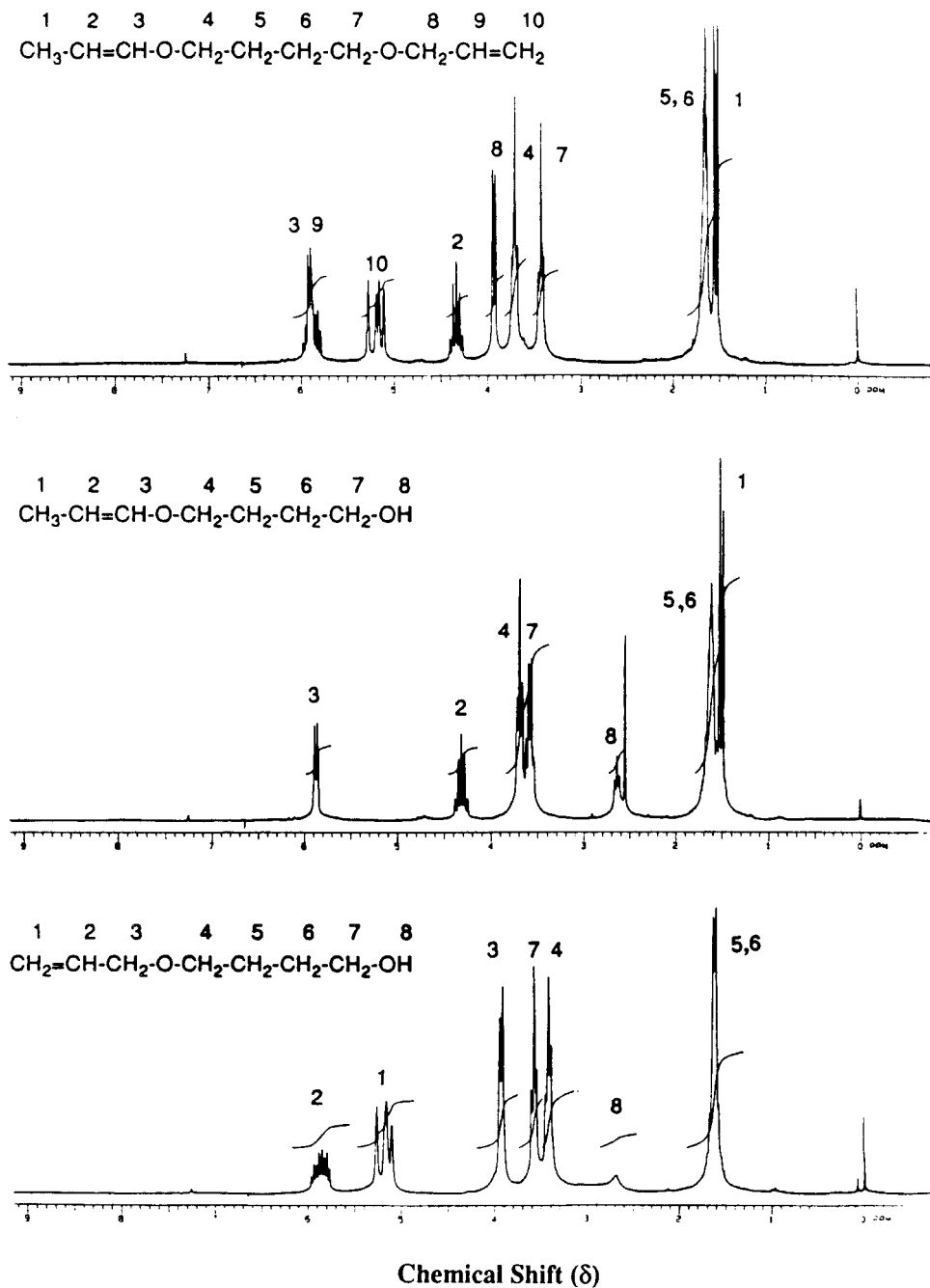
FIG. 1.   ¹H-NMR spectra for 4-allyloxybutan-1-ol, 4(1-propenoxy)butan-1-ol, and APB in CDCl₃.

Wilkinson's catalyst $(Rh[(C_6H_5)_3P]_3Cl)$ was employed as a catalyst for the hydrosilation reaction. The ^1H-NMR spectrum for Si2PE along with the proton assignments is given in Fig. 2.

The same synthetic approach was employed for the preparation of series of multifunctional silicon-containing monomers and oligomers whose structures are shown in Table 1. As noted in the table, the hydrosilation proceeded smoothly, chemoselectively, and in high yield in all cases. The PFS monomers and oligomers are all colorless, odorless, high boiling liquids. Although the isomerism is shown undefined, the double bonds in these compounds consist chiefly in the *Z* or *cis* configuration. In addition to the well-characterized Si—H-containing precursors shown in Table 1, a low molecular weight (DP = 30) poly(dimethylsiloxane-*co*-methylhydrosiloxane) copolymer having 7–8 pendant Si—H functional groups was also fitted with 1-propenyl ether groups by polymer analogous hydrosilation as shown in Eq. (6).

FIG. 2. ^1H-NMR spectrum of Si2PE in $CDCl_3$.

$$n \; CH_3 \sim CH = CH - O - (CH_2)_4 - O - CH_2 - CH = CH_2 \quad + \quad \left(\begin{array}{c} CH_3 \\ | \\ Si - O \\ | \\ CH_3 \end{array} \right)_m \left(\begin{array}{c} CH_3 \\ | \\ Si - O \\ | \\ H \end{array} \right)_n$$

$$\Big\downarrow \; Rh[(C_6H_5)_3P]_3Cl$$

$$\left(\begin{array}{c} CH_3 \\ | \\ Si - O \\ | \\ CH_3 \end{array} \right)_m \left(\begin{array}{c} CH_3 \\ | \\ Si - O \\ | \\ \end{array} \right)_n$$

$$(CH_2)_3 - O - (CH_2)_4 - O - CH = CH \sim CH_3$$

eq. 6

Electron-Beam Polymerization

It has been found that the PFS are readily and rapidly photopolymerized by exposure to UV irradiation in the presence of a variety of diaryliodonium and triarylsulfonium salts as cationic photoinitiators [19]. This is depicted in Eq. (7).
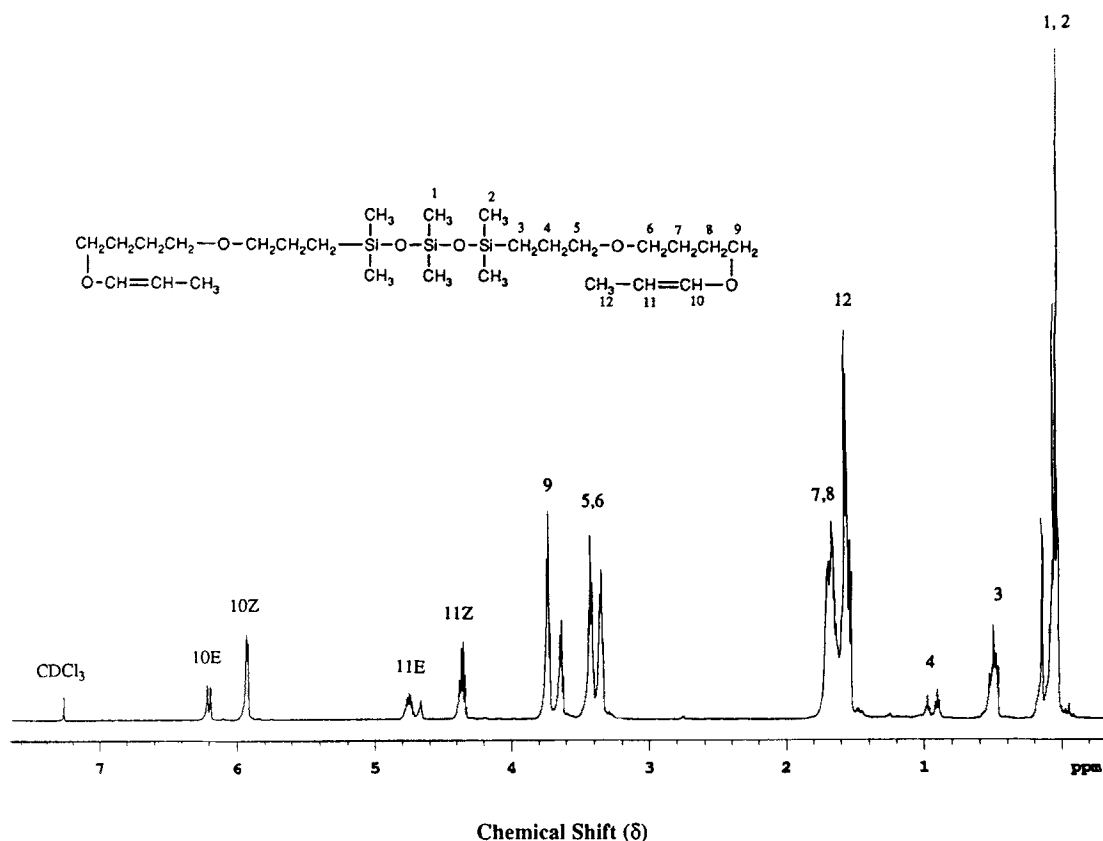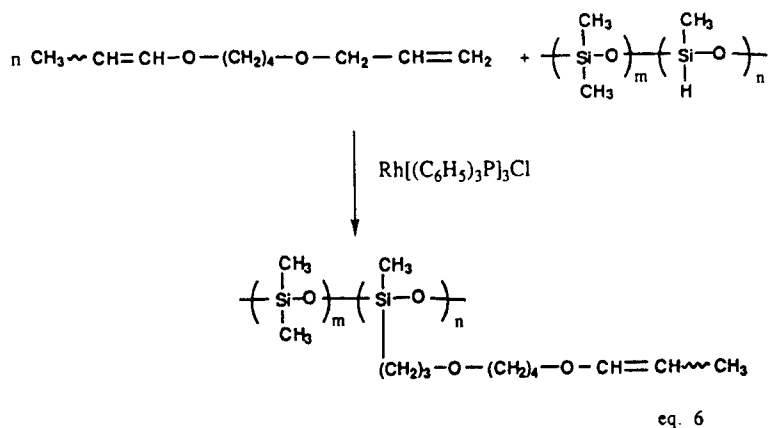
$$S - O - CH = CH \sim CH_3 \quad \xrightarrow[\text{or } Ar_3S^+ \, X^-]{\overset{h\nu}{Ar_2I^+ \, X^-}} \quad \begin{array}{c} S - O \\ | \\ \left(\begin{array}{c} CH - CH \\ | \\ CH_3 \end{array} \right)_n \end{array}$$
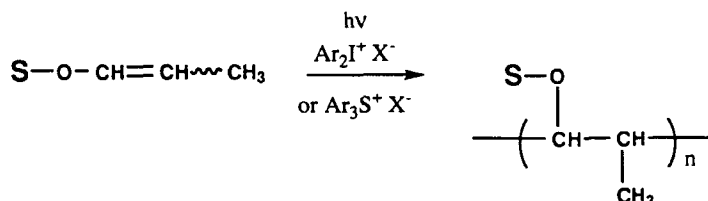
Where S represents a siloxane and a spacer group and X^- is a non-nucleophilic anion.

eq. 7

The rates of these polymerizations were shown be very high and to be comparable to 1-propenyl ethers which do not contain siloxane moieties.

With these data in hand, the possibility of high speed (low dose) electron-beam curing appeared promising. Accordingly, we conducted a brief study of the response of these novel monomers to low intensity electron-beam radiation. An Energy Sciences, Inc. Electrocurtin Model CB-150 apparatus was employed in this study. This instrument is ideal for these studies since it is capable of delivering energy doses reproducible from a minimum of 0.5 Mrad (5 kGy) to several tens of Mrads by adjusting either the current or the irradiation exposure time. The instrument is fitted with a conveyor which permits samples to be passed under the electron beam at various speeds for uniform irradiation. Irradiations can be performed in ambient air or under an atmosphere of inert nitrogen gas. Lastly, the instrument is self-shielded and requires no other special safety provisions for the operators.

As shown in a previous study [12] involving epoxy monomers, the electron-beam-induced cationic polymerization proceeds extremely sluggishly in the presence

of the pure monomers. Typically, irradiation doses of greater than 100 Mrad are required for the polymerization of these monomers. In contrast, when catalytic amounts of a diaryliodonium or triarylsulfonium salt photoinitiator were added, polymerization of the epoxy monomers proceeded at doses of from 1 to 3 Mrad. Similarly, the polymerization of PFS monomers and oligomers was not observed in these experiments in the absence of an onium salt photoinitiator. In this study we employed two different diaryliodonium salt photoinitiators whose structures are depicted below.

IOC10SbF₆   **IOC8PF₆**
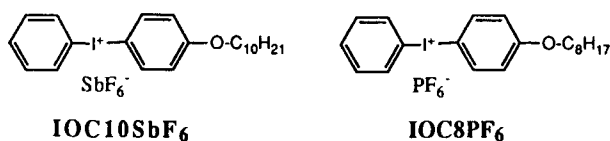
These onium salts represent examples of some of the most reactive photoinitiators which have been developed. The function of the long alkoxy side chains in these compounds is to provide solubility in the PFS monomers and oligomers shown in Table 1.

In the first study, nominally 3 mil (75 μm) films of the liquid PFS monomer Si2PE containing the above onium salt photoinitiators at the indicated concentrations were irradiated at room temperature under nitrogen. Immediately thereafter, the films were tested for their state of cure as indicated by tackiness. The results are shown in Table 2. In this table and in subsequent tables, (+) indicates the film was tack-free (±) means that it was slightly tacky, denoting partial polymerization, and (−) means no polymerization. As shown in Table 2, Si2PE undergoes facile electron-beam-induced cationic polymerization at low doses (0.5–4 Mrad). The dose appears directly related to the structure of the diaryliodonium salt employed. Using

TABLE 2.   Effect of Structure and Photoinitiator Concentration on the E-Beam-Induced Polymerization of Si2PE[a]

Photoinitiator	PI concentration, mol%	Dose, Mrad	Result[b]
−	−	2	−
IOC10SbF₆	0.4	1.0	+
IOC10SbF₆	0.4	0.5	+
IOC10SbF₆	0.2	0.5	+
IOC10SbF₆	0.1	0.5	+
IOC8PF₆	0.4	1	−
IOC8PF₆	0.4	2	−
IOC8PF₆	0.4	4	−

[a]Irradiated as 0.75 μm liquid coatings on poly(ethylene terephthalate) carrier films under nitrogen at 25°C.
[b](+) = tack-free; (−) = tacky.

IOC10SbF$_6$, the minimum dose required to produce a tack-free film using the Electocurtain apparatus is <0.5 Mrad at a photoinitiator concentration of 0.1 mol%. In contrast, IOC8PF$_6$ did not cause polymerization of this monomer at doses greater than eight times higher (4 Mrad). This anion dependence of the efficiency of various diaryliodonium and triarylsulfonium salt photoinitiators has been noted previously in both UV [20] and electron-beam-induced polymerizations [12]. Having established that IOC10SbF$_6$ was vastly superior to IOC8PF$_6$, all further studies were conducted using the former photoinitiator.

A study of the influence of structure and functionality of various PFS monomer and oligomers on their sensitivity toward electron-beam-induced cationic polymerization is given in Table 3. In every case, polymerization to the tack-free state took place at 0.5 Mrad and at 0.1 mol% IOC10SbF$_6$. Since reproducible doses below 0.5 Mrad were not possible with the Electrocurtain apparatus, no attempt was made to further reduce either the dose or the photoinitiator concentration. However, it is clear that these PFS monomers are all very highly reactive under electron-beam irradiation and that the sensitivity, particularly of the multifunctional monomers and oligomers, must lie considerably below 0.5 Mrad. These results compare well with the estimate by Hult and his coworkers [14] of a sensitivity of 0.2–0.4 Mrad for the electron-beam-induced cationic polymerization of the related vinyl ether monomers.

The previous electron-beam polymerization studies were all conducted in the presence of nitrogen as an inert atmosphere. A similar set of experiments was conducted in ambient air, and the results are depicted in Table 4. In the presence of oxygen, both the dose and the photoinitiator concentration must be raised in order to achieve sufficient polymerization to attain a tack-free film. Using Si2PE as a typical case, the dose must be increased over eightfold while the photoinitiator

TABLE 3.   Study of the Influence of Structure of PFS Monomers on their E-Beam-Induced Cationic Polymerization[a]

Monomer	PI concentration, mol%	Dose, Mrad	Result[c]
Si2PE	—	2	—
Si2PE	0.4	0.5	+
Si2PE	0.1	0.5	+
Si3PE	0.4	0.5	+
Si3PE	0.1	0.5	+
Si4PE	0.1	0.5	+
SiD4PE	0.1	0.5	+
Si-copolymer	0.4	0.5	+
Si-copolymer	0.1	0.5	+

[a]Irradiated as 0.75 μm liquid coatings on poly(ethylene terephthalate) carrier films under nitrogen at 25°C.

[b]Photoinitiator is IOC10SbF$_6$.

[c](+) = tack-free; (−) = tacky.

TABLE 4.   Effect of Oxygen on the E-Beam-Induced
Cationic Polymerization of PFS Monomers and Oligomers[a]

Monomer	PI concentration, mol%	Dose, Mrad	Result[c]
Si2PE	0.2	1	−
Si2PE	0.2	2	−
Si2PE	0.4	2	−
Si2PE	0.4	4	+
Si3PE	0.4	0.5	−
Si4PE	0.4	1	±
SiD4PE	0.4	2	−
Si-copolymer	0.4	1	−
Si-copolymer	0.4	2	±
Si-copolymer	0.1	3	+

[a]Irradiated as 0.75 μm liquid coatings on poly(ethylene ter-
ephthalate) carrier films under nitrogen at 25°C.
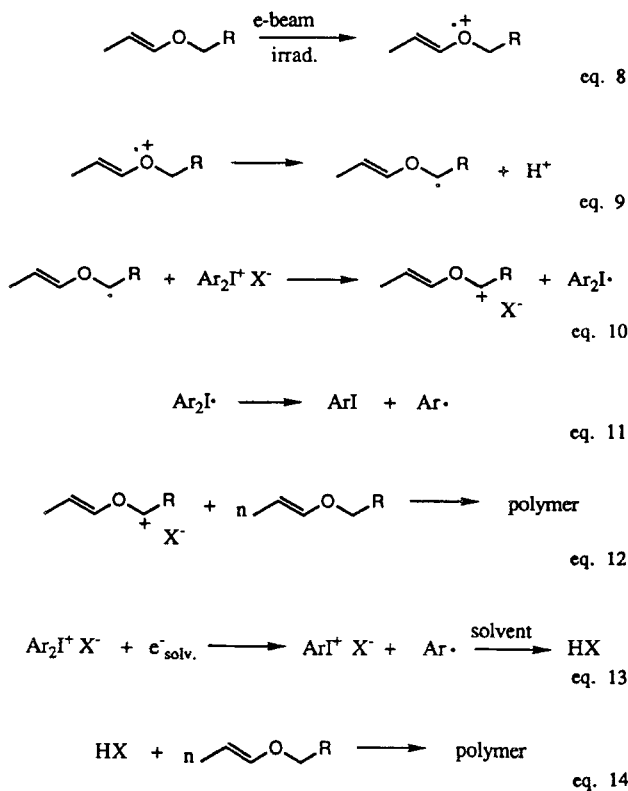[b]Photoinitiator is IOC10SbF$_6$.
[c](+) = tack-free; (−) = tacky.

concentration is raised fourfold. Similar trends were observed with tri-, tetra- and multifunctional PFS. Thus, the presence of oxygen has a marked effect in depressing the electron-beam polymerization of these materials.

Mechanistic Interpretation of the Results

Shown in Scheme 2 is the mechanism we propose for the electron-beam-induced polymerization of PFS. This mechanism is based upon our previous work in the area of photo [19] and electron-beam-induced [12] polymerizations as well as similar mechanisms proposed for the electron-beam-induced polymerizations of vinyl ethers by Hult and his coworkers [14]. Further, the mechanism is in accord with observations made during the studies described in this paper.

1-Propenyl ether monomers interact with electron-beam radiation to initially form a cation-radical species by removal of an electron from the ether oxygen as shown in Eq. (8). This reaction is well documented in the literature [21]. Subsequently, the cation radical species rapidly decays with the ejection of a proton and the formation of a stabilized α-ether radical (Eq. 9). The proton which is ejected can induce the cationic polymerization of the EFS monomers. However, such "free-cation" cationic polymerizations are typically very inefficient with respect to the electron-beam dose required and also greatly susceptible to inhibition by trace impurities. This is confirmed by the reluctance of these monomers to undergo polymerization in the absence of an onium salt photoinitiator. Instead, the α-ether radical which is formed can interact with a diaryliodonium salt photoinitiator $(Ar_2I^+ X^-)$ as depicted in Eq. (10) to reduce the onium salt producing the corresponding diaryliodine free radical. This latter species decays irreversibly to give an aryl iodide and an aryl free radical (Eq. 11). Simultaneously (Eq. 10), the α-ether free radical is

$$\text{CH}_2{=}\text{CH}{-}\text{O}{-}\text{CH}_2{-}\text{R} \xrightarrow[\text{irrad.}]{\text{e-beam}} \left[\text{CH}_2{=}\text{CH}{-}\overset{\cdot+}{\text{O}}{-}\text{CH}_2{-}\text{R}\right] \qquad \text{eq. 8}$$

$$\left[\text{CH}_2{=}\text{CH}{-}\overset{\cdot+}{\text{O}}{-}\text{CH}_2{-}\text{R}\right] \longrightarrow \text{CH}_2{=}\text{CH}{-}\text{O}{-}\overset{\cdot}{\text{C}}\text{H}{-}\text{R} + \text{H}^+ \qquad \text{eq. 9}$$

$$\text{CH}_2{=}\text{CH}{-}\text{O}{-}\overset{\cdot}{\text{C}}\text{H}{-}\text{R} + \text{Ar}_2\text{I}^+\text{X}^- \longrightarrow \text{CH}_2{=}\text{CH}{-}\text{O}{-}\overset{+}{\text{C}}\text{H}{-}\text{R} \;\; \text{X}^- + \text{Ar}_2\text{I}\cdot \qquad \text{eq. 10}$$

$$\text{Ar}_2\text{I}\cdot \longrightarrow \text{ArI} + \text{Ar}\cdot \qquad \text{eq. 11}$$

$$\text{CH}_2{=}\text{CH}{-}\text{O}{-}\overset{+}{\text{C}}\text{H}{-}\text{R} \;\; \text{X}^- + n\,\text{CH}_2{=}\text{CH}{-}\text{O}{-}\text{CH}_2{-}\text{R} \longrightarrow \text{polymer} \qquad \text{eq. 12}$$

$$\text{Ar}_2\text{I}^+\text{X}^- + e^-_{\text{solv.}} \longrightarrow \text{ArI}^+\text{X}^- + \text{Ar}\cdot \xrightarrow{\text{solvent}} \text{HX} \qquad \text{eq. 13}$$

$$\text{HX} + n\,\text{CH}_2{=}\text{CH}{-}\text{O}{-}\text{CH}_2{-}\text{R} \longrightarrow \text{polymer} \qquad \text{eq. 14}$$

SCHEME 2.

oxidized to the corresponding resonance stabilized α-ether carbenium ion (oxocarbenium ion). This latter species can then initiate the polymerization of PFS (Eq. 12). Equations (8)–(12) constitute the major process by which cationic polymerization of PFS monomers and polymers take place under electron-beam irradiation conditions. A secondary process shown in Eqs. (13) and (14) involves the direct reduction of the diaryliodonium salt by solvated electrons. In this case a protonic acid generated by the reduction process and interaction of the intermediates with the solvent or monomer initiates the cationic polymerization. The presence of free radicals and cations in these systems has been demonstrated by selective inhibition and retardation studies. The inclusion of tertiary amine bases completely inhibits the polymerization of PFS. This strongly supports the presence of cationic species as the ultimate initiators of polymerization. At the same time, the inclusion of free-radical retarders such as phenols was observed to slow but not completely inhibit the polymerization of PFS.

Several factors contribute to the efficiency of this mechanism in the initiation of cationic polymerization. First, the diaryliodonium salts possess low reduction potentials (-14 kJ·mol^{-1}) [22] which enables them to undergo a thermodynamically favored interaction with the α-ether radical (Eq. 10) to generate the initiating carbenium ion. Second, the reactivity of this latter species is determined not only by

$$\text{(structure)} + Ar_2I^+ X^- \longrightarrow \text{(structure)} + Ar_2I\cdot$$

eq. 10

$$Ar_2I\cdot \longrightarrow ArI + Ar\cdot$$

eq. 11

$$Ar\cdot + \text{(structure)} \longrightarrow \text{(structure)} + ArH$$

eq. 15
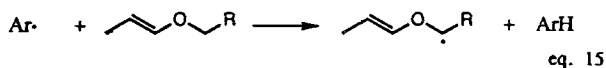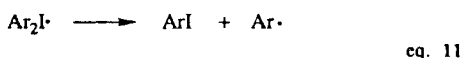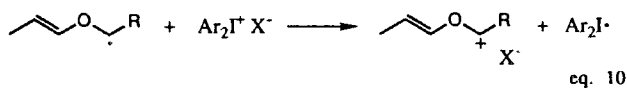
SCHEME 3.

its structure but also by the character of the accompanying anion. Maximum reactivity of the carbenium ion is attained with the SbF_6^- anion, due to both its stability and its low nucleophilicity. Even more important is the contribution made by a cycle or chain reaction which results in the free-radical-induced decomposition of the diaryliodonium salt photoinitiator. This cycle is shown in Scheme 3 and consists of the combination of Eqs. (10) and (11) in which the reduction of the diaryliodonium salt takes place and an aryl free radical is generated. The cycle is closed by abstraction of the α-ether proton by the aryl free radical which regenerates the α-ether free radical (Eq. 15). Once started, this cycle results in consumption of the diaryliodonium salt together with the continual generation of carbenium ions which initiate cationic polymerization. Thus, only a very few cation-radical or radical species need be produced by electron-beam irradiation for this cycle to be started. The resulting amplification effect accounts for the extraordinarily high sensitivity (<0.5 Mrad) of these cationic systems. In contrast, typical electron-beam-induced free-radical polymerizations of acrylate and methacrylate monomers require minimum radiation doses of 3–4 Mrad [23].

The combined mechanisms shown in Schemes 2 and 3 also account for the observed sensitivity of the polymerization of PFS monomers and oligomers to oxygen. Oxygen would be expected to intercept the α-ether and the aryl free radicals involved as intermediates in both of these mechanisms by formation of hydroperoxy radicals. The latter species cannot be further oxidized to the carbenium ions requisite for polymerization. Nor would such hydroperoxy radicals be expected to participate in the chain-induced decomposition of the diaryliodonium salts. Thus, while the electron-beam polymerization of PFS proceeds by a traditional cationic mechanism which is not usually affected by oxygen, free-radical intermediates involved in these polymerizations are consumed by reaction with oxygen, resulting in greatly diminished efficiency in its presence. Despite the attenuation in reactivity in the presence of oxygen, the PFS monomers and oligomers display excellent reactivity (~ 4 Mrad) and are highly suitable for high-speed coating applications.

CONCLUSIONS

A novel approach for the synthesis 1-propenyl ether functionalized siloxanes (PFS) has been devised. This preparative method takes advantage of the hydrosila-

tion of 1-allyloxy-4(1-propenoxy)butane with various Si—H functional siloxanes which takes place chemoselectively at the allyl group. The resulting PFS undergo rapid electron-beam-induced cationic polymerization in the presence of diaryliodonium salt photoinitiators. Investigations showed that the minimum dose required for induction of polymerization is less than 0.5 Mrad at a diaryliodonium salt concentration of 0.1 mol%. Consequently, the polymerizations of these monomers and oligomers are among the most rapid and efficient known to proceed by electron-beam irradiation. A mechanism involving the free-radical chain-induced decomposition of the diaryliodonium salt has been proposed to explain these results.

ACKNOWLEDGMENTS

REFERENCES

[1]   W. Noll, *Chemistry and Technology of Silicones*, Academic Press, San Diego, CA, 1968.

[2]   R. H. Bickford Jr. and J. Jackmann, *Proceedings Radtech '88-North America Conference*, 1988, p. 569.

[3]   J. E. Thompson and J. Cavezzan, *Proceedings Radtech '92-North America Conference*, 1992, p. 212.

[4]   H. K. Chu, R. P. Cross, D. I. Crossan, and E. K. Welch, US Patents 5,348,946 (September 20, 1994), 5,182,315 (January 26, 1993), and 5,179,134 (January 12, 1993), all to Loctite Corp.

[5]   J. V. Crivello and J. L. Lee, *J. Polym. Sci., Polym. Chem. Ed., 28*, 479 (1990).

[6]   J. V. Crivello, US Patent 4,310,469 (January 12, 1982).

[7]   J. V. Crivello, US Patent 4,138,255 (February 6, 1979).

[8]   J. V. Crivello and S. H. Schroeter, US Patent 4,026,705 (May 31, 1977).

[9]   K. Riding, *Proceedings Radtech '90-North America Conference*, 1990, p. 377.

[10] R. P. Eckberg, *Proceedings Radtech '88-North America Conference*, 1988, p. 576.

[11] C. Priou, A. Soldat, J. Cavezzan, J. P. Fouassier, and F. Castellanos, *Proceedings Radtech '94-North America Conference*, 1994, p. 187.

[12] J. V. Crivello, M. Fan, and D. Bi, *J. Appl. Polym. Sci., 44*, 9 (1992).

[13] J. V. Crivello, J. L. Lee, and D. A. Conlon, *J. Radiat. Curing, 1*, 6, (1983).

[14] A. B. Hult and P. E. Sundell, *Polym. Mater. Sci. Eng. Prepr., 60*, 453 (1989).

[15] S. C. Lapin, *Proceedings Radtech '88-North America Conference Proceedings*, 1988, p. 395.

[16] Ch. Herzig and B. Deubzer, *Proceedings Radtech Asia Conference*, 1993, p. 99.

[17] J. V. Crivello and J. L. Lee, *J. Polym. Sci., Polym. Chem. Ed., 27*, 3951 (1989).

[18] J. V. Crivello and K. D. Jo, *Ibid., 31*, 1483 (1993).

[19] J. V. Crivello, B. Yang, and W.-G. Kim, *Ibid., 33*, 2415 (1995).

[20] J. V. Crivello and K. Dietliker, *Chemistry and Technology of UV & EB Formulation for Coatings, Inks & Paints*, Vol. 3 (P. K. T. Oldring, Ed.), 1991, SITA Technology Ltd., London, p. 327.

[21] S. Arai and M. C. J. Sauer Jr., *Chem. Phys., 44*, 2297 (1966).

[22] P. E. Sundell, S. Jönsson, and A. Hult, *Polym. Prepr. 31*(2), 373 (1990).

[23] Kopchonof, Grozdov, Krajzman, Fakin, Ogonjdov, Shik, and Sidorenko, *Proceedings Radtech '90-North America Conference, 2*, 1990, p. 11.