

Synthesis of Novel Multifunctional Siloxane Oligomers Using Sol–Gel Techniques and Their Photoinitiated Cationic Polymerization

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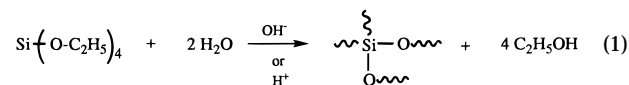
Employing modified sol–gel techniques, trialkoxysilanes bearing either epoxy or 1-propenyl ether functional groups can be condensed under well controlled conditions to yield a series of soluble multifunctional siloxane oligomers. The key to the success of this synthetic approach was the use of weakly acidic ion-exchange resins as catalysts. The novel multifunctional oligomers displayed exceptionally high reactivity in photoinitiated cationic polymerization using diaryliodonium salts as photoinitiators. Polymerization involved not only addition polymerization of the pendant epoxide or 1-propenyl ether groups but also acid-catalyzed hydrolysis and condensation of residual alkoxy groups along the siloxane backbone.

Introduction

For some time now, there has been considerable interest in this laboratory in the photoinduced cationic polymerization of siloxane-containing monomers and oligomers. Such monomers and oligomers have considerable potential in a wide diversity of applications including nonstick release coatings, adhesives, abrasion resistant coatings for plastics, optical fiber coatings and optical waveguides. In a recent series of articles, we described the preparation of epoxy functional^{1–3} and 1-propenyl ether functional^{4,5} siloxanes and their photoinitiated cationic polymerization. These monomers uniquely display the ability to undergo extremely rapid photoinduced cationic polymerization and to proceed to high conversions even in the case of multifunctional monomers and oligomers. In contrast, the photopolymerizations of analogous conventional multifunctional monomers characteristically proceed only to low conversions due to trapping of residual reactive functional groups within the rigid, cross-linked network as it is formed.⁶ The anomalous behavior in the case of the siloxane-containing monomers has been attributed to the high conformational flexibility of the siloxane (Si–O–Si) bond and to free-volume effects.⁷

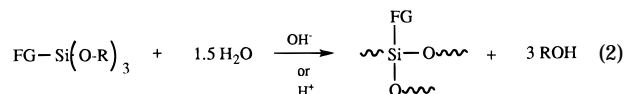
Since photopolymerizable siloxanes appear to have interesting properties and many very useful potential applications, we have been investigating a novel methodology for their synthesis. One very interesting and general method of preparing a variety of siloxanes is through the use of sol–gel techniques. Sol–gel tech-

niques are widely employed for the preparation of cross-linked, inorganic glasslike matrixes composed of Si–O–Si linkages.^{8–10} Typically, as shown in eq 1,



alkoxysilanes such as tetraethoxysilane (TEOS) are subjected to acid or base catalyzed hydrolysis–condensation in the presence of controlled amounts of water to yield a gel. The sol–gel process is, in fact, a rather complex process involving two basic reactions, first hydrolysis of the alkoxysilane to give a silanol followed by condensation of a silanol with an alkoxysilane or with another silanol to give the siloxane linkage. In TEOS, each of the four alkoxy groups are hydrolyzed at different rates, and further the condensation of each of the resulting silanols also proceeds at its own rate.

In most acid-catalyzed sol–gel processes, HCl is used, while NaOH and NH₄OH are often employed as base catalysts. Sol–gel chemistry can also be carried out as depicted in eq 2 using trialkoxysilanes to yield networks bearing functional groups (FG).



It occurred to us that it might be possible to use sol–gel chemistry to prepare siloxane or silsesquioxane monomers and oligomers bearing cationically polymerizable, functional groups. This area of sol–gel chemistry has been the subject of much current activity,^{11,12} and several review articles,^{13–16} have been published.

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Recently, we described one approach to the synthesis of epoxy functional monomers and oligomers bearing the T₈ silsesquioxane core using hydrosilylation chemistry.¹⁷ Selinger and Laine¹⁸ have reported the preparation of similar monomers using the same methodology.

The present article reports the development of a new sol-gel technique involving the use of weakly acidic ion-exchange resins as catalysts for the controlled preparation of a new series of soluble epoxy and 1-propenyl ether functional siloxane monomers and oligomers. The response of these materials to onium salt mediated cationic photopolymerization is also described.

Experimental Section

Materials and Analytical Procedures. [2-(3,4-Epoxy-cyclohexylethyl)]trimethoxysilane (**I**) and (3-glycidoxypropyl)-trimethoxysilane (**II**) were purchased from the Hüls America, Inc. All organic reagents employed in this investigation were reagent quality and were used as purchased from the Aldrich Chemical Co., Milwaukee, WI, unless otherwise noted. Ethylene glycol monovinyl ether (2-vinyloxyethanol) was obtained as a gift from the BASF Corp., Ludwigshafen, Germany. The preparation of (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate (**IOC10**) was carried out as described previously.¹⁹

Gel permeation chromatographic (GPC) analyses were carried out using a Hewlett-Packard HP-1090M HPLC equipped with a refractive index detector and a μ -styalgel column (particle size 5 μ m, mixed 24–34 Å pores). CHCl₃ was used as the eluent at a flow rate of 1.0 mL/min. All molecular weights are reported relative to polystyrene standards. Gas chromatographic (GC) analyses were performed on a Hewlett-Packard HP-5840A gas chromatograph equipped with a 15 m \times 0.53 mm \times 1.5 μ m film thickness cross-linked methylsilicone gum column and a flame ionization detector. ¹H NMR spectra were obtained using a Varian Unity-500 spectrometer at room temperature in CDCl₃. All chemical shifts are reported relative to tetramethylsilane as an internal standard.

Preparation of Epoxy Functional Oligomers. *Sol-Gel Condensation of 2-(3,4-Epoxy-cyclohexylethyl)trimethoxysilane (I).* A 50 mL round-bottom flask fitted with a magnetic stirrer, reflux condenser, and a thermometer was charged with 1.97 g (8 mmol) of **I**, 0.5–1.5 equiv of deionized water, 80 mg of Amberlite IRA-904 ion-exchange resin (Rhom and Haas, Philadelphia, PA), and 0.5 g of 2-propanol. The colorless solution was stirred and heated at 60 °C. Samples (0.5 g) of the reaction mixture were taken every several hours, cooled, and filtered, and the resulting colorless liquid combined with 0.5 g of 2-propanol and subjected to GPC and analysis. Then, the solvent was removed under reduced pressure and the resulting in a colorless, viscous liquid oligomer was further characterized by ¹H NMR spectroscopy and by RTIR analysis.

¹H NMR (CDCl₃) δ (ppm) 0.5, CH₂-Si; 1.2–2.2, aliphatic protons; 3.12, epoxy CH; 3.48, OCH₃.

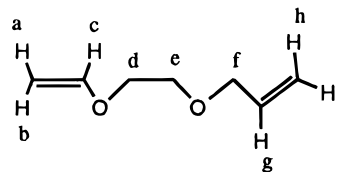
Sol-Gel Condensation of (3-Glycidoxypropyl)trimethoxysilane (II). Into the same apparatus described above were added 1.89 g (8.0 mmol) of **II**, 1.5 equiv (217 mg) of water, 80 mg of Amberlite IRA-904, and 0.5 g of 2-propanol. The colorless solution was stirred and heated at 60 °C. Samples (0.5 g) of the reaction mixture were taken every several hours, cooled, and filtered, and the resulting colorless liquid combined with 0.5 g of 2-propanol and subjected to GPC and analysis. Then,

the solvent was removed under reduced pressure, and the resulting colorless, viscous liquid oligomer was further characterized by ¹H NMR spectroscopy and by RTIR analysis.

¹H NMR (CDCl₃) δ (ppm) 0.59, CH₂-Si; 1.6, CH₂-CH₂-S; 2.5, epoxy CH₂; 2.7, epoxy CH; 3.07, OCH₂; 3.48, OCH₃.

Synthesis of 1-(1-Propenoxy)-2-(2-(trimethoxysilyl)ethoxy)ethane (V). A 100 mL round-bottom flask fitted with a reflux condenser and magnetic stirrer was charged with 8.8 g (0.1 mol) of ethylene glycol monovinyl ether, 14.5 g (0.12 mol) of allyl bromide, 4.8 g (0.12 mol) of NaOH, 0.9 g (3 mol %) of (*n*-Bu)₄NBr, and 20 mL of dried toluene. The suspension was stirred and heated at 65 °C for 12 h. After cooling the reaction mixture, the resulting pale yellow solution was separated from the white solids by decantation and washed four times with 50 mL portions of water in a separatory funnel. Removal of the solvent under reduced pressure followed by vacuum distillation (bp 30 °C/0.15 mmHg) gave the desired 1-(allyloxy)-2-vinyloxyethane as a colorless liquid.

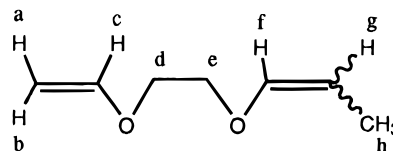
¹H NMR (CDCl₃) δ (ppm) 4.16–4.19 (m, H_{a,b}, 2H); 6.48 (m, H_c, 1H); 3.83 (m, H_d, 2H); 3.65 (m, H_e, 2H); 4.04 (m, H_f, 2H); 5.90 (m, H_g, 1H); 5.19 (m, H_h, 1H); 5.25 (m, H_i, 1H).



The entire amount of 1-(allyloxy)-2-(vinyloxy)ethane obtained in the above procedure was placed in a 50 mL round-bottom flask fitted with a magnetic stirrer and reflux condenser and 3 mg of (PPh₃)₃RuCl₂ was added. The resulting light brown-purple solution was refluxed at 130 °C for 2.5 h. Fractional vacuum distillation (bp 26 °C/0.15 mmHg) gave 1-(1-propenoxy)-2-(vinyloxy)ethane (mixture of cis and trans isomers) as a colorless liquid in an overall yield of 70% (9.17 g) from ethylene glycol monovinyl ether.

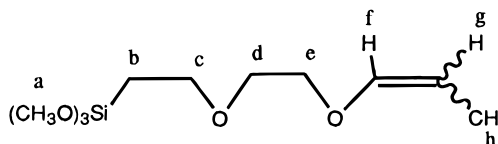
Elemental anal. Calcd for C₇H₁₂O₂: C, 65.60%; H, 9.44%. Found: C, 65.55%; H, 9.49%.

¹H NMR (CDCl₃) δ (ppm) 4.05 (m, H_a, 1H); 4.20 (m, H_b, 1H); 6.51 (m, H_c, 1H); 3.94 (m, H_d, 2H); 3.86 (m, H_e, 2H); 5.97 (m, H_f, 1H); 4.43 (m, H_g, 1H); 1.58 (m, H_h, 3H).



Into a 100 mL round-bottom flask were added 9.17 g (0.07 mol) of 1-(1-propenoxy)-2-(vinyloxy)ethane, 3 mg of (PPh₃)₃RhCl, 11.3 g of trimethoxysilane (0.09 mol), and 15 mL of dried toluene. The resulting purple solution was refluxed at 85 °C for 12 h. Fractional vacuum distillation yielded 1-(1-propenoxy)-2-(2-(trimethoxysilyl)ethoxy)ethane in 36% yield as a colorless liquid, bp 70 °C/0.15 mmHg.

¹H NMR (CDCl₃) δ (ppm) 3.54 (s, H_a, 9H); 1.08 (m, H_b, 2H); 3.60 (m, H_{c,d}, 4H); 3.84 (m, H_e, 2H); 6.14 (m, H_f cis); 5.95 (m, H_f trans); 4.85 (m, H_g cis); 4.36 (m, H_g trans); 1.54 (m, H_h, 3H).



1-(1-Propenoxy)-2-(2-(trimethoxysilyl)ethoxy)ethane was subjected to sol-gel condensation in the presence of Amberlite IRA-904 ion-exchange resin as described above.

Photopolymerization Studies. *Thin-Film Polymerizations.* Thin films (~25 μ m) of the liquid monomers containing 2.0 wt % of IOC10 photoinitiator were drawn onto glass or

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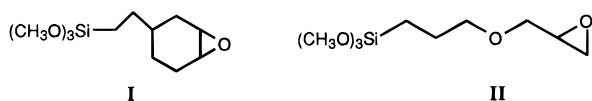
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steel panels and irradiated using a GE H3T-7 200 W medium-pressure mercury arc lamp mounted at a distance of 12 cm from the sample. This apparatus was equipped with a mechanical shutter that could be opened to expose the samples to UV irradiation.

Fourier Transform Real-Time Infrared Spectroscopy (RTIR). The course of the cationic photopolymerization of the monomers described in this paper were followed using real-time Fourier transform infrared spectroscopic analysis (RTIR). This method involves the monitoring of an appropriate IR band due to the polymerizing group while simultaneously irradiating the thin-film sample with UV light. Measurements were performed on a Midac Series M Fourier transform infrared spectrometer equipped with a liquid nitrogen cooled MCD detector. The instrument was fitted with a UVEXS Co. SCU 110 UV lamp equipped with a flexible liquid optic cable directed at a 45° angle onto the sample window. All studies were conducted using broad band, unfiltered UV light at an intensity of 1500 mJ cm⁻² min⁻¹. Samples were prepared by placing the liquid monomer or oligomer containing 2.0 wt % (4-(*n*-decyloxy)phenyl)phenyliodonium hexafluoroantimonate (**IOC 10**) between two poly(propylene) films and then mounting the sandwich in 5 cm × 5 cm slide frames. The progress of the polymerizations of the epoxy functional trialkoxysiloxanes was determined quantitatively by monitoring the decrease of the 885 cm⁻¹ band. The double bond peaks at 1660–1670 cm⁻¹ were employed to monitor the polymerization of the 1-propenyl ether functional trialkoxysiloxanes. The data were collected on a Bit-Wise Co. 486 PC computer, reduced, and plotted as conversion versus time curves with the aid of a Galactic Industries Corp. Grams 386, Version 3.0 software package. Conversions were determined by integration of the above-mentioned bands using one of the poly(propylene) peaks as an internal standard. Light intensity measurements were made with the aid of an International Light Co. Control-Cure radiometer.

Results and Discussion

General Synthetic Approach. Two trialkoxysilanes bearing epoxy functional groups whose structures are shown in **I** and **II** are commercially available. These

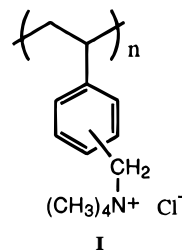


compounds are commonly employed as glass coupling agents to increase adhesion between epoxy matrixes and reinforcing glass fibers. We suggested that if it is possible to efficiently carry out sol-gel reactions using compounds **I** and **II**, oligomers or even silsesquioxane monomers bearing cationically polymerizable epoxy groups could be readily prepared. However, while conventional sol-gel chemistry is convenient and easily carried out, it suffers from certain drawbacks that make it less attractive for the preparation of photopolymerizable epoxy functional siloxane monomers and oligomers. First, the use of strong acid hydrolysis catalysts cannot be used for the synthesis of these materials since epoxy groups undergo spontaneous ring-opening reactions with these agents. At the same time, conventional basic catalysts are also problematic. Although epoxide groups do not directly react with inorganic bases, these bases are strong inhibitors for photoinduced cationic polymerizations. Further, it is difficult or impossible to remove conventional catalysts at the end of the sol-gel reaction since they may become bound to or entrapped in the polymer that is formed. Last, the rate and extent of the sol-gel reactions of **I** and **II** are dependent on the strength of the acid or base catalysts

used.^{16,20} Strong acids and bases give fast hydrolysis and condensation of alkoxy silanes and high conversions to polymers. If the sol-gel condensations of **I** or **II** are carried to high conversion, cross-linked matrixes inevitably result. Further, it is quite difficult to control fast sol-gel reactions to stop at intermediate stages and to reproducibly make soluble, low-viscosity, fluid oligomers. Indeed, even when such materials are obtained, they exhibit poor pot-lives and normally gel on standing due to further condensation. For these reasons, less active catalysts are desired.

All of the above problems were satisfactorily resolved through the use of weakly acidic anion-exchange resins as catalysts for the sol-gel condensation of **I** and **II**. Ion-exchange resins have been employed as catalysts for many different reactions,²¹ but applications in sol-gel chemistry have not been reported thus far. We have observed that excellent control over the complex sol-gel chemistry may be exercised with weakly acidic ion-exchange resins as catalysts. Condensation of the functionalized trialkoxysilanes in the presence of these catalysts proceeds at a convenient rate so that reaction times are not inordinately long and at the same time slow enough that adequate control can be maintained over the reaction to provide reproducible molecular weight control and to avoid gelation. The reaction may be terminated at any stage by quantitatively removing the catalyst by simple filtration. Last, the chemistry is broadly adaptable for the preparation of tailor-made siloxanes with various reactive, polymerizable pendant functional groups.

Sol-Gel Condensation of [2-(3,4-Epoxy cyclohexyl)ethyl]trimethoxysilane (I). We examined three weakly acidic gel and macroreticular ion-exchange resins as catalysts in the sol-gel condensation of **I**. All



these resins were in an easily handled bead form, have the general structure shown below, but differ in their cross-link density, porosity, and ion-exchange capacity. The cross-link density of the resins was controlled by the amount of divinylbenzene employed in their synthesis. All the resins were purchased and used in the chloride form.

Treatment of **I** with 1.5 equiv of water in the presence of a catalytic amount of a weakly ion-exchange resin at 45 °C for 9 h resulted in a colorless, viscous liquid. ¹H NMR spectroscopy was used to monitor the disappearance of the methoxy groups (band centered at 3.45 ppm) as a function of reaction time. Table 1 summarizes the results obtained with the three catalysts.

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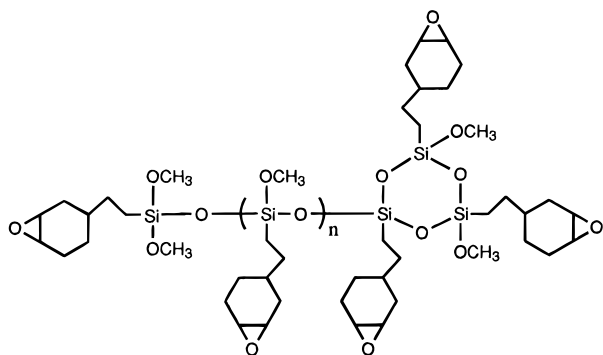
(22) We are indebted to one of the reviewers for supplying some of the data that appears in this table.

Table 1. Sol-Gel Reaction of I Catalyzed by Ion-Exchange Resins^{22a}

ion-exchange resin	type (porosity %)	water (%)	ion exchg capacity (mequiv/g)	conversion of methoxy groups (%)
Amberlyst A-27	macroporous 51	45	2.6	82
Amberlite IRA-400	gel		4.0	80
Amberlite IRA-904	macroporous 50	57	4.0	78

^a Reaction conditions, 45 °C, 9 h, 1.5 equivalents of water.

All three ion-exchange resins displayed similar catalytic activity in the sol-gel condensation of **I**. The fact that all of these varied resins gave the same results indicates that the chemical reaction is not limited by porosity or the ion-exchange capacity. It is interesting to note that despite the presence of sufficient water to hydrolyze all three methoxy groups of the starting material, that colorless, soluble, low-viscosity oligomers were obtained in each case. This would tend to suggest that the hydrolysis and condensation proceed in a discrete stepwise manner such that the rate of the reaction of the last of the three methoxy groups is considerably slower than that of the first two groups. This has led us to propose that the structure of the resulting oligomer is composed of a backbone consisting mainly of linear, branched, and condensed cyclic siloxane units. A depiction of the proposed structure of this oligomer is given below.



The degree of condensation can, therefore, be further controlled by varying the ratio of water to trialkoxysilane present in the reaction mixture. ¹H NMR spectroscopy showed that under the reaction conditions described here, no ring-opening side reactions at the highly reactive epoxy-cyclohexane groups took place. Removal of the ion-exchange catalyst by filtration provided products that appeared to be shelf stable and that did not increase in viscosity nor gel on standing for over 2 months. Further, preliminary studies showed that photopolymerization of **I** in the presence of (4-(*n*-decyloxy)phenyl)phenyliodonium hexafluoroantimonate (**IOC10**) proceeded vigorously to provide transparent, hard, glasslike films. On the basis of these results, we elected to employ one of these resins, Amberlite IRA-904, in all subsequent studies.

Figure 1 shows the progress of the GPC curves for the reaction of **I** with 0.5 equiv of water in the presence of Amberlite IRA-904 resin. The chromatogram consists of several peaks which could be assigned on the basis of their molecular weights relative to **I** as a standard. During reaction, oligomers are rapidly formed as **I** is

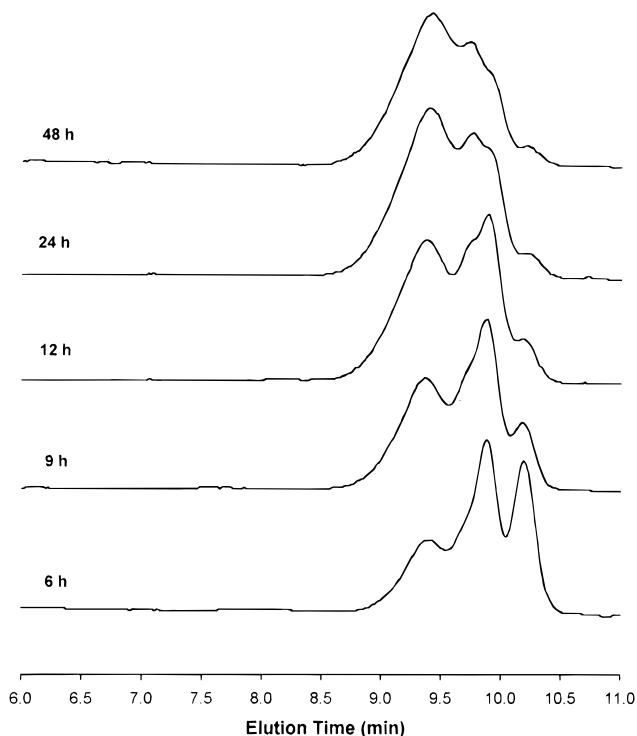
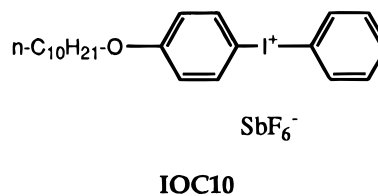


Figure 1. GPC study of the sol-gel condensation of **I** with time at 60 °C in the presence of 0.5 equiv of water.

consumed. After a 6 h reaction, the reaction mixture contains species with masses corresponding to mainly dimers, trimers, and tetramers. Within 24 h the reaction is essentially complete and thereafter little further reaction takes place.

Cationic Photopolymerization of Oligomers of I. Critical to the success of the photopolymerizations is the solubility of the onium salt photoinitiator in the epoxy functional monomers and oligomers produced by sol-gel reactions. It has been found that diaryliodonium salts bearing long alkoxy or alkyl side chains are particularly well suited for the polymerization of these materials because of their excellent solubility in these materials. For this study, we have employed the diaryliodonium salt photoinitiator shown below.



UV induced polymerization of thin (~25 μm) films of the oligomer (**I-0.5-24**) obtained after 24 h in the presence of 2 wt % of IOC10 as a photoinitiator gave hard, brittle, colorless transparent films. Previous work³ had shown that two independent polymerization processes occur simultaneously in the case of monomers such as **I** bearing both trialkoxysilane and epoxy groups. The photogenerated acid derived by UV irradiation of the diaryliodonium salt photoinitiator catalyzes the rapid ring-opening polymerization of the epoxy-cyclohexyl groups (eq 3).

At the same time, the slower acid-catalyzed condensation of the alkoxysilane groups takes place in the

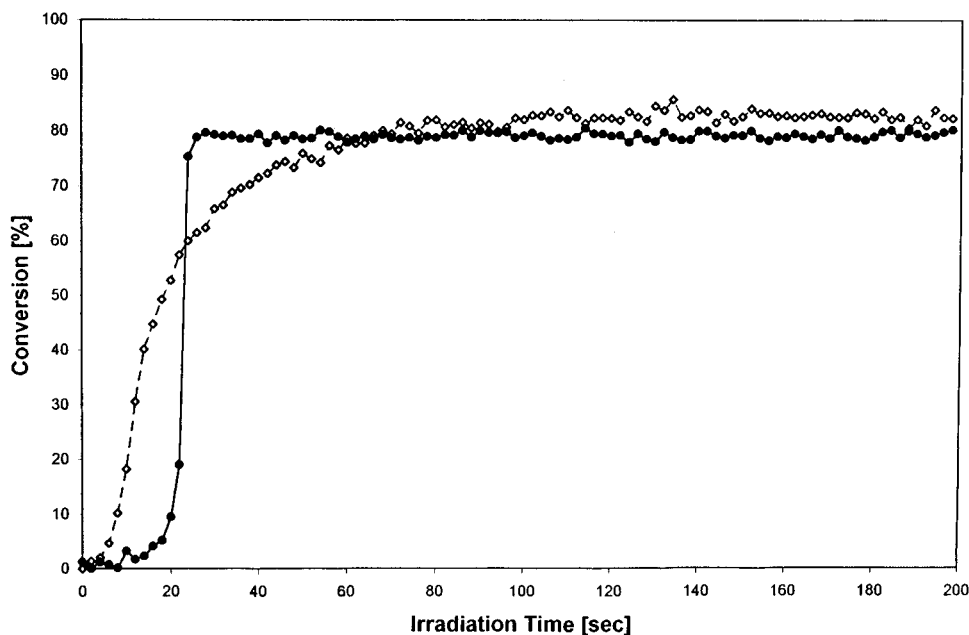
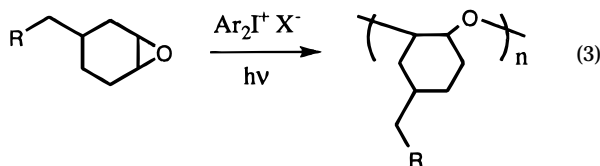
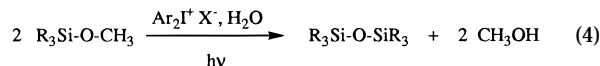


Figure 2. RTIR study of the photopolymerization of the polymerizations of oligomer **I-0.5-24** (●) and **I** (◇) in the presence of 2 wt % IOC10.



presence of atmospheric moisture to form Si–O–Si bonds (eq 4).



The rapid photopolymerization of these novel monomers and oligomers can be conveniently monitored using Fourier transform real-time infrared spectroscopy (RTIR). The decrease in the IR bands in the region 885 cm^{-1} assigned to the epoxy groups were followed continuously as a function of time while the sample was simultaneously irradiated with UV light. Thus, this method directly monitors the disappearance of the reactive epoxide groups as the polymerization proceeds. The polymerization studies described here were conducted at a light intensity of $1500 \text{ mJ cm}^{-2} \text{ min}^{-1}$ and at a photoinitiator concentration of 2 wt % to provide a system that polymerizes at a rate slow enough to allow kinetic analysis. The data were reduced and plotted as conversion versus irradiation time curves. The course of the slow alkoxy silane polymerization was not monitored by RTIR.

Figure 2 shows a RTIR study of the photoinduced polymerization of oligomer **I-0.5-24** produced by sol-gel condensation of **I** with 0.5 equiv of water for 24 h. Also shown in Figure 2 is the curve for the polymerization of epoxy functional trialkoxysilane precursor, **I**. The polymerization of the oligomer is preceded by approximately a 20 s induction period. This induction period is absent in the polymerization of the starting material **I**. It should be noted that the induction period is observed only at low light intensities. When higher incident light intensities are employed such as those

normally used for UV photopolymerizations, sufficient acid is generated to overcome the induction period immediately. We proposed that the induction period was due to trace amounts of free amine impurities present in the ion-exchange resin or by formation of amines by side reactions during the prolonged reaction time required to form the oligomer. To investigate this possibility further, Amberlite IRA-904 resin was extracted with four separate portions of toluene, stirring each portion for 1 h. After the last portion of toluene was removed by decantation, the beads were dried in vacuo at room temperature. The preparation and workup of resin **I-0.5-24** was repeated as described above with the extracted ion-exchange beads. RTIR of this resin showed that the induction period had been reduced from 20 s to approximately 8 s. These results strongly suggest that the ion-exchange resins contain small amounts of amine impurities adsorbed or weakly bound into the surface or pores of the cross-linked resins.

The induction period in the RTIR curve of oligomer **I-0.5-24** is followed by the extremely rapid polymerization of the epoxy groups, indicating that this oligomer is very reactive. The slope of the RTIR curve of the oligomer is considerably greater than that of the starting trialkoxysilane **I**. After 25 s of irradiation, the maximum epoxide conversion of 80% is attained, and the conversion does not increase on further irradiation. These results implied that during the first 20 s of irradiation the trace level of basic impurities is being consumed by photogenerated acid. Once these impurities are removed, catalytic polymerization of the oligomer should proceed with just a small additional increment of photogenerated acid. To test this hypothesis, the RTIR curves for the polymerization of the same epoxy functional oligomer after only 20 s of irradiation is compared with that in which the sample was continuously irradiated for 200 s. The results are shown in Figure 3. The two RTIR curves are essentially identical.

When the sol-gel condensation of **I** was carried out with 1.0 and 1.5 equiv of water, monitoring of the

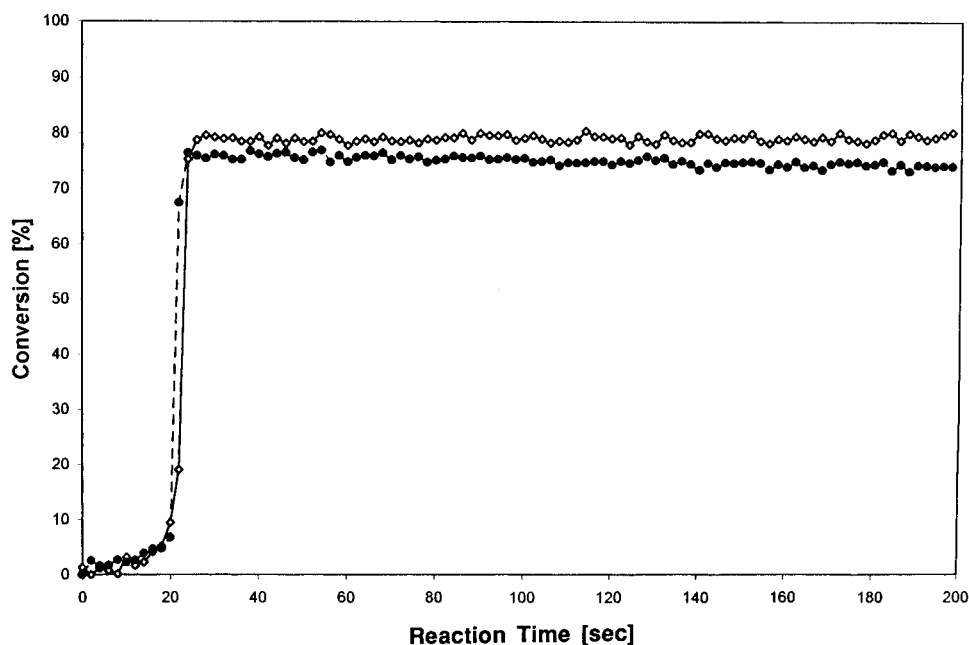


Figure 3. Comparison of the RTIR curves for the polymerization of **I-0.5-24** after 20 s (●) and 200 s (◇) irradiation.

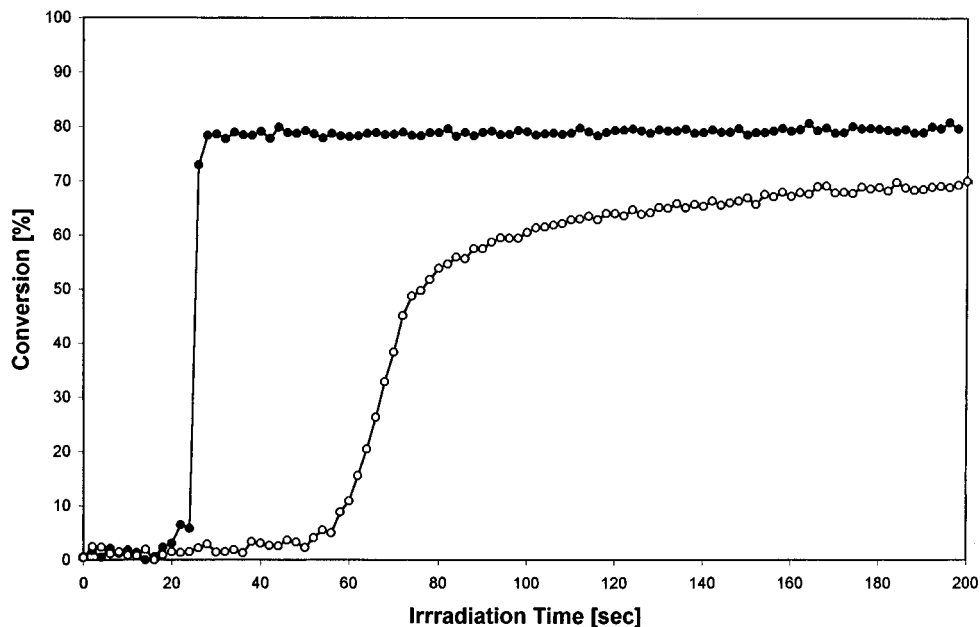


Figure 4. RTIR study of the photopolymerization of oligomer **I-1.0-12** (●) and oligomer **I-1.5-9** (○) in the presence of 2 wt % IOC10.

reaction by GPC analysis showed that the rate of the sol-gel process increased and resulted in a greater proportion of oligomers with higher molecular weights than in the previous reaction with 0.5 equiv of water (Figure 1). Reaction at 60 °C for 12 h leads to complete consumption of starting material. A broad distribution of oligomeric products is obtained in both cases with octamers as the major component of the mixture.

The RTIR curve for the photopolymerization of the oligomer obtained by condensing 1.0 equivalent of water with **I** for 12 h (**I-1.0-12**) is given in Figure 4. Again, the polymerization is preceded by a 20 s. induction period followed by the very rapid formation of a colorless cross-linked network with a maximum epoxide conversion of 81%. Using the same concentration of IOC10 (2 wt %), the photopolymerization of the oligomer obtained from the reaction of **I** with 1.5 equiv of water after 9 h (**I-1.5-9**) also rapidly polymerized under UV irradiation

(Figure 4), however, the induction time was much longer (50 s) and the conversion after 200 s continuous irradiation was lower (75%). The high viscosity of this oligomer may be responsible for both the slower rate and the lower conversion.

Sol-Gel Condensation of (3-Glycidoxypropyl)-trimethoxysilane (II). The sol-gel condensation of **II** with water catalyzed by Amberlite IRA-904 was slow compared to that of **I**. For example, the condensation of **II** with 1.5 equiv of water was conducted at 60 °C to achieve an appreciable rate. At that temperature, GPC analysis showed that the starting monomer **II** was completely consumed after 72 h. At this point, the product was a highly viscous fluid. The ¹H NMR spectrum of the product after 24 h (**II-1.5-24**) shows the presence of a band at 3.1 ppm assigned to the protons of the epoxy group and only a very small remaining methoxy band at 3.45 ppm. Irradiation of films of

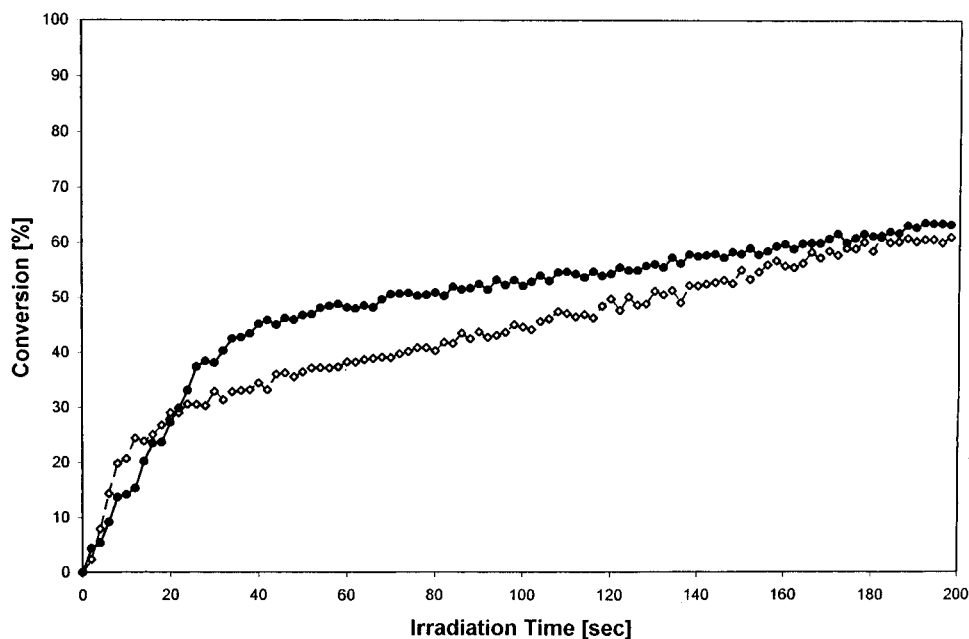


Figure 5. RTIR study of the photopolymerization of oligomer **II-1.5-24** (●) and **II** (◇) in the presence of 2 wt % IOC10.

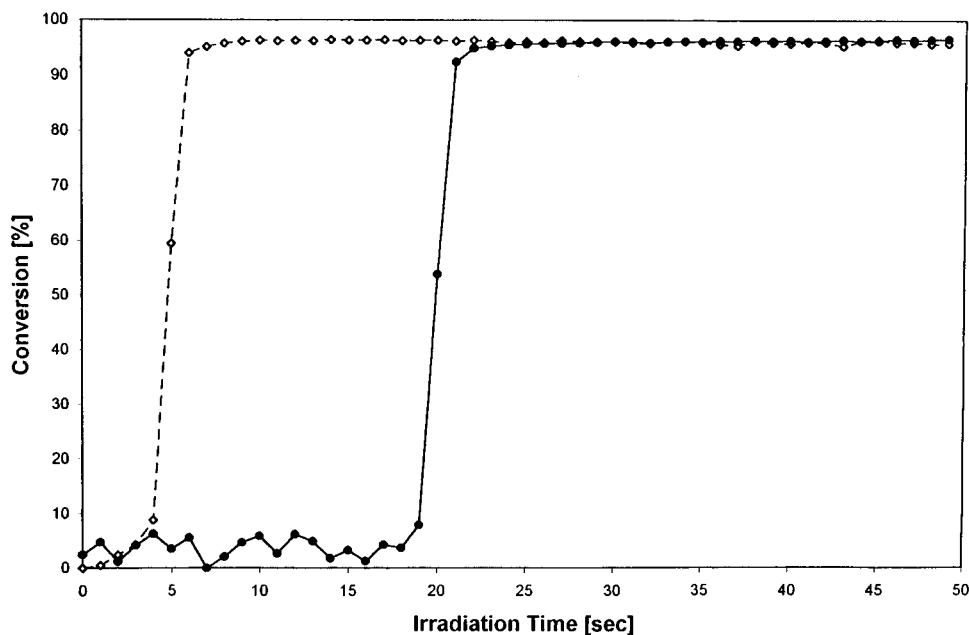
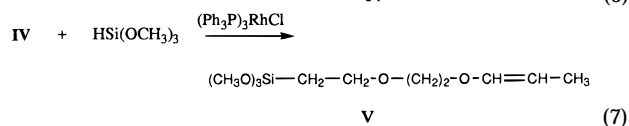
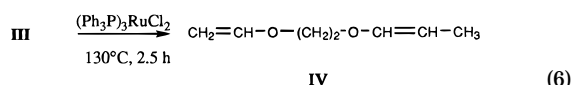
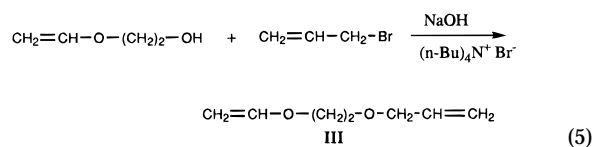


Figure 6. RTIR study of the photopolymerization of oligomer **V-1.0-1** (●) and **V** (◇) in the presence of 2 wt % IOC10.

oligomer **II-1.5-24** with 2 wt % **IOC10** undergo smooth polymerization to yield colorless cross-linked insoluble resins. Typically, the photopolymerized resins derived from **II** were softer than those from monomer **I**. Shown in Figure 5 are the RTIR curves for the photoinduced polymerization of oligomer **II-1.5-24** and for epoxy functional trialkoxysilane precursor **II** both in the presence of 2 wt % **IOC10**. Oligomer **II-1.5-24** appears to have a slightly higher reactivity, although both reach similar ultimate conversions.

Preparation and Sol-Gel Condensation of 1-(1-propenoxy)-2-(2-trimethoxysilylethoxy)ethane (V). It was of interest to determine whether the ion-exchange-catalyzed sol-gel chemistry described above could be extended to trialkoxysilanes bearing other cationically polymerizable functional groups. Vinyl and enol ethers are among the most reactive monomers known in cationic polymerization and are more reactive than

epoxides. Accordingly, the synthesis of a trimethoxysilane carrying a pendant 1-propenyl ether was carried out using the synthetic scheme shown in eqs 5–7.



Ethylene glycol monovinyl ether was condensed with allyl bromide under basic conditions in the presence of a phase-transfer catalyst as shown in eq 5. Subsequently (eq 6), the resulting allyl ether was isomerized in the presence of tris(triphenylphosphine)ruthenium(II) dichloride to give the desired 1-allyloxy-2-(vinylloxy)ethane. Chemoselective hydrosilylation (eq 7) of this latter compound with trimethoxysilane in the presence of a catalytic amount of tris(triphenylphosphine)rhodium(I) chloride afforded 1-(1-propenoxy)-2-(2-trimethoxysilyloxy)ethane (**V**) in good yield.

The Amberlite IRA-904 catalyzed sol-gel condensation of **V** in the presence of 1 mol equiv of water takes place very rapidly and is essentially complete after 1 h of reaction at 60 °C. At this point, the reaction mixture consisted mainly of oligomers up to octamers with a small amount of residual monomer. Extension of the reaction for 6 h produced no further observable change by GPC. Integration of the ¹H NMR spectrum of the reaction product after 1 h reaction (**V-1.0-1**) showed that the conversion of the methoxy groups had reached 58% (theoretical conversion 66.7%). Figure 6 shows the response of oligomer **V-1.0-1** to UV-induced photopolymerization in the presence of 1 wt % of **IOC10**. Also given in this figure is the RTIR curve for the polymerization of 1-propenyl ether functional trialkoxysilane precursor **V**. In these studies, the course of the photoinduced cationic polymerization was followed by monitoring the double-bond absorption band of 1-propenyl group at 1660–1670 cm⁻¹. Again, one can see that while **V** displays only a 3–4 s induction period, the induction period for **V-1.0-1** is approximately the same (~20 s) as that observed for the oligomers derived from **I** and **II**. These results lend further credence to the proposal that the origin of the inhibition is due to trace amounts of basic impurities carried into the reaction mixture by the ion-exchange resin. The rates of polymerization for both of these materials as given by the

slopes are very high. Both photopolymerizations also proceed to very high conversions (~97%). Thin photopolymerized films of **V-1-1** were hard, transparent, and insoluble in all common solvents.

Conclusions

A new practical and attractive sol-gel technique has been employed to transform a variety of trialkoxysilane coupling agents to multifunctional oligomers bearing epoxy and 1-propenyl ether functional groups. Key to the success of these reactions is the use of weakly acidic cross-linked ion-exchange resins as catalysts for the sol-gel condensations. The oligomers which are formed range from low- to high-viscosity fluids. The oligomers are shelf stable once the ion-exchange resin catalysts are removed. Further, onium salt cationic photoinitiators are readily soluble in these oligomers and photopolymerizations take place readily under UV irradiation to give colorless cross-linked network polymers. Real-time infrared spectroscopic studies showed that the photoinitiated cationic polymerization of these oligomers is extremely rapid and those oligomers bearing either epoxy-cyclohexyl or 1-propenyl ether groups are especially reactive. Very high conversions of the functional groups of these latter oligomers is obtained during photopolymerization. Using the above-described novel sol-gel approach, the preparation of a wide variety of photopolymerizable oligomers with unique and interesting properties can be potentially achieved. Some of the applications of this chemistry are now under investigation.

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