

Photopolymerization of a Novel Tetraoxaspiroundecane and Silicon-Containing Oxiranes

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ABSTRACT: New multifunctional silorane-based systems were investigated, with respect to their photoreactivity, as potential matrix resins for low-shrinkage/stress dental composites. The objective of this investigation was to synthesize and evaluate the reactivity of a silicon-analogue oxaspirocyclic monomer with silorane-based matrix resin systems during visible-light polymerization. The experimental formulations contained (1) a silicon-containing 1,5,7,11-tetraoxaspiro[5.5]undecane (TOSU-IV), (2) a phenylmethylsilane containing two cyclohexyloxiranyl groups, (3) a cyclotetra-siloxane containing four cyclohexyloxiranyl groups, and (4) a photocationic initiator system. Three main aspects were studied: (1) the photoreactivity of the tetraoxaspiroundecane (TOSU)/silorane reactant mixtures with differential scanning photocalorimetry, (2) oxirane ring-opening reactions of siloranes during binary photopolymerization with

Fourier transform infrared (FTIR), and (3) oxaspirocyclic ring-opening reactions of the TOSU reactant during homophotopolymerization and binary photopolymerization with FTIR and NMR. A diallyl ether precursor of TOSU-IV was also included in selected studies. The main findings were as follows: (1) a feasible route for the successful synthesis of a silicon analogue (TOSU-IV) was developed; (2) TOSU-IV was compatible and photoreactive, making possible the reduction of polymerization stress in silorane-based matrix resins; and (3) spectroscopic evidence for both oxirane and oxaspirocyclic ring opening during the visible-light photopolymerization of the test formulations was found. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 336–344, 2007

Key words: cationic polymerization; dental polymers; photopolymerization; ring-opening polymerization; stress

INTRODUCTION

Polymeric dental restorative chemistry has been dominated by free-radical methacrylate-based systems for over 50 years. Bowen,¹ who introduced bis(glycidyl methacrylate) systems, had previously researched epoxides (oxiranes) as possible matrix resin candidates. Concerns about water stability, biocompatibility, and initiator systems prevented their further development as restoratives until the 1990s. Oxiranes have seen use in clinical dentistry as root-canal sealants.²

A variety of organosilicon compounds with oxirane functionality were first synthesized and polymerized by Sato et al.³ Similar compounds were studied in the early 1990s.^{4–8} 3M-ESPE adapted and innovated this technology for applications in dentistry.⁹ This is a major step forward in restorative dentistry, as the new silorane composites exhibit greater hydrophobicity

and significantly reduced polymerization stress and shrinkage, with average mechanical properties and good biocompatibility.^{10–12}

Siloranes contain oxiranes and, therefore, can be polymerized via cationic initiation. Metal halide salts of complex arylonium cations,^{5,13–15} which efficiently generate protons upon irradiation, initiate the polymerization. For these initiators to function in a dental system with visible light, they must also contain a photosensitizer, typically a molecule such as camphorquinone (CQ). Also, the addition of ethyl 4-dimethylaminobenzoate (ED) and similar compounds to the photoinitiator system greatly enhance the photoreactivity of oxirane resin systems.¹⁶

The literature on oxaspirocyclic monomers with potential for expansion in polymerization has been extensively reviewed.^{17,18} These monomers polymerize cationically and are generally compatible with oxirane-based systems. Cationically initiated reactions at the TOSU center commence with an essentially irreversible protonation of one of the spiro oxygens to form a carbocation that becomes the polymerizing species. We have carried out extensive theoretical calculations on both the homopolymerization and copolymerization of spiroorthocarbonates.^{19–21}

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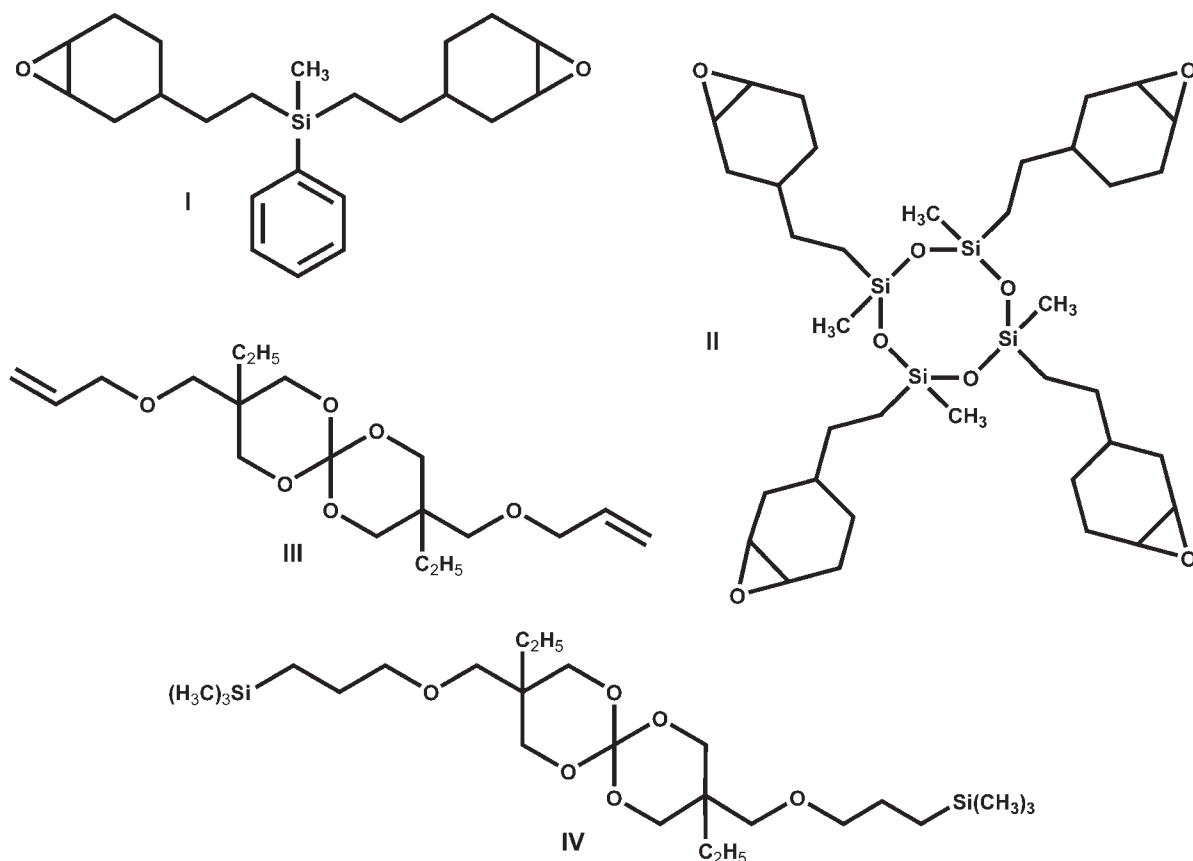


Figure 1 Structures of the siloranes (I and II) and developmental monomers (III and IV).

The development of low-stress/low-shrink dental resins has been a major focus of our research for more than a decade.^{22–27} We have recently synthesized and evaluated several new oxaspirocyclic monomers containing silicon to further reduce polymerization shrinkage and stress in silorane systems. One of our initial hybrid monomers²⁸ has been found to significantly reduce polymerization stress²⁹ when incorporated into a silorane-based matrix system. This article focuses on the synthesis and characterization of the hybrid silicon-containing monomer and its reactivity during photoinitiated cationic polymerization with and without siloranes.

EXPERIMENTAL

Materials

Monomer structures are shown in Figure 1. Silicon-containing oxiranes, methylbis[2-(7-oxabicyclo[4.1.0]hept-3-yl)ethyl]phenylsilane (I or Ph-Sil) and 2,4,6,8-tetramethyl-2,4,6,8-tetrakis[2-(7-oxabicyclo[4.1.0]hept-3-yl)ethyl]-1,3,5,7-tetraoxa-2,4,6,8-tetrasilacyclooctane (II or Tet-Sil), and a 1 : 1 (w/w) blend of I and II (Sil-Mix) were obtained from 3M ESPE (St. Paul, MN). 3,9-Diethyl-3,9-bis(allyloxymethyl)-1,5,7,11-tetraoxaspiro[5.5]undecane (III) and 3,9-diethyl-3,9-bis(trimethylsilyloxypropyl)-1,5,7,11-tetraoxaspiro[5.5]undecane (IV) were synthesized at the Midwest Research Institute according to the method described in the Methods section. The photoinitiator system components (Fig. 2) were phenyl[*p*-(2-hydroxytetradecyloxy)phenyl]iodonium hexafluoroantimonate (PI; OMAN072, Gelest, Tullytown, PA), CQ (Aldrich, Milwaukee, WI), and ED (Fisher/Acros, Hanover Park, IL). As for the

piro[5.5]undecane (III) and 3,9-diethyl-3,9-bis(trimethylsilyloxypropyl)-1,5,7,11-tetraoxaspiro[5.5]undecane (IV) were synthesized at the Midwest Research Institute according to the method described in the Methods section. The photoinitiator system components (Fig. 2) were phenyl[*p*-(2-hydroxytetradecyloxy)phenyl]iodonium hexafluoroantimonate (PI; OMAN072, Gelest, Tullytown, PA), CQ (Aldrich, Milwaukee, WI), and ED (Fisher/Acros, Hanover Park, IL). As for the

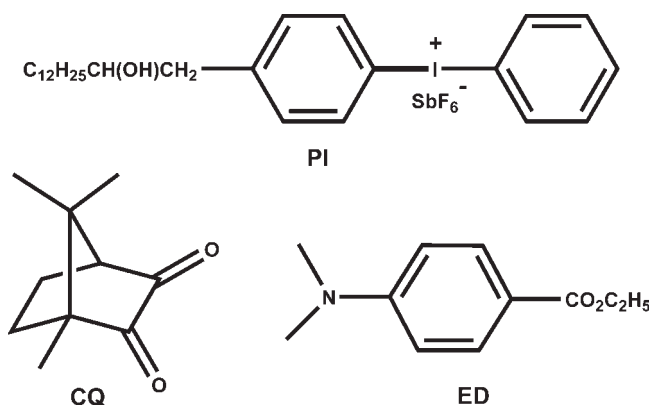


Figure 2 Structures and acronyms for the photoinitiator system components.

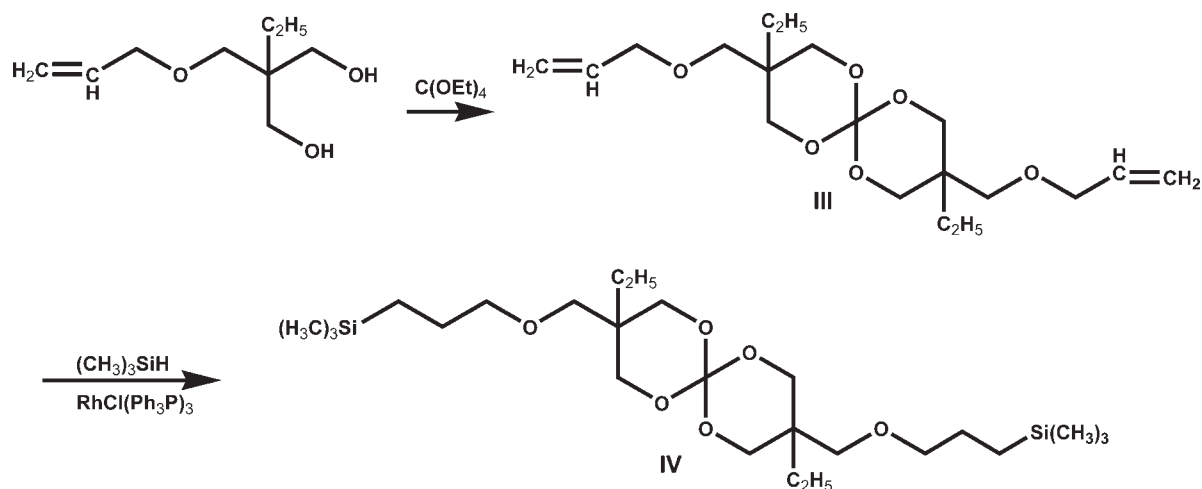


Figure 3 Synthesis scheme for tetraoxaspiro[5.5]undecanes **III** and **IV**.

synthesis reagents, trimethylolpropane allyl ether was obtained from Aldrich, and anhydrous *p*-toluene sulfonic acid (PTSA) was prepared by the drying of the monohydrate (Aldrich) at 100°C *in vacuo* for 6 h.³⁰ Tetraethylortho-carbonate (TEOC) was synthesized at the Midwest Research Institute according to a reported procedure.³¹ Wilkinson's catalyst, tris(triphenylphosphine)rhodium chloride, was obtained from Strem (Newburyport, MA); trimethylsilane was acquired from Gelest, and the solvents and silica gel were acquired from Fisher.

Methods

Synthesis and characterization of the oxaspirocyclic monomers (**III** and **IV**)

The two-step synthetic sequence is shown in Figure 3. The general transesterification method (step 1) was similar to that used by Endo et al.³⁰ The hydrosilylation procedure (step 2) was similar to that reported by Crivello and Bi.³²

Step 1. **III** was prepared as follows. To a three-necked, 1-L, round-bottom flask equipped with a magnetic stirring bar, a Dean-Stark trap with a reflux condenser, and a thermometer, a mixture of toluene (500 mL) and the starting trimethylolpropane allyl ether (98%, 8.89 g, 50 mmol) was added. The solution was brought to reflux for 2 h to remove water azeotropically. The mixture was allowed to cool below 70°C, and then anhydrous PTSA (0.09 g) was added. The mixture was allowed to further cool to room temperature, and then TEOC (5.39 mL, 25 mmol) was added slowly. The resulting mixture was then brought to reflux to azeotropically remove the byproduct ethanol generated during the reaction. The reaction mixture was allowed to reflux for an additional hour and then allowed to cool to room temperature. Triethylamine (2 mL) was added, and

the resulting mixture was stirred at room temperature for 1.5 h and concentrated under reduced pressure; this resulted in a light yellow liquid (14.84 g). The crude product was purified by flash chromatography (silica gel, 10–20% ether/hexanes), and 8.92 g (> 99% yield) of **III** was obtained as a colorless liquid.

Purity: ~ 96% by gas chromatography (GC). ¹H-NMR (CDCl₃, 400 MHz, δ): 5.93–5.81 (m, 2H), 5.29–5.21 (dd, 2H, *J* = 12.9, 1.2 Hz), 5.17–5.12 (dd, 2H, *J* = 7.8, 0.9 Hz), 3.99–3.95 (d, 4H, *J* = 3.9 Hz), 3.85–3.66 (m, 12H), 3.47 (s, 4H), 1.42–1.35 (q, 4H, *J* = 5.7 Hz), 0.85–0.79 (t, 6H, *J* = 5.7 Hz). ¹³C-NMR (CDCl₃, 400 MHz, δ): 134.74, 116.36, 114.75, 72.13, 69.25, 67.39, 66.97, 36.16, 23.42, 7.11. FTIR (cm⁻¹): 3081, 2966, 2882, 1646, 1456, 1364, 1261, 1228, 1189, 1112, 1071, 1014, 927.

Step 2. **IV** was prepared as follows. To a flame-dried, three-necked, 250-mL, round-bottom flask equipped with a magnetic stirring bar, a thermometer, a reflux condenser fitted with a dry-ice/acetone cold finger, and an addition port, the diallyl ether intermediate (8.91 g, 25 mmol), toluene (80 mL), and Wilkinson's catalyst [tris(triphenylphosphine)rhodium chloride; 2.5 mg] were added. Into the mixture at room temperature, trimethylsilane gas (4.95 g, 66.7 mmol) was bubbled very slowly via the addition port with stirring over a period of 3 h. The resultant mixture was slowly heated to 80°C and held at this temperature for 3.5 h. The reaction was monitored by thin-layer chromatography (silica gel, 50% ether/hexanes). The mixture was then allowed to stir at room temperature overnight, filtered, and concentrated under reduced pressure to give a turbid, yellowish liquid (13.85 g). The crude material was purified by column chromatography (silica gel, 5–10% ethyl ether/hexanes). The desired hydrosilylation product **IV** was obtained in a 73.6% yield (9.29 g) as a colorless liquid that solidified upon sitting overnight.

Purity: $\sim 96\%$ by GC. mp (differential scanning calorimetry): 44.27°C . $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, δ): 3.78–3.59 (m, 8H), 3.38 (s, 4H), 3.34–3.28 (t, 4H, $J = 5.1$ Hz), 1.52–1.43 (m, 4H), 1.36–1.28 (q, 4H, $J = 5.7$ Hz), 0.8–0.72 (t, 6H, $J = 5.7$ Hz), 0.43–0.37 (m, 4H), -0.08 (s, 18H). $^{13}\text{C-NMR}$ (CDCl_3 , 400 MHz, δ): 114.78, 74.30, 69.66, 67.45, 67.03, 36.19, 23.84, 23.49, 12.41, 7.16, -1.86 . FTIR (cm^{-1}): 2955, 2875, 1461, 1366, 1250, 1225, 1188, 1114, 1070, 1010, 860, 754, 693. ANAL. Calcd for $\text{C}_{25}\text{H}_{52}\text{O}_6\text{Si}_2$: C, 59.48%; H, 10.38%. Found: C, 60.07%; H, 10.89%.

Preparation of the experimental matrix resin formulations

Reaction mixtures (~ 2 g) were formulated with a 4.1 wt % photoinitiator system (3 wt % PI, 1 wt % CQ, and 0.1 wt % ED), except where noted. Formulated mixtures were heated for 5 min in an oil bath at 60°C and stirred magnetically to dissolve the photoinitiator system and **IV** when included. Formulations were prepared and stored away from ambient light and tested on the day on which they were prepared.

Evaluation of the photoreactivity via differential scanning photocalorimetry (photo-DSC)

Photoreactivity assessments were made with an EXFO Novacure light-curing unit (Mississauga, Ontario, Canada) interfaced with a PerkinElmer Diamond differential scanning calorimeter (Shelton, CT). The experimental conditions were as follows: 25°C , N_2 atmosphere, 400–500-nm light, 3-mm quartz light guides, and 500 mW/cm output measured 15 mm from the sample surface. The sample weights were 15–18 mg. Standard Al pans were used. An empty pan was placed in the reference position. The irradiation time was 10 min after a 1-min equilibration. After the initial run, the sample was reirradiated for an additional 10 min. This second curve was subtracted from the initial exotherm curve to zero out artifacts due to the beginning and ending of irradiation and to compensate for the heat capacity differences between the sample pan and empty reference pan. Integrations were from time $t = 1.1$ min (lamp shutter opened) to $t = 11.1$ min (lamp shutter closed). The enthalpies of mixtures containing **III** or **IV** were measured and compared with those calculated for comparable formulations containing an inert diluent in the silorane at the same addition levels. The effect of doubling the photoinitiator content from 3 to 6 wt % was also determined for selected mixtures.

Analysis of oxirane ring opening via FTIR spectroscopy

All FTIR spectra were acquired with a PerkinElmer BX II FTIR spectrophotometer. The identification of

the location of the oxirane absorption band in the IR spectrum of siloranes was achieved by methanolysis. A sample was dissolved in CH_2Cl_2 and exposed to CH_3OH in the presence of a catalytic amount of zinc tetrafluoroborate hydrate overnight. The mixture was evaporated onto a salt plate. An FTIR spectrum was acquired and compared to a pre-exposure spectrum. There was a significant decrease in the oxirane absorption region at $882\text{--}886\text{ cm}^{-1}$. This band was selected as the absorption to monitor for following the oxirane ring-opening reaction.

The analytical samples contained siloranes **I**, **II**, or Sil-Mix with or without 50 mol % **III** or **IV**. A thin film was brushed onto a salt plate. Irradiation (10 min at $23\text{--}25^\circ\text{C}$ and 40–45% relative humidity) was provided by a 3M XL2500 curing light positioned 1 cm above the sample surface. The light intensity was measured at 360 mW/cm^2 on the sample surface. The oxirane band absorption (A_{oxirane}) and an internal reference band absorption (A_{ref}) were assessed before and after irradiation. The oxirane conversion (α) was calculated according to eq. (1):³³

$$\alpha = \left\{ \left[\frac{(A_{\text{oxirane}}/A_{\text{ref}})_0}{(A_{\text{oxirane}}/A_{\text{ref}})_t} \right] / \frac{(A_{\text{oxirane}}/A_{\text{ref}})_0}{(A_{\text{oxirane}}/A_{\text{ref}})_0} \right\} \times 100\% \quad (1)$$

where subscripts 0 and t represent preirradiation and postirradiation, respectively.

Assessment of oxaspirocyclic ring opening via NMR and FTIR

NMR studies. NMR spectra were acquired with a Bruker Advance Ultrashield FT-NMR spectrometer (Billerica, MA). A reaction mixture consisting of **IV** and the photoinitiator system was heated to $55\text{--}60^\circ\text{C}$ to liquefy and then allowed to cool to room temperature. A 300-mg sample was transferred to an 8 mm i.d. \times 8 mm H, cylindrical, glass mold and irradiated for 20 min (3 mm ; 500 mW/cm^2) with a 3M XL 2500 lamp. A small amount was transferred to an NMR tube and taken up in CDCl_3 , and the $^{13}\text{C-NMR}$ spectrum was acquired and compared with the preirradiation spectrum. The residual irradiated material was stored in the dark for 24 h and resampled, and the NMR spectrum was acquired and compared with the pre- and postirradiation spectra.

FTIR studies. The FTIR spectra of the bulk-polymerized samples of **IV** analyzed in the $^{13}\text{C-NMR}$ studies were acquired and compared with the preirradiation spectra.

RESULTS AND DISCUSSION

Photoreactivity of the oxaspirocyclic and silorane reactions

All exothermal profiles for the photopolymerization of selected monomer compositions exhibited a rapid

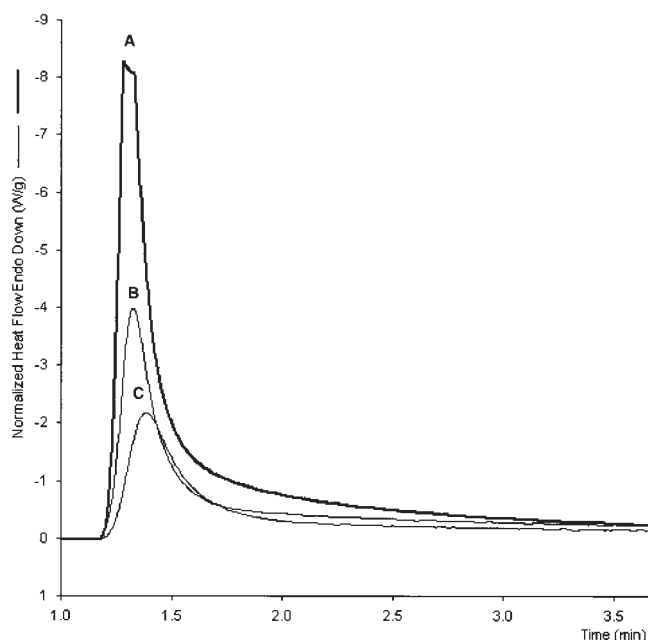


Figure 4 Photoreactivity exotherm profiles for Sil-Mix with (A) 0, (B) 10, and (C) 25 mol % tetraoxaspiro[5.5]undecane IV.

rise in the heat that evolved up to a maximum and then a slower rate of decline (Fig. 4). This behavior is characteristic of some network-forming cationic polymer systems and is associated with the gel effect, which arises from an increase in the rate of diffusion-controlled termination reactions, resulting from a steady increase in the viscosity, which reduces the mobility of growing polymer chains.³⁴ Initially, there is a rapid increase in the concentration of growing oligomer chains, and propagation is favored over termination. The later decrease in the reaction rate may also be caused by the depletion of

monomers in the system and the fact that the propagation reaction becomes diffusion-controlled because of the reduction of the monomer mobility as solidification is approached. Net photopolymerization enthalpies for selected silorane and silorane/tetraoxaspiroundecane (TOSU) mixtures were studied under controlled reaction conditions.

The results of the experimental and calculated net enthalpy (ΔH) values for selected silorane/TOSU reactant ratios and photoinitiator dosage levels are given in Table I. An inspection and comparison of the ΔH values reveals the following information about the relative photoreactivity of the systems studied: (1) all test formulations containing a TOSU had ΔH values less than that calculated for a pure dilution effect and (2) doubling the photoinitiator content (from 3 to 6 wt %) had only a minimal effect (a 5–7% increase in ΔH). Our modeling and computational studies of 1,5,7,11-tetraoxaspiroundecanes indicate that ring protonation and ring opening proceed via both exothermic and endothermic processes. The reduced enthalpies of mixtures containing TOSUs may be a direct effect of TOSU ring-opening polymerization that is necessary for possible volume expansion and stress reduction to take place. Net photopolymerization exotherms for Sil-Mix and Sil-Mix/TOSU-IV formulations at 90/10 and 25/75 (mol/mol) reactant ratios and a 3% photoacid dosage level are shown in Figure 4. The results indicate that Sil-Mix is the most reactive component in this series of formulations and that the incorporation of TOSU-IV into Sil-Mix gave experimental ΔH values that were markedly less than the calculated ΔH values: for the 10% TOSU mix, the experimental ΔH value was 71% of the calculated ΔH value, and for the 25% TOSU mix, ΔH was 59% of the calculated ΔH value. The incorporation of 20% TOSU-III into Sil-Mix yielded an experimental ΔH value that was

TABLE I
Photo-DSC Enthalpies of Polymerization for Siloranes With and Without Tetraoxaspiroundecanes

Test mixture	3 wt % PI		6 wt % PI	
	ΔH_{exp} (J/g) ^a	ΔH_{calc} (J/g) ^b	ΔH_{exp} (J/g) ^a	ΔH_{calc} (J/g) ^b
100% Sil-Mix	-193	—	185	—
10% IV	-124	-174	-127	-166
25% IV	-86	-145	-87	-139
20% III	-124	-154	NT	NT
100% Ph-Sil I	-208	—	NT	NT
50% III	-78	-104	NT	NT

NT, not tested.

^a Experimental enthalpy measured by the integration of the area under the baseline-corrected, normalized photopolymerization exotherm profile curve from time $t = 1.1$ min to $t = 11.1$ min.

^b Calculated enthalpy for the addition of an inert diluent instead of III at 20 or 50 mol % or IV at 10 or 25 mol %. It assumes that the entire heat of reaction comes from the oxirane functionality and is based on measured experimental values for 100% silorane.

TABLE II
Oxirane Conversions of Siloranes With and Without Tetraoxaspirodecanes

Silorane	Tetraoxaspirodecane comonomer	Oxirane conversion (%) ^a	Reference band (cm ⁻¹)
Ph-Sil (I)	—	31	1428
Ph-Sil (I)	III (50 mol %)	36	1455
Ph-Sil (I)	IV (50 mol %)	22	1428
Tet-Sil (II)	—	13	1258
Tet-Sil (II)	III (50 mol %)	27	1455
Tet-Sil (II)	IV (50 mol %)	3	1228
Sil-Mix	—	28	1428
Sil-Mix	IV (50 mol %)	22	1455

^a Based on the peak height of the 884–886-cm⁻¹ absorption band in comparison with the indicated reference band before and after visible-light photopolymerization.

81% of the calculated ΔH value. However, the incorporation of TOSU–III at 50% into Ph-Sil gave an experimental value that was 75% of the calculated value. The coefficient of variation for replicate ($n = 3$) enthalpy determinations (same mix; same day) in our laboratories was 1.8%.

Oxirane ring-opening reactions of the silorane reactants

Oxirane conversion results for siloranes with and without 50 mol % III or IV irradiated as thin films on salt plates are shown in Table II. Aromatic silane I has dioxirane functionality and is less viscous than cyclo-siloxane II, which has tetraoxirane functionality. On a weight basis, approximately the same number of oxirane groups are available, as the molecular

weight of I (370.60) is roughly half that of II (737.23). Viscosity differences may explain why the oxirane conversion for I (31%) is over twice that of II (13%).

The addition of experimental monomer IV (low-melting solid) or liquid unsaturated intermediate III to the siloranes resulted in some analytical challenges. The fine structure in the 1400–800-cm⁻¹ region of the spectra of III and IV occluded some primary reference bands in the silorane spectra and partially occluded the primary oxirane absorption (882–884 cm⁻¹). Spectral regions of interest for the Sil-Mix/IV reaction mixture before and after photopolymerization are shown in Figure 5. The hydroxyl region peak at 3445 cm⁻¹ could have resulted from the opening of either the oxaspirocyclic rings of IV or the oxirane rings of the siloranes. The carbonyl region peak at

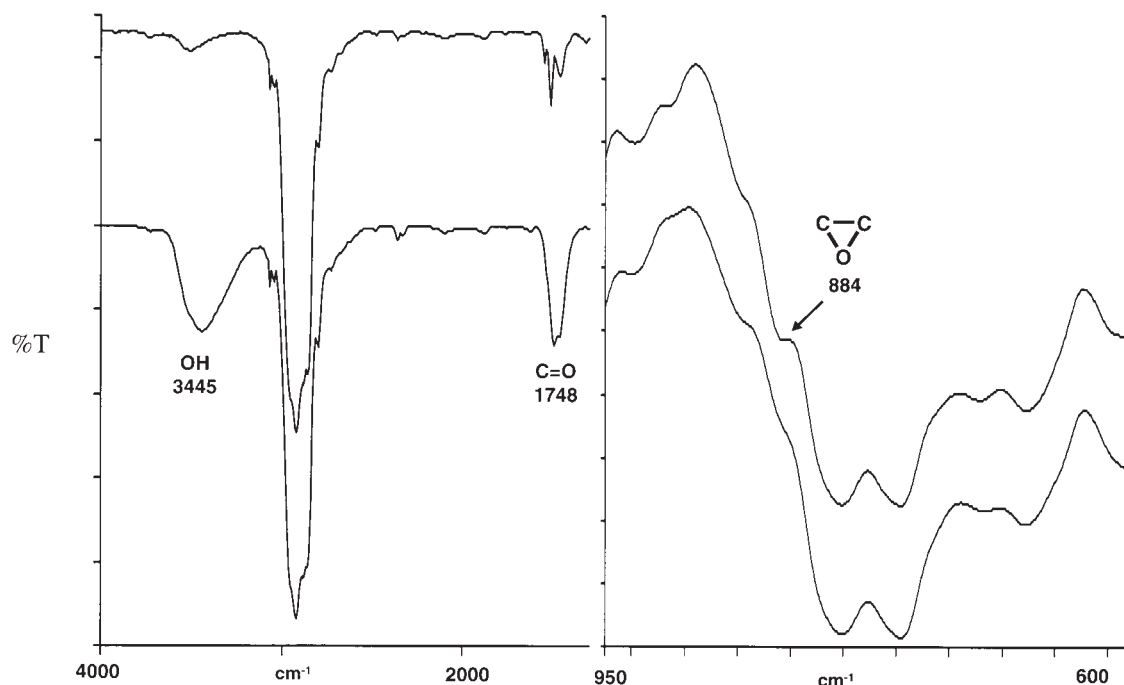


Figure 5 Selected FTIR spectroscopy regions of an equimolar Sil-Mix/IV mixture before and after visible-light irradiation for 10 min as a thin film on a salt plate (T = transmittance).

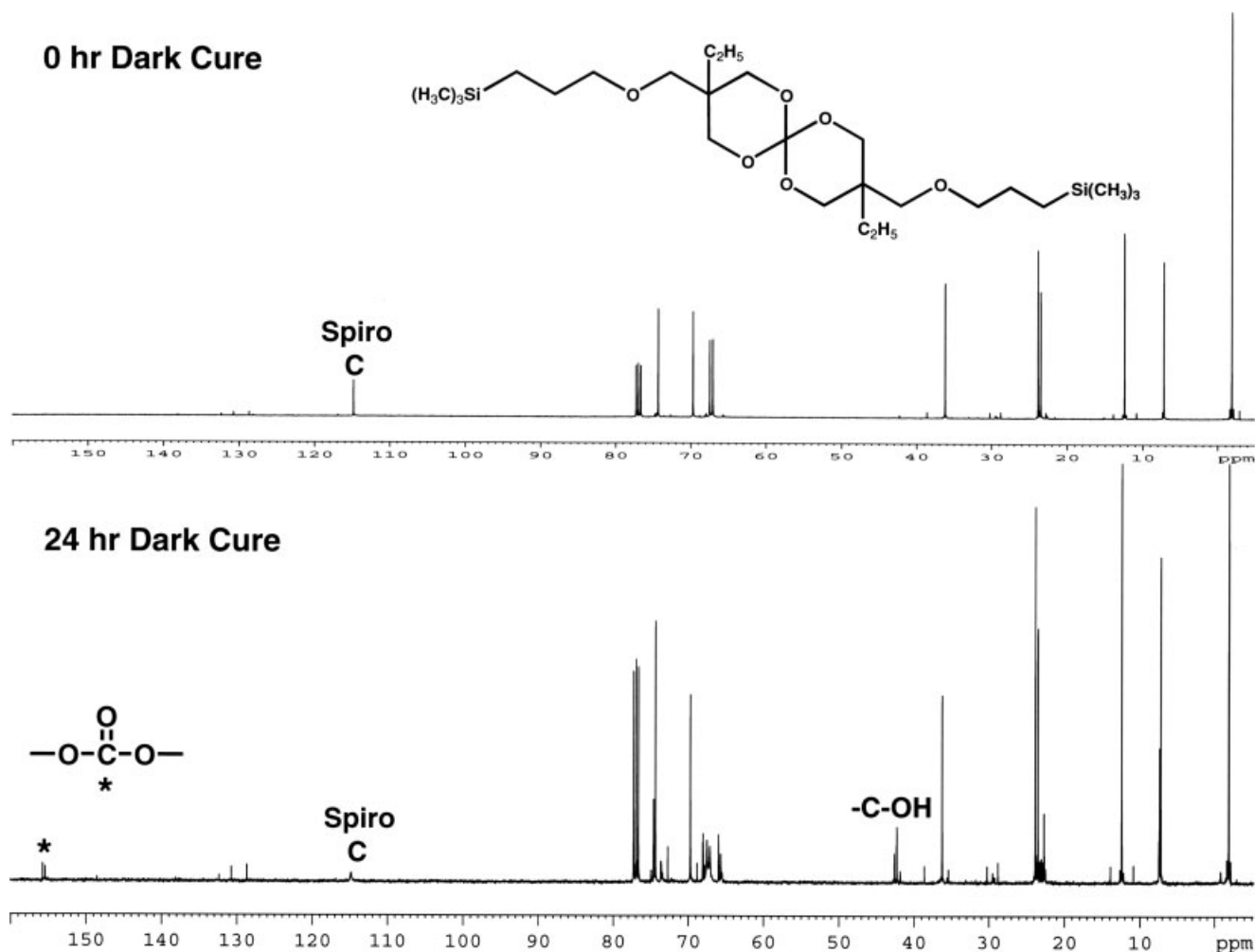


Figure 6 ^{13}C -NMR spectra of tetraoxaspiro[5.5]undecane IV after 20 min of visible-light irradiation with a 0-h dark cure (top) and a 24-h dark cure (bottom).

1748 is typically associated with the opening of the oxaspirocyclic rings in tetraoxaspiroundecanes to produce linear carbonate species. There was no evidence of reactivity at the double-bond absorption peak (1647 cm^{-1}) in the unsaturated intermediate III mixtures containing it and the siloranes. The band is small and difficult to quantitate. Oxygen inhibition of free-radical polymerization at the unsaturated sites may have been a factor as the measurements were made in a laboratory atmosphere. The increased oxirane conversion noted in the mixtures containing III may be due to a decrease in the viscosity and a corresponding increase in the molecular mobility.

Oxaspirocyclic ring-opening reactions of silicon analogue TOSU IV

The ^{13}C -NMR spectra of IV immediately following irradiation (0-h dark cure) and after a 24-h dark cure are shown in Figure 6. No significant changes were

noted in the NMR spectrum of IV after the irradiation (0-h dark cure). The spiral carbon peak (114.8 ppm) was still intact, and there were no new peaks that would have indicated oxaspirocyclic ring opening (top spectrum). There were significant changes in the spectrum of the residual bulk-polymerized sample that was stored in the dark for 24 h and reanalyzed (bottom spectrum, Fig. 6). The spiral carbon peak (114.8 ppm) was greatly diminished and considerably broadened. The two new peaks at $\sim 155\text{ ppm}$ were thought to be due to linear carbonate $\text{C}=\text{O}$ species and hydroxyl $-\text{C}-\text{OH}$ peaks (41.8–42.6 ppm). Also, several differences in the 65–69 ppm region were noted. All the changes were consistent with oxaspirocyclic ring opening to form oligomeric carbonate species.

The FTIR spectrum of IV after irradiation and NMR analysis (bottom; 0-h dark cure) is compared with its preirradiation spectrum (top) in Figure 7. There were new peaks at 3445 (OH) and 1748 cm^{-1}

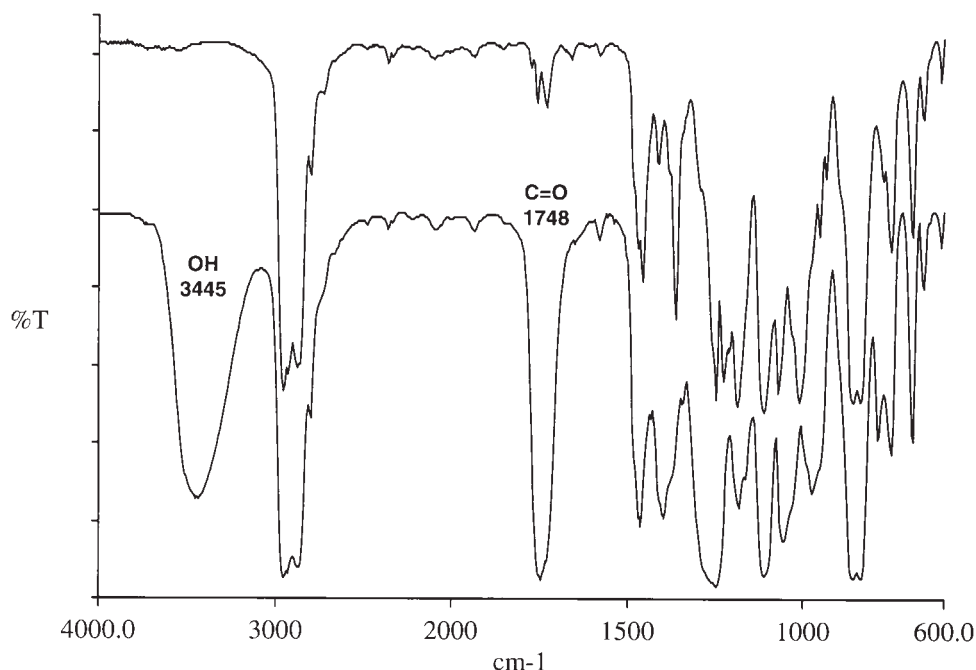


Figure 7 FTIR spectra of tetraoxaspiro[5.5]undecane **IV** after 20 min of visible-light irradiation with a 0-h dark cure (top) and a 24-h dark cure (bottom) after ^{13}C -NMR analysis (T = transmittance).

(C=O) and in the fingerprint region at 1463, 1397, 1058, 975, and 790 cm^{-1} . The spectrum of the 24-h-dark-cure NMR sample did not have any significant changes from the spectrum of the 0-h-dark-cure sample. There were notable changes in the FTIR spectra of **IV** shortly after irradiation, but the changes in the NMR spectrum were much slower to manifest.

Experimental irradiation times

Because the photoreactivity of **IV** alone or in combination with Sil-Mix was not known before this study was undertaken, irradiation times were chosen to allow adequate time for the evidence of reaction to be determined. The experimental irradiation times were much longer than those traditionally used in a clinical setting to cure conventional composite restoratives. The sample mass and morphology as well as the irradiation time and intensity can have a significant effect on the reaction rate and degree of cure.

CONCLUSIONS

Oxaspirocyclic monomers that have the potential to reduce photopolymerization stress and shrinkage can be made more compatible with silorane-based resin systems by the incorporation of silicon into their structures. There is evidence that both oxirane and oxaspirocyclic ring opening occurs during photopolymerization.

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