Silsesquioxanes as Synthetic Platforms. 3. Photocurable, Liquid Epoxides as Inorganic/Organic Hybrid Precursors

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Octameric silsesquioxanes, $(RSiO_{1.5})_8$, are rigid structures that closely resemble specific crystalline forms of silica and zeolites and offer appealing properties currently being exploited by many research groups.[1−14] Through their eight Si vertexes, these cubes may be covalently linked to a plethora of organic functional groups creating libraries of single-phase inorganic/organic hybrids that when polymerized mimic silica-reinforced composites.[12,15,16] To be effective for single-phase composite processing, e.g., for use as dental restoratives,[7,8] the cubes must be soluble or liquid and readily polymerizable. Methacrylates and epoxides are typical functional groups that can be used to meet this latter requirement. Efforts to prepare simple methacrylate derivatives were successful but gave products that were too reactive for practical use (e.g., short shelf-life).[15] More robust epoxide derivatives can be synthesized by epoxidation of (vinyl-$SiO_{1.5})_8$ (T_8^V) and (vinyl-$Me_2SiOSiO_{1.5})_8$ ($Q_8M_8^V$).[16] These epoxides are soluble in common solvents but are crystalline solids and therefore not practical for processing dense, single-phase nanocomposites. Furthermore, they give very brittle materials on polymerization with Lewis acid catalysts or simple diamines.[16] To improve processability and impart the potential for toughening, we targeted the synthesis of liquids with epoxide groups tethered via flexible spacers to the cube. We report here the synthesis and characterization of simple, photochemically curable, *liquid*, epoxy-functionalized cubes.

Plueddemann et al. and Crivello et al. have shown that, under the appropriate conditions, alkenes will hydrosilylate exclusively in the presence of epoxide functionality.[17,18] On the basis of these reports, $(HMe_2SiOSiO_{1.5})_8$ ($Q_8M_8^H$) and $(HSiO_{1.5})_8$ (T_8^H) were reacted with 4 or 8 equiv of allyl glycidyl ether (AGE) using Karstedt's catalyst [Pt(dvs)]. Four sets of products, $Q_8M_4^HM_4^E$, $Q_8M_8^E$, $T_4^HT_4^E$, and $T_1^HT_7^E$, were isolated.[19] As with the methacrylates and vinyl-derived epoxides,[15,16] $T_4^HT_4^E$ and $Q_8M_4^HM_4^E$ likely consist of a series of products (mono → septa substituted) that average four substitutions per cube.

Efforts to fully substitute T_8^H gave only $T_1^HT_7^E$ based on NMR, TGA, and FTIR analyses. Higher temperatures and longer reaction times led only to isomerization of AGE to the unreactive vinyloxy analog.[8] Bassindale et al. have reported complete substitution of T_8^H using a variety of 1-alkenes.[9]

Although several mass spectral analytic approaches were attempted, only $T_4^HT_4^E$ responded. Chemical ionization (NH_3) mass spectra of $T_4^HT_4^E$ show only mono → tetra substituted cubes, although higher MW cubes (penta → septa) must exist based on NMR, TGA, and SEC results (see below).[20]

NMRs (^1H, ^{13}C and ^{29}Si) of both $Q_8M_4^HM_4^E$ and $Q_8M_8^E$ are straightforward (see supporting information), indicating exclusive β-addition without the side reactions common to allyloxy moieties during hydrosilylation.[8]

(1) (a) Agaskar, P. A. *Inorg. Chem.* **1991**, *30*, 2707. (b) Agaskar, P. A. *Colloids Surf.* **1992**, *63*, 131. (c) Agaskar, P. A. *Synth. React. Inorg. Met.-Org. Chem.* **1990**, *20*, 483. (d) Agaskar, P. A. *J. Am. Chem. Soc.* **1989**, *111*, 6858.

(2) (a) Hasegawa, I.; Motojima, S. *J. Organomet. Chem.* **1992**, *441*, 373. (b) Hasegawa, I. *J. Sol-Gel Sci. Technol.* **1994**, *2*, 127.

(3) Voronkov, M. G.; Lavrent'yev, V. I. *Top. Curr. Chem.* **1982**, *102*, 199.

(4) Bartsch, M.; Bornhauser, P.; Calzaferri, G. *J. Phys. Chem.* **1994**, *98*, 2817.

(5) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741.

(6) Kreuzer, F. H.; Maurer, R.; Spes, P. *Makromol. Chem. Macromol. Symp.* **1991**, 50, 215.

(7) Sellinger, A.; Laine, R. M. *Polym. Prepr.* **1994**, *35*, 665.

(8) Laine, R. M.; Sellinger, A.; Chu, V.; Viney, C. *J. Polym. Sci.: Part A, Polym. Chem.* **1994**, *32*, 3069.

(9) (a) Bassindale, A. R.; Gentle, T. R. *J. Mater. Chem.* **1993**, *3*, 1319. (b) Schmidt, H.; Reinert, T.; Endres, K.; Hoebbel, D. *Mater. Res. Soc. Symp. Proc.* **1994**, *346*, 863.

(10) Calzaferri, G.; Herren, D.; Imhof, R. *Helv. Chim. Acta* **1991**, *74*, 1278.

(11) Agaskar, P. A.; Day, V. W.; Klemperer, W. G. *J. Am. Chem. Soc.* **1987**, *109*, 5554.

(12) (a) Lichtenhan, J. D.; Vu, N. Q.; Carter, J. A.; Gilman, J. W.; Feher, F. J. *Macromolecules* **1993**, *26*, 2141. (b) Haddad, T. S.; Lichtenhan, J. D. *Am. Chem. Soc. Polym. Prepr.* **1994**, *35*, 708. (c) Lichtenhan, J. D.; Mantz, R. A.; Jones, P. F.; Carr, M. J. *Am. Chem. Soc., Polym. Prepr.* **1994**, *35*, 523. (d) Haddad, T. S.; Lichtenhan, J. D. *J. Inorg. Organomet. Polym.* **1995**, *3*, 237.

(13) Herren, D.; Burgy, H.; Calzaferri, G. *Helv. Chim. Acta*, **1991**, *74*, 24.

(14) Yuchs, S .E.; Carrado, K. A. *Inorg. Chem.* **1996**, *35*, 261.

(15) Sellinger, A.; Laine, R. M. *Macromolecules* **1996**, *29*, 2327

(16) Laine, R. M.; Zhang, C. *J. Organomet. Chem.*, in press.

(17) Chung, P. H.; Crivello, J. V.; Fan, M. *J. Polym. Sci.: Part A, Polym. Chem.* **1993**, *31*, 1741.

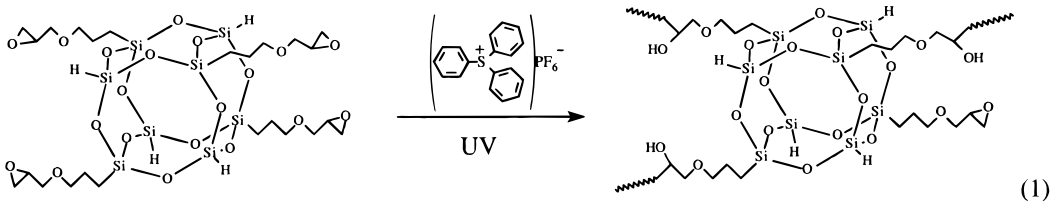
(18) (a) Plueddemann, E. P.; Fanger, G. *J. Am. Chem. Soc.* **1959**, *81*, 2632. (b) Crivello, J. V.; Bi, D. *J. Polym. Sci.: Part A, Polym. Chem.* **1994**, *32*, 683.

(19) Complete experimental, TGA, and SEC figures are available in supporting information. All reactions were performed under N_2 atmosphere using dry solvents. $(HSiO_{1.5})_8$ and $(HMe_2SiOSiO_{1.5})_8$ were synthesized from known procedures (see supporting information).[1,2] Platinum divinyltetramethyldisiloxane [Pt(dvs), Karstedt's catalyst, United Chemical Technologies] was used as 2.0 mmol solutions in xylene. ASHP cationic photoinitiator (Cyracure 313, Union Carbide) was used as a 50% solution in propylene carbonate. The preparation of $Q_8M_4^HM_4^E$ is typical. $(HMe_2SiOSiO_{1.5})_8$ (0.50 g, 0.49 mmol) was added to a magnetically stirred 25 mL Schlenk flask. Toluene (5 mL) was added and the solution stirred for ≈5 min. AGE (0.23 mL, 1.96 mmol) was then added followed by 5 drops of 2.0 mM Pt(dvs). The reaction was stirred for 4 h at 50 °C and cooled, and dry activated charcoal added. After stirring for 5 min, the mixture was filtered through a 0.45 μm Teflon membrane into a vial and stored as ≈10 wt % clear solution. Removal of solvents affords an opaque viscous liquid, yield 0.68 g (94%). ^1H NMR (360 MHz, $CDCl_3$, 25 °C) δ Si*H* 4.72 (septet, J = 2.77 Hz, 4H), (epoxy) CH_2O$(CH_2)_3$ diastereotopic 3.72, 3.66 (dd, J = 3.17 Hz, 4.3H) (due to peak overlap, all resonances between 3.5 and 3.3 are integrated as one peak, 13.6H) 3.45, 3.41 (dd, J = 2.74 Hz), $SiCH_2CH_2CH_2O$ 3.43 (m), OCH_2CH (epoxy) 3.14 (m, 3.7H), CH_2 (epoxy) diastereotopic 2.79 (dd, J = 4.97 Hz, 3.9H), 2.59 (dd, J = 2.67 Hz, 4H), $SiCH_2CH_2CH_2O$ 1.64 (m, 8H), $SiCH_2CH_2CH_2O$ 0.61 (m, 8.3H), $(CH_3)_2$SiH 0.25 (d, J = 2.72 Hz, 24H), $(CH_3)_2SiCH_2$ 0.15 (s, 26H); ^{13}C NMR (90 MHz, $CHCl_3$, 25 °C) δ $SiCH_2CH_2CH_2O$ 74.1, 73.9, (epoxy) $CH_2O(CH_2)_3$ 71.4, OCH_2CH (epoxy) 50.7, CH_2 (epoxy) 44.2, $SiCH_2CH_2CH_2O$ 22.9, $SiCH_2CH_2CH_2O$ 13.5, $(CH_3)_2SiH$ −0.05, $(CH_3)_2SiCH_2$ −0.60; ^{29}Si NMR (71.5 MHz, $CHCl_3$, 25 °C) δ $(CH_3)_2SiCH_2$ 13.9, $(CH_3)_2SiH$ −1.1, $SiOSi(CH_3)_2H$ −107.8, $SiOSi(CH_3)_2CH_2$ −108.1. Size-exclusion chromatography (SEC) polystyrene standards, THF solvent, toluene reference; M_n = 1260, M_w = 1290, PDI = 1.02, calc MW = 1475 g/mol. FTIR (neat film, cm^{-1}) 3035, 2962, 2934, 2874 (m, C−H str); 2142 (m, Si−H str); 1257 (s, C−O−C str); 1095 (vs, Si−O str); 902 (s, C−O−C bend).

(20) MWs corresponding to mono → tri substituted $(HSiO_{1.5})_{10}$ also appear in the mass spectrum due to the presence of T_{10}^H in the initial cube. T_{10}^H (5%) is produced during the synthesis of T_8^H. Pure T_8^H can be isolated, however at the expense of overall yield (≈15% vs ≈25%).

S0897-4756(96)00149-4 CCC: $12.00

Scheme 1



(1)

Table 1. Thermogravimetric Analysis (TGA) and Size Exclusion Chromatography (SEC) Data

precursor cube	R	TGA (SiO_2 ceramic yields) calc	exp	SEC[a] PS equiv M_n	calc MW	PDI
$T_4{}^HT_4{}^E$	H, AGE	54.4	54.6	780	881	1.14
$T_1{}^HT_7{}^E$	H, AGE	39.2	40.9	984	1224	1.07
$Q_8M_4{}^HM_4{}^E$	H, AGE	65.1	63.9	1260	1475	1.02
$Q_8M_8{}^E$	AGE	49.7	48.5	1480	1931	1.05

[a] Polystyrene equivalents, THF solvent, toluene reference.

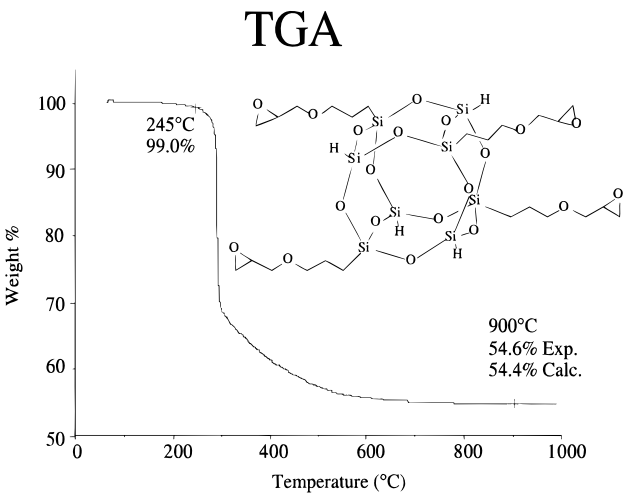


Figure 1. TGA trace for tetrakis(propyl glycidyl ether) silsesquioxane, ($T_4{}^HT_4{}^E$).

J-modulated ^{13}C and heteronuclear correlation (HETCOR) NMR techniques[21] for $T_4{}^HT_4{}^E$ and $T_1{}^HT_7{}^E$ indicate both α- and *β*-addition products. The amount of α-addition product varies with the choice of solvent system and catalyst. For example, toluene with triphenylphosphine (PPh_3), toluene, and toluene/*n*-butyl ether (1/1) as solvent gives 10, 20, and 35% α-isomer, respectively (see supporting information). Similar studies with $Q_8M_8{}^H$ always give the *β*-product regardless of solvent composition.

TGA analyses (Table 1 and Figure 1) confirm the NMR results. The estimated substitution patterns (from NMR) permit calculation of theoretical SiO_2 contents, which for all cubes deviate <2 wt % from theory, as found for other derivatives.[15,16] The TGA and NMR results are further substantiated by the narrow polydispersities (PDI) found from SEC analyses (Table 1, Figure 2, and supporting information). The narrow PDI imply that cross-coupled products are absent. Furthermore, it is likely that the various substituted species within $Q_8M_4{}^HM_4{}^E$ and $T_4{}^HT_4{}^E$ have very similar hydrodynamic radii and are encompassed in the narrow SEC responses.[15,16] DSC profiles show no thermal events prior to decomposition at ≈225−250 °C.

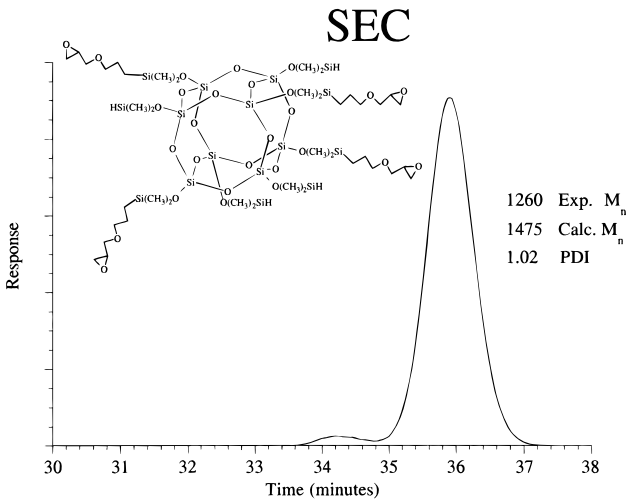


Figure 2. SEC trace for tetrakis(dimethylsiloxypropyl glycidyl ether) silsesquioxane, ($Q_8M_4{}^HM_4{}^E$).

Preliminary photoinduced cationic polymerization studies were run using catalytic triaryl sulfonium hexafluorophosphate (ASHP). Toluene solutions of cubes (≈ 20 wt %) using ASHP (0.5 mol %) were coated onto glass slides, dried and exposed to UV light (3−5 min, air; see Scheme 1).

The resulting insoluble, hybrid polymers can be peeled off the slide and characterized (e.g., by FTIR). Polymerization is initiated by in situ formation of $H^+PF^-_6$ and results in *ν*(OH) (FTIR) absent in uncured cubes.[22] Experiments run without ASHP show no signs of curing. More complete polymerization studies will be reported later.

In conclusion, novel epoxide silsesquioxanes were synthesized by the Pt-catalyzed hydrosilylation of AGE, with $Q_8M_8{}^H$ and $T_8{}^H$. The reactions are high yield (>90%) and form relatively pure products as determined by ^1H, ^{13}C, and ^{29}Si NMR, TGA, FTIR, and SEC. The products can be chemically, or photochemically cured to give hard, scratch- and solvent-resistant materials containing up to 65% masked silica.

Supporting Information Available: Experimental details and TGA and SEC figures (14 pages). Ordering information is given on any current masthead page.

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(21) Derome, A. E., *Modern NMR Techniques for Chemistry Research*; Pergamon Press: Elmsford, NY, 1990; p 143.

(22) (a) Crivello, J. L. In *Radiation Curing in Polymer Science and Technology*; Fouassier, J. P., Rabek, J. F., Eds.; Elsevier: New York, 1993; Vol. II, p 435.