Silsesquioxanes as synthetic platforms. II. Epoxy-functionalized inorganic–organic hybrid species [1]

Chunxin Zhang, Richard M. Laine *

Departments of Chemistry, Materials Science and Engineering, and Macromolecular Science and Engineering Center, University of Michigan, Ann Arbour, MI 48109-2136, USA

Abstract

The vinyl cubic polyhedral silsesquioxanes (vinyl$SiO_{1.5})_8$ and [(vinyl$Me_2SiO)SiO_{1.5}]_8$ were epoxidized using ten equivalents of m-chloroperoxybenzoic acid (m-CPBA) per cube. The [(vinyl$Me_2SiO)SiO_{1.5}]_8$ compound converts, quantitatively, to the octaepoxide, [(epoxy$Me_2SiO)SiO_{1.5}]_8$ as demonstrated by ^1H, ^{13}C, and ^{29}Si solution NMR, chemical and mass spectral analysis. The (vinyl$SiO_{1.5})_8$ cube was likewise fully epoxidized as determined by NMR; however, efforts to isolate it always led to intractable gels. Partial epoxidation was achieved using only three equivalents of m-CPBA. The partially epoxidized compound, when characterized by Cl mass spectra, chemical analysis and NMR, was shown to have an average of two epoxy groups per cube. Both polyepoxides readily polymerized in the presence of Lewis acid catalysts or on reaction with simple amines, which suggests their potential as coupling agents in the synthesis of novel inorganic–organic hybrids.

Keywords: Silicon; Multifunctional silsesquioxane epoxides; Epoxidation; Vinyl silsesquioxanes; Expoxide coupling agents

1. Introduction

Polyhedral silsesquioxanes offer access to new materials with well-defined properties for applications ranging from models of silica surfaces and zeolites, to low density/low dielectric planarization coatings in ULSI, to inorganic–organic hybrid polymers [1–7]. Of particular interest are the cubic silsesquioxanes $(RSiO_{1.5})_8$ (referred to simply as 'cubes'), which offer up to eight reactive sites, one at each vertex. In principle, each site can be functionalized differently, thus cubes can be prepared with diverse sets of functional groups. The resulting multifunctional cubes might serve as precursors to inorganic–organic hybrid materials with highly-delineated properties. To realize this potential, we are exploring methods of preparing polyfunctional, processable and polymerizable cubes [8].

Our intent is to develop soluble and/or liquid cubes containing functional groups for adhesion, light sensitization, binding catalysts, copolymerization for fabrication of nanocomposites and/or for liquid crystalline

properties [9]. In a preliminary report, we described the synthesis, characterization and properties of methacryloyl-substituted cubes: $[H_4(methacryloyl)_4Si_8O_{12}]_8$ and $[(HMe_2SiO)_4(methacryloylSiMe_2O)_4Si_8O_{12}]$ [8]. These cubes (average substitution of four methacryloyl groups) are low viscosity liquids that cure readily to give clear, abrasion resistant monoliths and coatings on heating or on exposure to UV light in the presence of a sensitizing agent. As these cubes are relatively susceptible to polymerization, we sought more robust compounds that were still easily polymerized. Thus, we report here on the synthesis of epoxide analogs.

2. Results and discussion

Epoxy-functionalized cubes can be synthesized via epoxidation of octavinylsilsesquioxane $((vinylSiO_{1.5})_8$, 1) and octa(vinyldimethylsiloxy)silsesquioxane $([(vinylMe_2SiO)SiO_{1.5}]_8$, 2). Cube 1 was prepared following a modified literature procedure [10], which furnished 1 in ca. 50% yield. Cube 2 can be prepared via several routes [11], that involve coupling $Si_8O_{20}^{8-}$ with vinyldimethylchlorosilane (vinylMe_2SiCl) to produce 2. The route used here provides pure samples of 2 in

---

80–90% yields. Solutions of $Si_8O_{20}^{8-}$ were prepared by hydrolytic condensation of either tetraethoxysilane (TEOS) [11] or silicon glycolate $[Si(eg)_2]$ [12] in the presence of Me_4NOH.

Compounds 1 and 2, when treated with ten equivalents of *m*-chloroperoxybenzoic acid (*m*-CPBA, Scheme 1) in refluxing CH_2Cl_2 for 40 h, convert quantitatively to the corresponding octaepoxy cubes; $((epoxySiO_{1.5})_8$, 3) and octa(epoxydimethylsiloxy)silsesquioxane $([(epoxyMe_2SiO)SiO_{1.5}]_8$, 4), as indicated by NMR analysis. Compound 4 was easily isolated as a microcrystalline, white powder and was readily characterized using standard techniques (see Section 3.

In contrast, attempts to remove byproduct *m*-chlorobenzoic acid (*m*-CBA) from 3 by washing with a potassium phosphate buffer (pH 7.5) [13] gave only intractable gels. However, when 1 was reacted with three rather than ten equivalents of *m*-CPBA, a partially epoxidized product was isolated. Efforts to recrystallize the epoxidized product were unsuccessful. Recrystallization from hot MeOH, CH_2Cl_2 or CH_3CN gave white powders in ca. 80% yield; however, no separation of the various epoxides was obtained. NMR analysis indicates an average ratio of vinyl to epoxy groups of ca. 6:2, suggesting that two vinyl groups out of eight

were epoxidized on each cube. However, mass-spectral analysis (NH_3 CI) indicates a mixture of mono-, di-, tri-, tetra- and penta-epoxy cubes with relative intensities (parent ions) of 73%, 100%, 69%, 24% and 4% respectively. A parent peak for 1 is also observed with an intensity of 19%. If all the parent ions have comparable stabilities under CI conditions, then the average ratio of vinyl to epoxy groups by mass spectroscopy is also ca. 6:2. C and H elemental analyses also give values that are nearly exact for the diepoxy cube, again supporting this 'average' degree of epoxidation. For the di-epoxy cube, minimization of steric hindrance might lead to preferential formation of the 'trans' shown in Scheme 1; however, we have no proof for this at present.

Cubes 3' and 4 were polymerized using $ZnCl_2$, BF_3OEt_2 initiators or ethylene diamine as a crosslinking reagent at ambient temperature in CH_2Cl_2. Insoluble polymers resulted from all trials [14]. In contrast, cubes 1 and 2 were stable under identical reaction conditions, suggesting that polymerization occurs solely via the epoxy functionality.

The facility with which these polyepoxide compounds are made, and their stability compared with the tetramethacryloyl cubes, suggest that they may be of
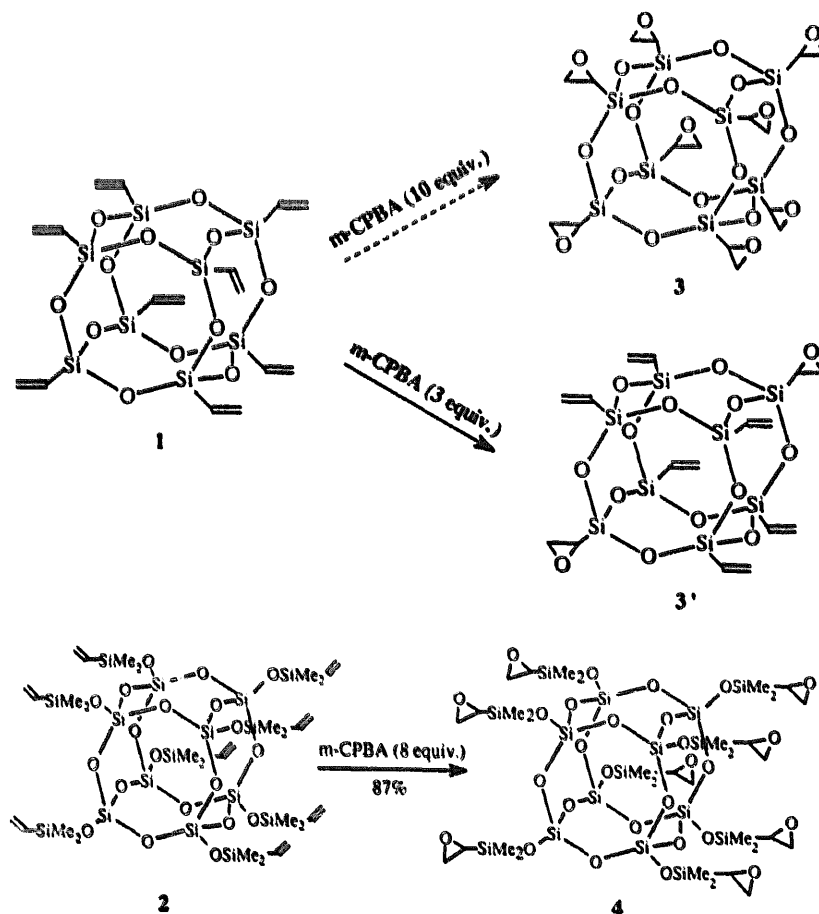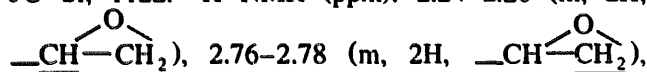

Scheme 1.

considerable use in the synthesis of a wide variety of hybrid materials, especially novel nanocomposites.

3. Experimental details

3.1. Partial epoxidation of 1

Octavinylcube **1** 1.000 g (1.581 mmol) and *m*-CPBA 1.170 g (4.744 mmol) were dissolved in 15 ml CH_2Cl_2 in a 25 ml Schlenk flask equipped with a magnetic stirrer and a reflux condenser. As the reaction proceeded, *m*-CBA precipitated. The reaction was then stopped after being refluxed for 40 h, and the flask was cooled in ice leading to further precipitation of *m*-CBA, which was filtered off. The filtrate was washed with 0.2 M phosphate buffer (pH 7.5) and dried over anhydrous Na_2SO_4. CH_2Cl_2 was removed by rotary evaporation. The white solid obtained was recrystallized from methanol, and 0.83 g was recovered (80% of theoretical). NMR analysis indicates an average of about two vinyls epoxidized. Selected data for this product are as follows. IR (KBr, cm^{-1}): $vC-H$, 3066, 2961; $vC=C$, 1603; $\delta C-H$, 1409, 1275; $vC-O$ of epoxy, 1233, 878; $vO-Si$, 1122. ^1H NMR (ppm): 2.24–2.26 (m, 2H, $\_CH-CH_2$), 2.76–2.78 (m, 2H, $\_CH-CH_2$), 2.89–2.91 (m, 2H, $\_CH-CH_2$), 5.89–6.13 (m, 18H, vinyl-Hs). ^{13}C NMR (ppm): 38.13–38.52 (CH_2 of epoxy), 44.35 (CH of epoxy), 127.65–128.58 (CH_2 of vinyl), 137.85–138.34 (CH of vinyl). ^{29}Si NMR (ppm): -79.4 to -80.3 [SiO_3C(vinyl), 6Si], -77.2 to -77.8 [SiO_3C(epoxy), 2Si]; Anal. Found (%): C, 28.94; H, 3.68. Calc. for diepoxide (%): C, 28.90; H, 3.64; Mass spectrum (CI with NH_3): 730 ($M_{penta} + NH_4^+$, 4%), 714 ($M_{tetra} + NH_4^+$, 24%), 698 ($M_{tri} + NH_4^+$, 69%), 682 ($M_{di} + NH_4^+$, 100%), 666 ($M_{mono} + NH_4^+$, 73%), 650 ($M_{vinylcube} + NH_4^+$, 19%).

3.2. Full epoxidation of 2

Cube **4** was synthesized from 1.352 g (1.102 mmol) cube **2** and 2.524 g (11.682 mmol) *m*-CPBA following the same procedure as that for the partially epoxidized cube. The reaction was stopped when all the vinyl groups were epoxidized as shown by NMR analysis. Isolation and purification of **4** followed the same procedure as that for the partially epoxidized cube. Selected data for **4** are as follows. IR (KBr, cm^{-1}): $vC-H$, 3044, 2961; $\delta C-H$, 1405; $vC-O$ of epoxy, 1237, 878; $vO-Si$, 1097. ^1H NMR (ppm): 0.18 (s, 3H, CH_3), 0.24 (s, 3H, CH_3), 2.22 (dd, $J = 4.0, 5.6$ Hz, 1H, CH), 2.65 (dd, $J = 4.0, 5.6$ Hz, 1H, CH_2), 2.91 (dd, $J = 5.6, 5.6$ Hz, 1H, CH_2). ^{13}C NMR (ppm): -2.77 (CH_3), -2.16

(CH_3), 42.93 (CH_2), 42.27 (CH). ^{29}Si NMR (ppm): -109.45 (SiO_4), 6.98 ($SiOC_3$). Anal. Found (%): C, 28.02; H, 5.33. Calc. (%): C, 28.38; H, 5.33. Mass spectrum (EI): 1354 (M + 2^+, 1.3%), 1352 (M^+, 0.6%), 1058 (22%), 1043 (100%), 1028 (30%), 969 (34%).

References

[1] R.H. Baney, M. Itoh, A. Sakakibara and T. Suzuki, *Chem. Rev.*, 95 (1995) 1409.
[2] D.A. Loy and K.J. Shea, *Chem. Rev.*, 95 (1995) 1431.
[3] S.-P. Jeng, K. Taylor, T. Seha, M.-C. Chang, J. Fattaruso and R. H. Havemann, *VLSI Technol. Symp. Dig.*, (1995) 61.
[4] (a) M. Bartsch, P. Bornhauser and G. Calzaferri, *J. Phys. Chem.*, 98 (1994) 2817. (b) H. Burgy, K.W. Tomroos and G. Calzaferri, *Inorg. Chem.*, 32 (1993) 4914.
[5] (a) F.J. Feher and T.L. Tajima, *J. Am. Chem. Soc.*, 116 (1994) 2145 and references cited therein. (b) F.J. Feher, D.A. Newman and J.F. Walzer, *J. Am. Chem. Soc.*, 111 (1989) 1741. (c) F.J. Feher and D.A. Newman, *J. Am. Chem. Soc.*, 112 (1990) 1931.
[6] (a) P.A. Agaskar, *Colloids Surf.*, 63 (1992) 131. (b) K.J. Shea, D.A. Loy and O. Webster, *J. Am. Chem. Soc.*, 114 (1992) 6700. (c) C. Zhang, R. Baranwal and R.M. Laine, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, 36 (1995) 342.
[7] (a) D. Herren, H. Burgy and G. Calzaferri, *Helv. Chim. Acta, 74* (1991) 24. (b) A.R. Bassindale and T.E. Gentle, *J. Mater. Chem.*, 3 (1993) 1319. (c) B.J. Hendan, and H.C. Marsmann, *J. Organometal. Chem.*, 483 (1994) 33. (d) S.E. Yuchs and K.A. Carrado *Inorg. Chem.*, 35 (1996) 261. (e) V.W. Day, W.G. Klemperer, V.V. Mainz and D.M. Millar, *J. Am. Chem. Soc.*, 107 (1985) 8262. (f) M. Moran, C.M. Casado and I. Cuadrado, *Organometallics*, 12 (1993) 4327. (g) P. Jutzi, C. Batz and A. Mutluay, *Z. Naturforsch. Teil B:*, 49 (1994) 1689. (h) A. Sellinger and R.M. Laine, *J. Mater. Chem.*, in press.
[8] A. Sellinger and R.M. Laine, *Macromolecules, 29* (1996) 2327.
[9] (a) A. Sellinger, R.M. Laine, C. Viney and V. Chu, *J. Polym. Sci. Part A: Polym. Chem.*, 32 (1994) 3069. (b) A. Sellinger and R.M. Laine, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, 35 (1994) 665.
[10] K. Olsson, *Ark. Kemi, 13* (37) (1958) 367.
[11] (a) I. Hasegawa, K. Kuroda and C. Kato, *Bull. Chem. Soc. Jpn.*, 59 (1986) 2279. (b) I. Hasegawa and S. Sakka, *J. Mol. Cryst. Liq.*, 34 (1987) 307. (c) I. Hasegawa, S. Sakka, Y. Sugahara, K. Kuroda and C. Kato, *J. Chem. Soc. Chem. Commun.*, (1989) 208. (d) I. Hasegawa and S. Motojima, *J. Organomet. Chem.*, 441 (1992) 373. (e) S.E. Yuchs and K.A. Carrado, *Inorg. Chem.*, 35 (1996) 261.
[12] A. Sellinger, D. Treadwell and R.M. Laine, in preparation.
[13] N.N. Schwartz and J.H. Blumbergs, *J. Org. Chem.*, 29 (1964) 1976.
[14] C. Zhang and R.M. Laine, unpublished results, 1996.