Silsesquioxane–Siloxane Copolymers from Polyhedral Silsesquioxanes

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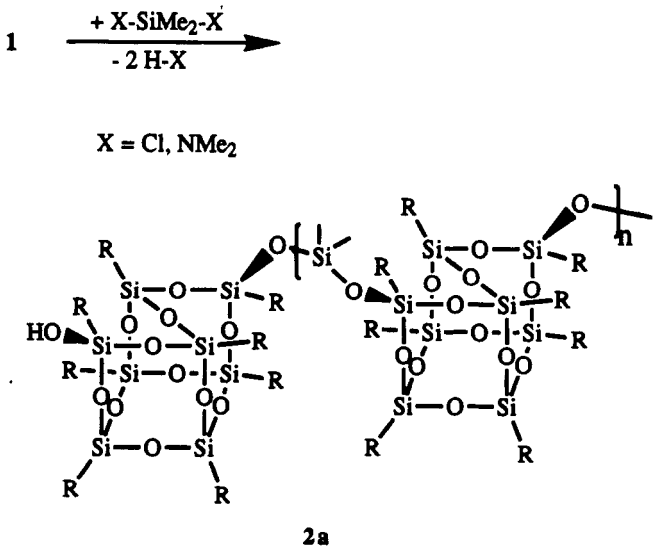
Introduction. Silsesquioxane-based polymers are a potentially useful class of materials for numerous applications.[1] Despite the past and present interest in these materials, a general synthetic route which affords rational control over their properties has not been developed. Previous synthetic routes have largely relied upon the in situ formation of the silsesquioxane or have utilized commercially available silsesquioxanes with unordered (unknown) structure, molecular weight, and molecular functionality.[1] Consequently, these approaches have produced polymers and networks for which the basic molecular structure is unknown and from which little information regarding structure–property relationships can be drawn.

Results and Discussion. In order to design processible silsesquioxane-based polymeric materials with tailorable material properties, we have utilized the silsesquioxane monomer shown in Figure 1.

This molecule possesses a well-defined structure and composition which includes two reactive hydroxyl groups that can be converted into additional functionalities.[2] We are currently exploring the potential for derivatives of 1 and other related incompletely condensed polyhedral oligosilsesquioxanes to function as monomers and macromers for additional polymer synthesis.[3]

The reaction of 1 with a variety of difunctional silane or siloxane comonomers affords polymers with discrete silsesquioxane units incorporated into the polymer backbone. These polymerizations proceed through condensation of the reactive hydroxyl groups on 1 with the functionality on the comonomer. The formation of strong silicon–oxygen bonds in the polymer and loss of reaction byproducts may help drive these polymerizations.



2a

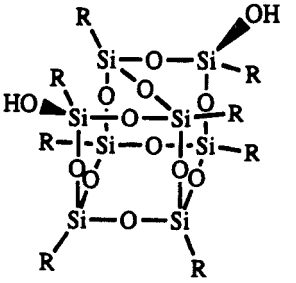


Figure 1. Silsesquioxane monomer (R = *c*-C_6H_{11}).

Table I
Composition and Thermal Properties of Polymers 2a–e

polymer	comonomer	T_g (°C)	T_m (°C)	T_{dec} (°C)
2a	$SiMe_2$	40		490
2b	$SiMe(CH_2{=}CH)$	48		490
2c	$SiMe_2(CH_2)_2SiMe_2$	40		420
2d	$SiMe_2O(SiMe_2O)_2SiMe_2$	23	114	495
2e	$SiMe_2O(SiMe_2O)_nSiMe_2$[a]	58	94	510

[a] Oligomer average n = 3.4.

Reactions of 1 with bis(dimethylamino)silanes or siloxanes provided a more efficient synthetic route to these polymers than reactions between 1 and dichlorosilanes or -siloxanes. By analogy to reported condensation polymerizations involving related silanol systems,[4] reactions of 1 with diureidosilanes and -siloxanes should provide yet another synthetic route to this new family of silsesquioxane-based polymers.

The series of polymers reported in Table I were produced in a one-step synthesis by reacting 1 with the bis(dimethylamino) derivatives of the comonomers listed. In a subsequent step the polymers can be chain terminated with trimethylsilyl groups.[5] All of the polymers in Table I show high solubilities (>55% w/w in $CHCl_3$ and THF) and appear to have excellent long-term shelf life. Additionally, the polymers have the physical appearance of clear plastics when hot pressed or deposited from solution as films.[6]

The decomposition temperatures (T_{dec}) listed for **2a–e** have been identified by TGA and represent a 10% mass loss for the sample while under N_2. The T_{dec} values of **2a–e** are significantly higher than that (350 °C) reported for poly(dimethylsiloxane).[7] The T_{dec} values for **2a** and **2b**, however, are nearly identical to that reported for the 1,4-bis(dimethylsilyl)benzene–dimethylsiloxane copolymer prepared by Lenz and Divornic.[4d,8] Therefore, incorporation of this silsesquioxane segment into siloxane polymers enhances the thermal stability of the siloxane linkage. However, the observed 10% mass loss for **2a–e** in air occurs at lower temperatures (typically at 300–350 °C) than those in nitrogen and than those observed for the related silarylene–siloxane copolymers (typically near 500–550 °C).[4c,8] The stability of **2a–e** to atmospheric oxidation could likely be enhanced by substituting the cyclohexyl groups on 1 for phenyl.[3]

Differences between the molecular weights and the polydispersities of the polymers listed in Table II prohibit making strong comparisons between polymer composition and its effect on the corresponding $T_{g,m}$ values. However, a correlation between the increased length and flexibility of the comonomer and a decrease in the observed T_m for these polymers is evident.[9] This indicates that the material

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Table II
Molecular Weight Values for Polymers 2a–e

polymer	$M_n^a \times 10^{-3}$	$M_n^b \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n^b	DP
2a	7.61	11.5	15.5	1.34	11
2b	34.7	37.5	61.2	1.63	34
2c	23.4	18.5	32.7	1.77	16
2d	34.3	28.1	114	4.06	21
2e	43.4	46.7	203	4.35	34

[a] From ^{29}Si NMR measurements. [b] From GPC measurements.

properties of these silsesquioxane-based polymers can be controlled through variations of the comonomers. A more detailed evaluation of the thermal, mechanical, and structure–property relationships of these systems is underway.

This series of polymers is especially amenable to characterization by NMR given their high solubilities and can reveal information relating to the composition, sequence, and molecular weight of **2a–e**. The ^{1}H NMR spectra of **2a–e** are similar in that each contains broad cyclohexyl resonances at δ 1.71, 1.21, and 0.70 (5:5:1) and silicon methyl resonances at or near δ 0.10. Additional resonances for the vinyl protons (δ 5.97) of **2b** and methylene protons (δ 0.48) of **2c** are also observed. The ^{29}Si resonances for **2a–e** are consistent with the polymer formulations and span the M, D, and T regions of the silicon spectrum.[10] The ^{29}Si spectra are also useful in that ratios between the repeat units and the trimethylsilyl end group provide a measure of the number-average molecular weights for **2a–e**.[11]

Molecular weight determinations for **2a–e** were also obtained from refractive index and light scattering measurements. The average M_n value obtained from successive measurements of an individual polymer sample is within 20% of the M_n value measured by NMR.[12]

This new family of polymers also functions as highly processible preceramics. Heating an un-cross-linked sample of **2a** to 900 °C under nitrogen results in its conversion into a glassy black ceramic material in 56% yield. Analysis of this residue by ESCA and ^{29}Si MAS NMR has confirmed the presence of SiO_2 and SiOC in the resulting ceramic.[13]

A general route has been established for the synthesis of soluble, well-defined silsesquioxane–siloxane-based copolymers. Control over the properties of these materials is possible though variations of the individual monomer segments in the copolymers. This family of silsesquioxane-based materials shows additional promise as a new class of nonnetwork (processable) preceramics. A detailed description of the structure–property relationships for this new class of polymers and on their conversion to silicon-based ceramics will be forthcoming.

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Supplementary Material Available: Tables of ^{29}Si NMR chemical shifts for polymers **2a–e** and GPC, UV–vis, thermal data, and ^{1}H and ^{29}Si NMR spectra for **2d** (10 pages). Ordering information is given on any current masthead page.

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(5) In a typical polymer synthesis, a 250-mL flask was charged with 1 (7.79 g, 7.08 mmol) and bis(dimethylamino)octamethyltetrasiloxane (2.61 g, 7.01 mmol). Freshly distilled xylene was quickly added to the mixture, and the reaction was stirred and heated 117 °C under nitrogen for 24 h. After removing the solvent and volatiles under reduced pressure, the polymer was dissolved in a minimum of THF (25 mL) and precipitated into excess methanol (1 L). Subsequent purification was accomplished by redissolving the polymer in a minimum of hexane (20 mL) followed by precipitation into excess methanol (1 L). End capping of the polymer was accomplished by dissolving the polymer in THF, adding an excess of *N,N*-(dimethylamino)trimethylsilane (700 mg, 6 mmol) to the solution, and heating at 80 °C for 2 h. Solvent and volatiles were then removed under reduced pressure. The polymer was dissolved in hexane (20 mL) and precipitated into an excess of methanol (1 L). Excess solvent was decanted, and the remaining white solid was dried under vacuum for 3 h (9.67 g, 96% of theoretical yield). Spectroscopic analysis of the product was consistent with the formation of **2d**: ^{1}H NMR ($CDCl_3$) 1.72 (br, 40 H), 1.23 (br, 40 H), 0.71 (s, 8 H), 0.10 (s, 25 H); ^{29}Si NMR ($CDCl_3$) –69.46 (s, 2 Si), –68.10 (s, 4 Si), –66.34 (s, 2 Si), –21.59 (s, 2 Si), –21.31 (s, 2 Si), 8.15 (s, 0.34 Si).

(6) A disk-shaped sample of **2d** was irradiated from 200 to 800 nm. A transparency cutoff for this sample was observed at 256 nm.

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(9) Determination of the thermal properties of the polymers was carried out using a Du Pont 2000 controller with TGA 951 and TMA 2940 attachetments. A well-defined T_m was not observed for polymers **2a–c** before the onset of polymer decomposition. Further characterization of the thermal properties for this new class of polymers is underway.

(10) A detailed sequence analysis (by NMR) for this class of polymers has not been completed.

(11) All ^{29}Si NMR spectra were taken at 59.6 MHz on a Bruker AMX 300 (300-MHz ^{1}H) instrument in $CDCl_3$ with 0.02 mmol of $Cr(acac)_3$. Chemical shifts (δ) are given in ppm and are reported relative to tetramethylsilane.

(12) Molecular weight determinations were made using a GPC equipped with a DAWN-F detector (Wyatt Technology). We observed excellent reproducibility of values for M_w (±6%) and significant fluctuations (±32%) in the M_n values. Poor reproducibility in M_n measurements using the DAWN-F detector has also been reported for polyurethane samples. See: Samuels, M. Q.; Coughlin, C. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33*, 1138–1139.

(13) (a) Heating 8.3 mg of **2a** to 900 °C under N_2 produced 4.6 mg of residue. ESCA analysis of a finely ground sample of this residue found the following: 13.3, SiO_2; 7.4, SiOC; 34.2, C. (b) Mantz, R. M.; Jones, P. J.; Gilman, J. G.; Lichtenhan, J. D., work in progress.