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THE CATALYTIC SYNTHESIS OF INORGANIC POLYMERS FOR HIGH TEMPERATURE APPLICATIONS AND AS CERAMIC PRECURSORS

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ABSRACT:

Polysilsesquioxanes, $-[RSi(O)_{1.5}]_x$- exhibit many properties that are potentially quite useful for industrial applications. These properties include high temperature stability ($\approx 600°C$ in O_2); good adhesion and, liquid crystal-like behavior for some derivatives. Moreover, $[MeSi(O)_{1.5}]_x$, polymethylsilsesquioxane has been used successfully as a precursor for the fabrication of carbon fiber/"black glass" $(SiO_2/SiC/C)$ composites and "black glass" fibers.

Current methods of preparation depend on hydrolysis of $RSiCl_3^n$ or $RSi(OR)_3^n$. Unfortunately, this approach leads to several products that are difficult to purify because polysilsesquioxanes exhibit a great propensity for forming gels. We describe here a simple catalytic approach to the synthesis of polymethylsilsesquioxane copolymers of the type $-[MeRSiO]_{.3}[MeSi(O)_{1.5}]_{.7}$- where R = H, OMe, OEt, OnPr and OnBu. The R = H copolymer is produced by catalytic redistribution of $-[MeHSiO]_x$- oligomers using dimethyltitanocene, Cp_2TiMe_2 as the catalyst precursor.

Following catalytic redistribution, the resulting copolymer, $-[MeHSiO]_{.3}[MeSi(O)_{1.5}]_{.7}$-, is reacted *in situ* with alcohols to produce $-[Me(R'O)SiO]_{.3}[MeSi(O)_{1.5}]_{.7}$- (where R' = Me, Et, nPr and nBu) which serve as masked forms of the polymethylsilsesquioxane. These new copolymers have been characterized by ^{1}H, ^{13}C and ^{29}Si NMR TGA and DTA. The NMR studies allow us to assign structures for the copolymer.

These new copolymers exhibit improved tractability. Their high temperature properties are all quite similar; although, the MeO-, EtO- and especially the nPrO- derivatives give much higher ceramic yields than expected.

Keywords: Polymers, Ceramic Materials, copolymers, catalysis, ... Polysiloxanes, silicon, Oxygen

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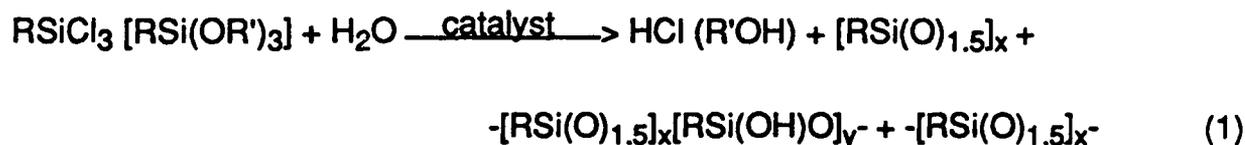
Richard M. Laine

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INTRODUCTION

Polysilsesquioxane polymers,[1] -[RSi(O)$_{1.5}$]$_x$-, are a very poorly exploited area of polysiloxane chemistry despite the fact that they exhibit a variety of potentially useful properties including: high temperature stability in air;[2] good adhesion to a wide variety of substrates[3] and, in some instances, liquid crystal-like behavior.[1] Furthermore, -[MeSi(O)$_{1.5}$]$_x$, polymethylsilsesquioxane has been used as a preceramic polymer for fabrication of silicon carbide powders,[4] "black glass" (70% SiO$_2$/20% SiC/10% C) composite matrices for carbon fibers[5] and for the fabrication of black glass fibers.[6]

The primary problems associated with using polysilsesquioxanes for engineering applications concern: (1) the lack of good, high yield synthetic routes and, (2) the highly crosslinked nature of the polymers which limits their tractability and ease of purification. Literature syntheses generally rely on the hydrolysis of RSiCl$_3$ or RSi(OR')$_3$:[1]
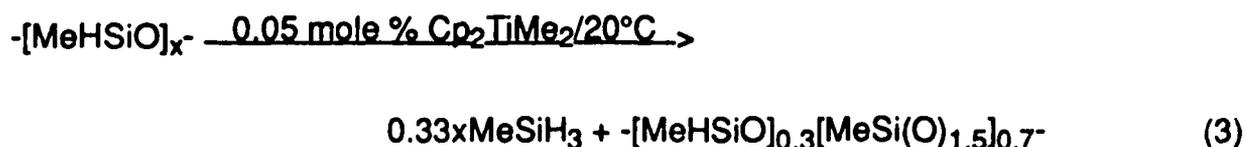
$$RSiCl_3 \ [RSi(OR')_3] + H_2O \xrightarrow{\text{catalyst}} HCl \ (R'OH) + [RSi(O)_{1.5}]_x +$$

$$-[RSi(O)_{1.5}]_x[RSi(OH)O]_y- + -[RSi(O)_{1.5}]_x- \qquad (1)$$

These reactions usually lead to the coincident formation of polyhedral oligosilsesquioxanes, [RSi(O)$_{1.5}$]$_x$, where x = 8, 10, 12; polysilsesquioxanes with partially condensed monomer units, -[RSi(O)$_{1.5}$]$_x$[RSi(OH)O]$_y$-, and polyhedral polysilsesquioxane itself. Because polysilsesquioxanes exhibit a strong propensity to form intractable gels with organic solvents, there are significant problems with purification which result in low yields. Thus, this synthetic route is unattractive for the rapid, large-scale preparations.

Harrod and coworkers have recently developed a novel titanium catalyzed redistribution reaction, as illustrated in reaction (2),[7] that can

$$3MeHSi(OEt)_2 \xrightarrow{\text{0.05 mole \% Cp}_2\text{TiMe}_2\text{/20°C}} MeSiH_3 + 2MeSi(OEt)_3 \qquad (2)$$
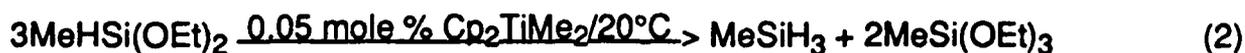
also be used to prepare methylsilsesquioxane copolymers, reaction (3):[2,8]

$$-[MeHSiO]_x- \xrightarrow{\text{0.05 mole \% Cp}_2\text{TiMe}_2\text{/20°C}}$$

$$0.33x MeSiH_3 + -[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}- \qquad (3)$$

The copolymer -$[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}$- forms as a gel if neat oligomethylhydridosiloxane, Me_3SiO-$[MeHSiO]_x$-H ($M_n \sim$ 2K D), is exposed to the catalyst. Fortunately, gelation can be avoided if polymerization is conducted in toluene with a greater than 5:1 toluene to -$[MeHSiO]_x$- volume ratio. The resulting polymer can be used to prepare coatings, fibers and monolithic shapes.[8] At lower volume ratios, gels form quite readily.

Although the 5:1 volume ratio solutions can be used for some applications, the gel-like material that results on solvent removal limits the copolymer's utility for some applications, e.g. as a matrix material for composites. As such, we sought to modify the copolymer's physical characteristics by taking advantage of the reactive Si-H bonds. Reactions at these bonds should permit one to vary the side chains on the copolymer backbone and thereby control some of its physical properties.

The long term objectives of the work described here are to prepare tractable silsesquioxane copolymers that exhibit improved high temperature performance and that are also useful for the fabrication of polymer and ceramic, membranes and fibers. This report concerns preliminary studies on the modification of the -$[MeHSiO]_x[MeSi(O)_{1.5}]_y$- copolymer by alcoholysis of Si-H bonds.

RESULTS AND DISCUSSION

The copolymer produced in reaction (3) either neat or in toluene gives the same results when characterized by magic angle spinning (MAS), multinuclear NMR, solution NMR, diffuse reflectance infrared fourier transform spectroscopy (DRIFTS), chemical analysis, TGA or DTA. These extensive studies are described elsewhere.[2,7] For illustration purposes, the TGA of -$[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}$- is shown below (Figure 1). This Figure also contains the elemental analyses (at selected temperatures) as the polymer is heated in nitrogen at 5°C/min to 900°C.

At 400°C, the elemental analysis corresponds to pure -$[MeSi(O)_{1.5}]_x$- without any of the starting monomer. This is confirmed by the MAS ^{29}Si NMR which shows a single peak at -65.7 δ relative to TMS.[2] Consequently, the 20% weight loss at temperatures below 400°C corresponds to the depolymerization and volatilization of almost all of the -$[MeHSiO]_x$- units.
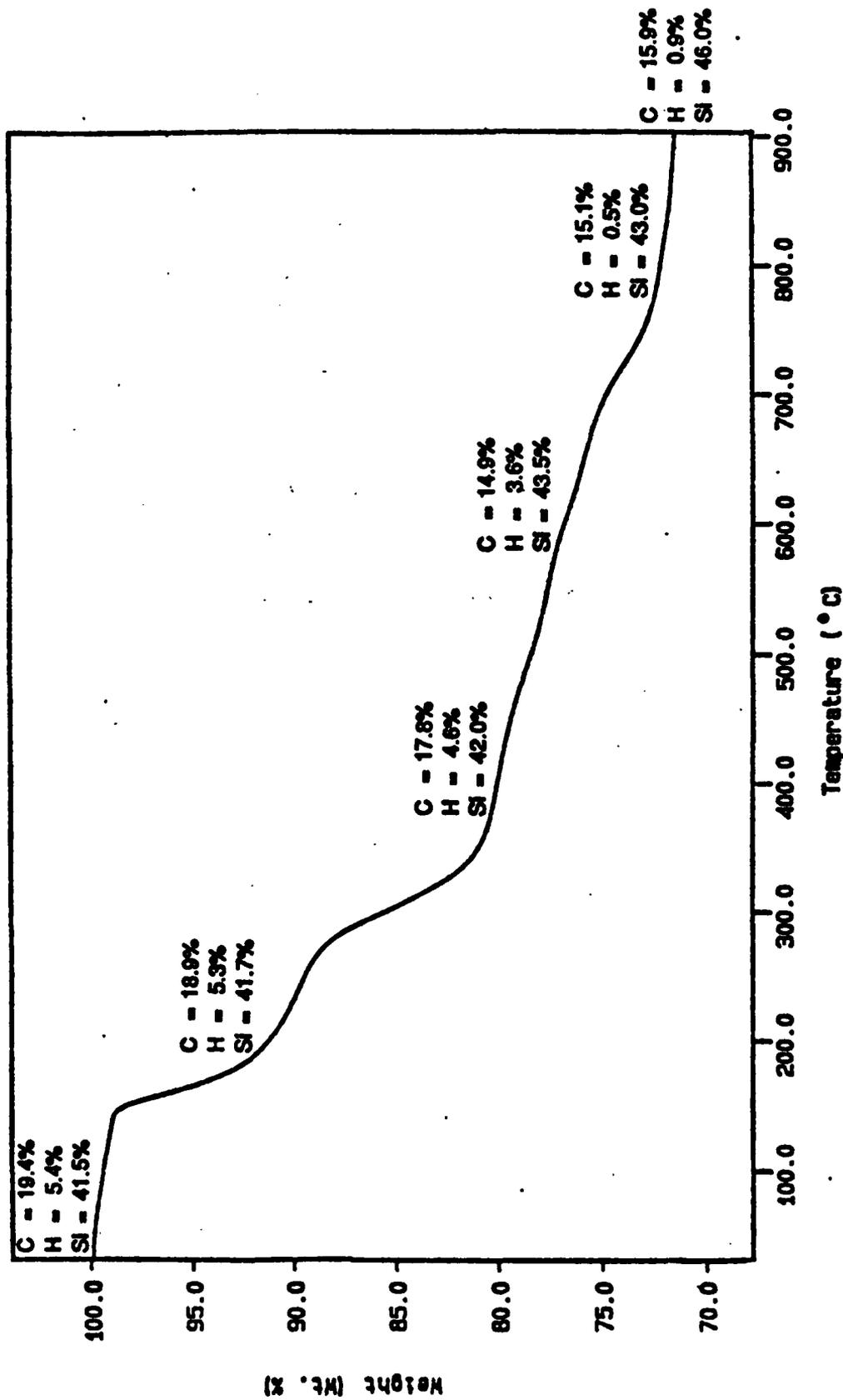
Figure 1. Thermogravimetric Analysis of -[MeHSiO]$_3$[MeSi(O)$_{1.5}$]$_7$ as a Function of Temperature. The TGA heating schedule was 5°C/min in N$_2$. Bulk samples for the analyses were heated in a similar manner.

C = 19.4%
H = 5.4%
Si = 41.5%

C = 18.9%
H = 5.3%
Si = 41.7%

C = 17.8%
H = 4.6%
Si = 42.0%

C = 14.9%
H = 3.6%
Si = 43.5%

C = 15.1%
H = 0.5%
Si = 43.0%

C = 15.9%
H = 0.9%
Si = 46.0%

Temperature (°C)

Weight (Wt. %)

Copolymer Preparation and Characterization

Efforts to modify the $-[MeHSiO]_x[MeSi(O)_{1.5}]_y-$ copolymer began with attempts to promote alcoholysis of the Si-H groups, reaction (4),[9,10] *in situ*, following completion (72 h) of reaction (3).

$$-[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}- + ROH \xrightarrow{\text{0.5 mole \% Cp}_2\text{TiMe}_2/20°C}$$

$$H_2 + -[Me(RO)SiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}- \qquad (4)$$

The motivation for the alcoholysis experiments was to create a polysilsesquioxane wherein some of the T groups, $[MeSi(O)_{1.5}]$, are masked as the alkoxy derivative, $[MeSi(O)OR]$. In this way, the yield of T groups in the polymer would increase significantly. Moreover, if R is a long chain alkyl group it would also be possible to introduce more flexibility and perhaps reduce or eliminate the elastomeric or gel character.

To our surprise, the addition of alcohols rapidly extinguishs the royal blue Ti(III) color of the original active catalyst system that forms in reaction (3) leaving a yellow solution. If the alcohol is MeOH, then rapid, almost violent H_2 evolution ensues coincident with the color change. The reaction can be somewhat exothermic depending on the initial catalyst concentration.

Removal of the solvent and characterization by NMR indicates that almost all of the Si-H bonds react with alcohol converting the remaining silicons to T groups. NMR characterization, Table 1, confirms the 30:70 composition of the initial copolymer in that the integrated ratios of the alkoxy groups to T groups in the product copolymer are nearly the same.

To date, we have made the derivatives R = Me, Et, Pr, nBu and bis-1,4-(2-hydroxyethoxy)benzene (hydroquinone). These alcohols exhibit reactivities with the copolymer strictly in accord with the size of the alkyl group. The MeOH reaction is quite vigorous and is over in minutes to hours while the nBuOH reaction requires two to three days. The hydroquinone reaction results in extensive crosslinking that makes further characterization impossible. The other copolymers are moderately (MeO-) to completely (nBuO-) tractable following solvent removal; however, it is expedient to redissolve the polymer in the corresponding alcohol as these polymers still show a tendency to gel with time (days to weeks).

The alkoxy copolymers have been characterized by ^1H, ^{13}C and in part

OR'	^{29}Si(δ)	^{13}C(δ)	^{1}H(δ) (integration)
Starting oligomer	-34.6	1.75 OSi(CH$_3$)$_3$ 1.04 SiCH$_3$	4.69 (3.43) MeHSiO 0.18 (1.02) OSi(CH$_3$)$_3$ 0.10 (9.68) HSiCH$_3$
H (72 h)	-33.5, -34.4, -35.9 -57.2, -65.5	1.68 OSi(CH$_3$)$_3$ 0.66 HSiCH$_3$ -3.27 OSiCH$_3$	4.68 (8) SiH 0.18 (x) OSi(CH$_3$)$_3$ 0.13 (80-x,y) HSiCH$_3$ 0.10 (y) OSiCH$_3$
OCH$_3$		49.70 OCH$_3$ 1.54 OSi(CH$_3$)$_3$ -3.29 br OSiCH$_3$ -5.10 br MeOSiCH$_3$	4.70 (1.7) SiH 3.48 (17) OCH$_3$ 0.13 (49-x) OSiCH$_3$ 0.10 (x) MeOSiCH$_3$
OCH$_2$CH$_3$		57.99 OCH$_2$ 18.16 CH$_2$CH$_3$ 0.70 br ROSiCH$_3$ -3.25 br OSiCH$_3$	3.76 (7) OCH$_2$ 1.20 (10) CH$_2$CH$_3$ 0.12 SiCH$_3$
O(CH$_2$)$_2$CH$_3$	-36.7, -57.9, -66.3	64.02 OCH$_2$ 25.55 OCH$_2$CH$_2$ 10.27 CH$_2$CH$_3$ 1.65 OSi(CH$_3$)$_3$ -3.12 OSiCH$_3$ -4.52 ROSiCH$_3$	4.70 (3) HSiCH$_3$ 3.65 (6.4) OCH$_2$ 1.55 (8) OCH$_2$CH$_2$ 0.87 (8) CH$_2$CH$_3$ 0.12 (33-x) OSiCH$_3$ 0.10 (x) OSiCH$_3$
O(CH$_2$)$_3$CH$_3$	-36.5 w, -57.94, -64.33, -66.45	62.10 OCH$_2$ 34.50 OCH$_2$CH$_2$- 18.94 CH$_2$CH$_3$ 13.82 CH$_2$CH$_3$ -3.0 ->-3.5 OSiCH$_3$	3.68 (8.6) OCH$_2$ 1.50 (9) OCH$_2$CH$_2$ 1.34 (8) CH$_2$CH$_3$ 0.89 (11) CH$_2$CH$_3$ 0.12 (30) SiCH$_3$

Table 1. NMR Spectra for -[-Me(OR)SiO]$_x$[MeSi(O)$_{1.5}$]$_y$-. Spectra taken in CDCl$_3$ using TMS as an internal standard.

by ^{29}Si as recorded in Table 1. The ^{13}C shifts of the alkoxy carbon bound directly to the oxygen are quite similar (except for MeO). Consequently, characterization by ^{29}Si was not deemed essential in all instances. The proton and carbon spectra are all standard values for alcohols or alkoxy substituents. However, the ^{29}Si results are interesting because they provide some understanding of the polymer backbone structure if we use published ^{29}Si peak assignments for standard siloxane monomer units.[11]

The ^{29}Si and ^{13}C spectra for $Me_3SiO[MeHSiO]_xH$, ($M_n \approx 2K$ D), the starting oligomer, are very simple. The MeHSiO ^{29}Si peak appears at -34.6 δ. The product, $-[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}$, obtained from Ti catalyzed redistribution, shows several ^{29}Si peaks in the same vicinity, -33 to -36 δ. It also shows two peaks at -57.2 and -65.5 δ. These results, when coupled with the reproducible 30:70, $[MeHSiO] : [MeSi(O)_{1.5}]$ ratio, suggest a polymer structure consisting of open cubes of T groups bridged by one or two -MeHSiO- groups as depicted below. By visual inspection, the peak at
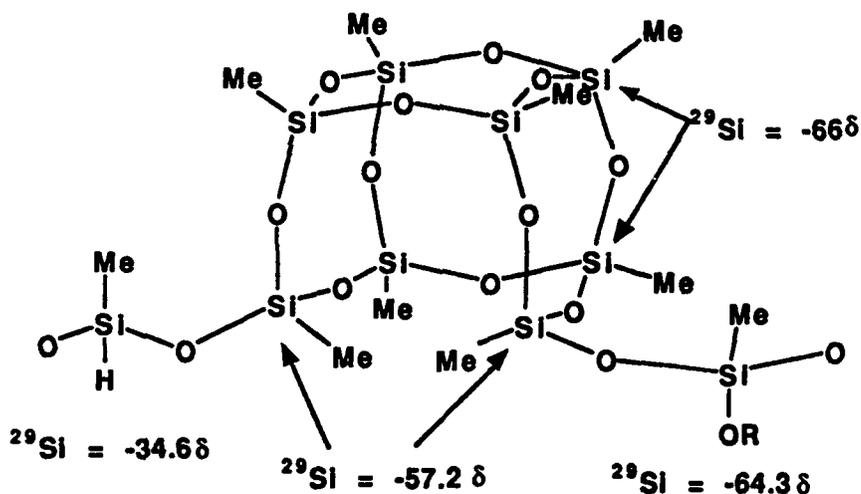
-57.2 δ is much smaller than the peak at -65.5 δ. Consequently, we assign this peak to the open silicons in the cube and the -65.5 δ peak to the remaining T group silicons in the cube. In the nBuO- derivative, the -34.6 δ peak is replaced by the appearence of a peak at ca. -64 δ. This peak appears to overlap with the T groups in the cube in the nPrO derivative. We assign this peak to the alkoxy substituted silicons.

High Temperature Studies

TGA studies indicate that the high temperature stability of the alkoxy derivatives is very similar to that of the starting copolymer. The 900°C ceramic yields for the set of copolymers are 76% (MeHSiO), 75%

[Me(MeO)SiO], 74% [Me(EtO)SiO], 78% [Me(nPrO)SiO] and 62% for the [Me(nBuO)SiO] derivative. As in Figure 1, most of the weight loss occurs below 400-450°C. If weight loss in the alkoxy derivatives occurs by a mechanism similar to that found for the hydrido copolymer, then weight loss must occur by depolymerization and volatilization of Me(RO)SiO groups. One would expect increasing weight losses with increases in the size of the R' group. Clearly this is not the case with the R' = Me, Et or nPr derivatives. In these cases, the ceramic yields are comparable to that of the original copolymer. Even in the nBuO- derivative, the mass of the group increases from 60 D (MeHSiO) to 132 D [Me(OnBu)SiO]. If complete loss of 60 D leads to a ceramic yield of 75% then complete loss of 132 D should lead to a ceramic yield of <50%. These results inidcate that the ceramic products from pyrolysis of these materials retain the carbons in the alkoxy groups.

This is in contrast to studies by Fox et al.[4] on the pyrolysis of the polyalkylsilsesquioxanes, $-[RSi(O)_{1.5}]_x-$, where increasing the size of R from Me to Et to Pr resulted in drops in the 900°C ceramic yields from 86% (Me) to 47% (Et) to 44% (nPr). In all instances, except for the Me derivative, our ceramic yields are much higher.

It is likely that these differences arise because the bond dissociation energy for Si-C bonds is approximately 85-90 kcal/mole whereas O-C bond dissociation energies are typically around 100 kcal/mole.[12] Thus, the decomposition mechanisms for the two types of polymers are quite different. The important point to be made is that proportionately, the EtO- and nPrO- derivatives incorporate more carbon in the ceramic product than the EtSi and nPrSi derivatives, which should result in a higher proportion of SiC in the final composite ceramic/black glass.

ACKNOWLEDGEMENTS

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