SAN096-1282C

CONF-960807--17

NEW HYBRID POLYSILANE/POLYSILOXANE NANOCOMPOSITES.§

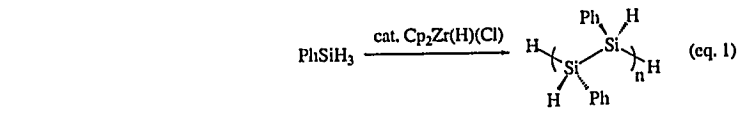
Gregory M. Jamison,†* Douglas A. Loy,†* Kimberly A. Opperman,† James V. Beach† and Robert M. Waymouth.‡*

†Sandia National Laboratories, Albuquerque, NM 87185-1407
‡Department of Chemistry, Stanford University, Stanford, CA 94305-5080

INTRODUCTION

Polysilanes are saturated organosilicon macromolecules which display polyene-like electronic properties derived from σ-bond delocalization along the catenated silicon backbone.[1] Potential commercial applications of polysilanes include display devices, NLO materials, semiconductors, photoresists and photoconductors.[2] While Würtz coupling of dichlorosilane monomers is currently the best synthetic route for large scale preparation of high molecular weight polysilanes, drawbacks include using stoichiometric quantities of molten alkali metal, low polymer yields and significant amounts of hazardous waste. These reaction conditions also limit one's choice of side group to the most robust organic substituents.

Titanocene- and zirconocene-catalyzed polymerization of phenylsilane under mild conditions provides an attractive route to oligophenylsilanes with degrees of polymerization approaching 40 (eq. 1),[3] making the resulting oligomers amenable for many electronic applications.



(eq. 1)

n ~ 20

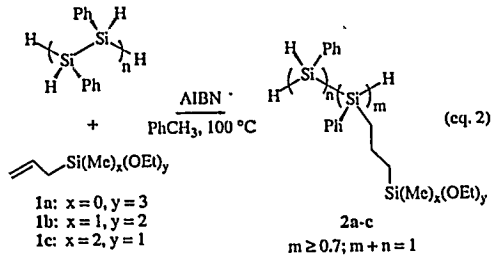
While only arylsilanes can be polymerized by this route, the resulting oligophenylsilane can be functionalized by free radical hydrosilation of olefins, carbonyls and imines.[4] Substitution along the polysilane backbone with sol-gel precursors should generate soluble functionalized polymer and ought to yield, after sol-gel polymerization, materials where the chromophore is entrained within a relatively inert siloxane matrix, an attractive strategy for utilizing polysilanes under thermally demanding or photooxidative conditions. Here we describe the extension of this approach to include (alkoxysilyl)propyl functionalities as latent sol-gel polymerizable residues, and the preparation of a new class of hybrid organic-inorganic polysilane-siloxane materials, derived from the sol-gel polymerization of functionalized polysilanes 2a-c (eq. 2).

EXPERIMENTAL

General. Allyltriethoxysilane was obtained from Aldrich and distilled from calcium hydride under argon prior to use. Allylmethyldiethoxysilane and allyldimethylethoxysilane were prepared by ethanolysis of their respective chloride precursors (Gelest) by procedures analogous to those described elsewhere.[5] Polyphenylsilane was prepared by the method described earlier by Waymouth[6] using zirconocene hydride chloride (Aldrich) and phenylsilane (Acros). Anhydrous toluene and THF were from Aldrich (Sure/Seal™). AIBN (Kodak) was recrystallized from ethanol prior to use.

Free Radical Hydrosilation of Allyl(ethoxy)silanes. In a typical experiment, 5.0 g (47 mmol) of polyphenylsilane (M_w = 4887, M_w/M_n = 1.23), 11.74 g (57 mmol) of allyltriethoxysilane and 0.77 g (4.7 mmol, 10 mol% based on polyphenylsilane) AIBN were dissolved in 50 mL dry

§This work was supported by the United States Department of Energy under Contract No. DE-AC04-94AL85000.



(eq. 2)

1a: x = 0, y = 3
1b: x = 1, y = 2
1c: x = 2, y = 1

2a-c
m ≥ 0.7; m + n = 1

toluene and heated at reflux for four hours. Following cooling to room temperature the reaction volume was reduced to approximately 10 mL and then transferred via cannula to a flask of vigorously stirred, dry methanol (100 mL). Repeated precipitations (3x) yielded 2.41 g of functionalized polymer 2a as a pale yellow, waxy material. M_w = 10,635, M_w/M_n = 1.23 (polystyrene standard).

Sol-Gel Polymerization of Poly(ethoxysilylpropyl)(phenyl)-silanes. In a typical experiment, 2.5 g (8.05 mmol) of poly(triethoxysilylpropyl)(phenyl)silane 2a was dissolved in 4 mL dry THF in a 10 mL volumetric flask. In a separate vial, 0.42 mL of 1N HCL solution was dissolved in 2 mL dry THF. The acid/THF solution was added to the polysilane solution and the total volume adjusted to 10 mL. After thoroughly mixing, the solution was allowed to stand overnight, protected from light, during which time the mixture gelled to hybrid material 3a. Polysilane xerogels were processed by crushing the gel in a vast excess of water and filtering. Two additional washes with water and finally with diethyl ether, followed by vacuum drying at 100 °C yielded the final material as a white solid. Aerogels were processed by supercritical CO_2 extraction.

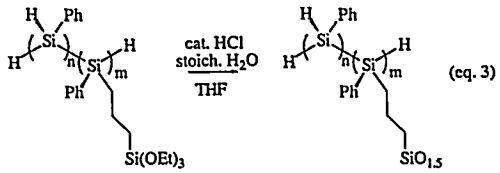
RESULTS

Poly(alkoxysilylpropyl)(phenyl)silanes. Free radical-initiated hydrosilation of allyl(ethoxy)silanes 1a-c with polyphenylsilane leads to efficient backbone elaboration with little degradation of the silicon catenate (eq. 2). GPC analysis of functionalized poly(triethoxysilylpropyl)(phenyl)silane 2a indicates that a small amount of degradation, probably to form stable cyclic oligomers, has taken place, but that the majority of material remains as linear polymer of modest molecular weight (for 2a, M_w = 10,635; M_w/M_n = 1.23).

Integration of the ^{1}H NMR spectrum of functionalized polysilanes 2a-c yields information regarding the degree of polysilane backbone substitution; in all cases hydrosilation of allyl silanes 1a-c yielded polysilanes with 70% or greater substitution. This is corroborated by inspection of the infrared spectra (comparison of the intensity of the Si-H stretching band relative to the aromatic fingerprint region) to give a semi-quantitative value for the amount of backbone silicon substitution. The sol-gel precursors have also been characterized by solution ^{13}C and ^{29}Si NMR.

Polysilane/Polysiloxane Hybrid Materials. Hydrolysis-condensation of the ethoxysilane groups under acid-catalyzed conditions (5 mol% HCl, in ethanol) yields opaque white gels 3a-c within 4 hours (eq. 3). (It is interesting to note that under basic conditions no gels form, and in fact polysilane backbone degradation takes place). The gels can be processed to give nonporous xerogels by washing with excess water and vacuum drying, or processed as aerogels by solvent extraction under a supercritical CO_2 atmosphere to give materials with modest surface areas; the dried samples were ground prior to analyses.

All dried gels were determined to be amorphous by x-ray diffraction analysis. Solid state ^{13}C NMR spectra (CPMAS NMR) of the xero- or aerogels confirm the retention of the aromatic and aliphatic (propyl) organic groups under the sol-gel reaction conditions. For example, the ^{13}C NMR of xerogel 3b displays aromatic resonances at approximately 137 and 127 ppm; two aliphatic signals appear at 20 and 0 ppm, assigned to the



2a 3a (eq. 3)

propylene chain and the terminal methyl group of the siloxane D^n silicons (n = 1, 2, *vide infra*).

^{29}Si CPMAS NMR reflects two general types of silicon environment; polysilane backbone silicons generate a broad signal at -34 ppm in 3b, and both partially condensed D^1 and fully condensed D^2 siloxane silicons can be identified at -17 and -20 ppm, respectively (Fig. 1).

When the solutions are cast as thin films, solid state UV-Vis spectroscopy confirms the retention of the polysilane backbone, reflected in the characteristic long wavelength absorption at $\lambda = 320$ nm for 3a (Fig. 2). The polysilane-polysiloxane composites also display typical photobleaching behavior upon irradiation with UV light.[7]

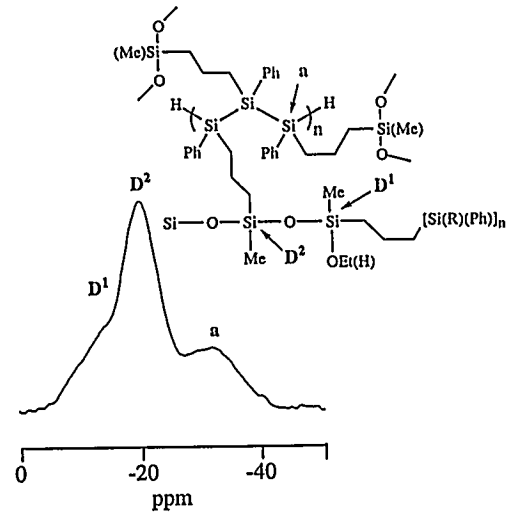


Figure 1. ^{29}Si CPMAS NMR sectrum of hybrid polysilane-polysiloxane xerogel 3b.

Nitrogen sorption analysis of the polysilane-polysiloxane nanocomposites indicate that the xerogels are nonporous. However, mesoporous aerogels of modest surface area (Type IV isotherm; ≈ 420 m^2/g for aerogel of 3a; BET) result from supercritical CO_2 processing of the polysilane-polysiloxane wet gels. Scanning electron microscopy

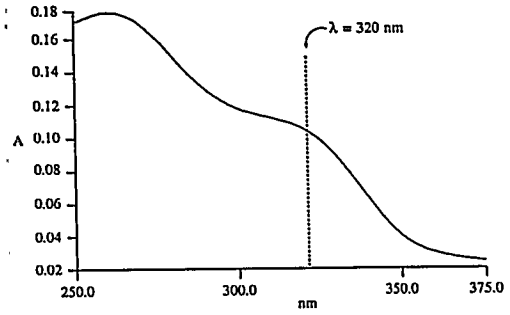


Figure 2. Solid state UV-Vis spectrum of polysilane-polysiloxane 3a.

corroborates the aerogel mesoporosity, displaying granular fracture surfaces with particle diameters approximately 60 nm across.

SUMMARY

AIBN-initiated functionalization of polyphenylsilane with allyl(ethoxy)silanes generates (ethoxysilylpropyl)polysilanes in good yield. Amorphous polysilane-polysiloxane hybrid nanocomposites can be prepared by the mild, acid-catalyzed sol-gel hydrolysis-condensation of polysilane-based precursors 2a-c at the pendant alkoxysilane residues. UV-Vis and multinuclear NMR spectroscopies establish the retention of the polysilane chromophore and attached organic residues; NMR also reflects the degree of condenstion at the siloxane silicon nuclei. The bulk morphology of the resulting dried gels can be influenced by the choice of solvent removal from the wet gel. Aqueous extraction of solvent results in nonporous xerogels, while solvent removal by supercritical CO_2 yields mesoporous aerogels with retention of the wet gel surface area.

In hybrid materials 3a-c the polysilane chromophore is homogeneously dispersed in, and covalently bound to, a highly crosslinked siloxane matrix. The demonstrated ability to homogeneously entrain polysilanes within glass matrices holds great potential for fabricating sophisticated electronic, NLO and photoconducting devices.

REFERENCES

[1] For a review on polysilanes and their properties: Miller, R. D.; Michl, J. *Chem. Rev.* 1989, *89*, 1359.
[2]. Hayase, S. *CHEMTECH* 1994, *24*, 19.
[3]. Tilley, T. D. *Acc. Chem. Res.* 1993, *26*, 22 and references cited therein.
[4]. Hsiao, Y.-L.; Waymouth, R. M. *J. Am. Chem. Soc.* 1994, *116*, 9779.
[5]. Jamison, G. M.; Loy, D. A. and Shea, K. J. *Chem. Mater.* 1993, *5*, 1193.
[6]. Banovetz, J. P.; Stein, K. M.; Waymouth, R. M. *Organometallics* 1991, *10*, 3430.
[7]. Beach, J. V.; Loy, D. A.; Hsiao, Y.-L.; Waymouth, R. M. *ACS Symp. Ser.* 1995, *614* (*Microelectronics Technology*), 355.

DISCLAIMER

New Hybrid Polysilane/ Polysiloxane Nanocomposites

Gregory M. Jamison, Douglas A. Loy,
Kimberly A. Opperman and James V. Beach

Properties of Organic Materials Department
Sandia National Laboratories
Albuquerque, New Mexico 87185-1407

Robert M. Waymouth

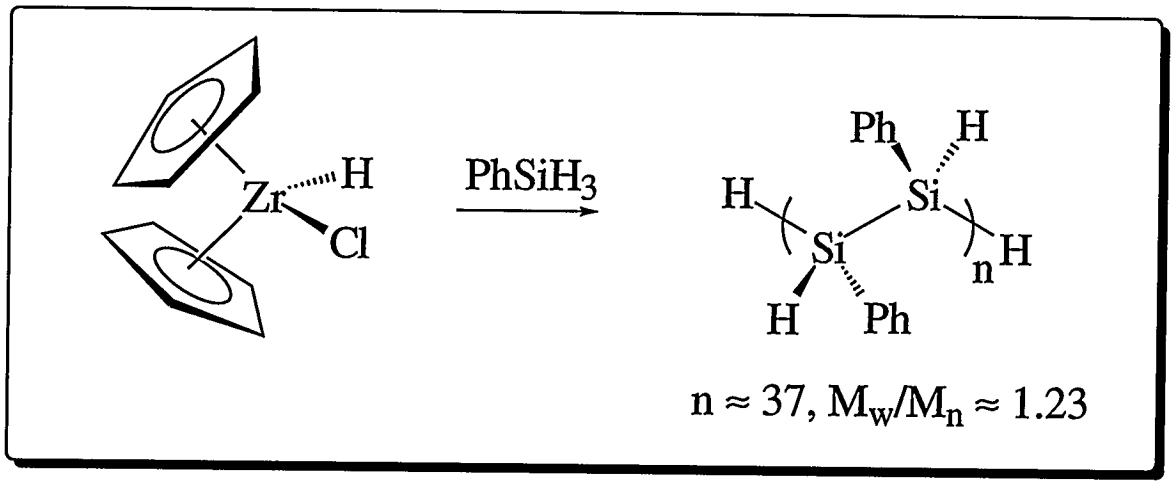
Department of Chemistry
Stanford University
Stanford, California 94305-5080

This work supported by the United States Department of Energy under Contract No. DE-AC04-94AL85000.

Background

- Polysilanes $[Si(R)(R')]_n$ display polyene-like electronic characteristics by virtue of σ-conjugation associated with the saturated, all-silicon backbone ($\lambda_{\sigma-\sigma^*} \approx 320\text{-}360$ nm).

- Zirconocene-catalyzed Si-H σ-bond metathesis of phenylsilane generates oligophenylsilane as a safe, economically attractive alternative to reductive coupling of dichlorosilanes.

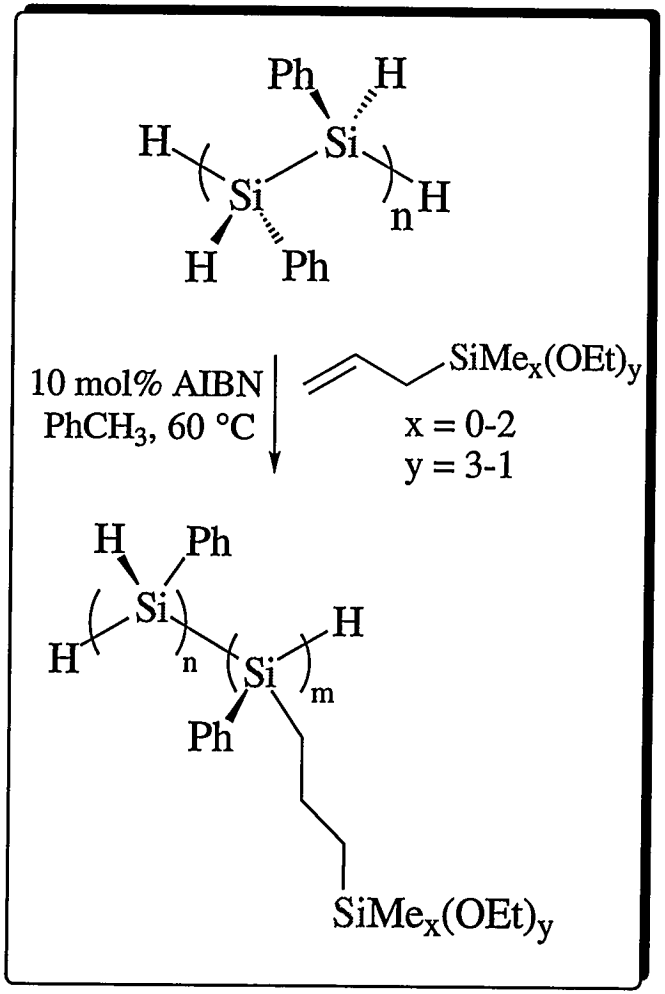


$n \approx 37$, $M_w/M_n \approx 1.23$

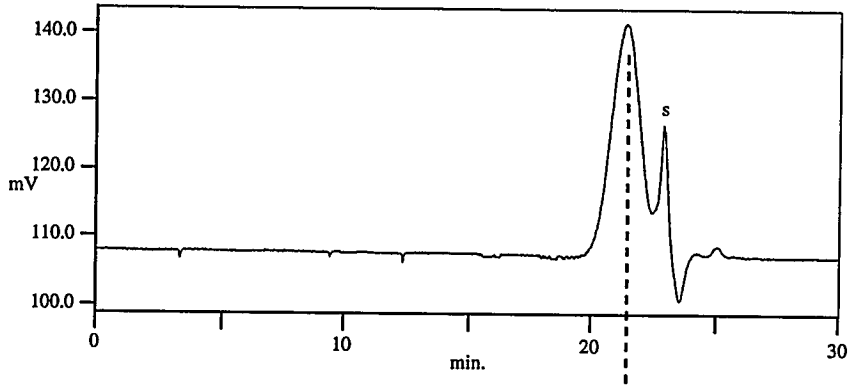
Harrod et. al.
J. Am. Chem. Soc. **1986**, *108*, 4059.

- Other advantages include greater latitude in chemically functionalizing oligophenylsilane by taking advantage of the reactivity of the Si-H bond.

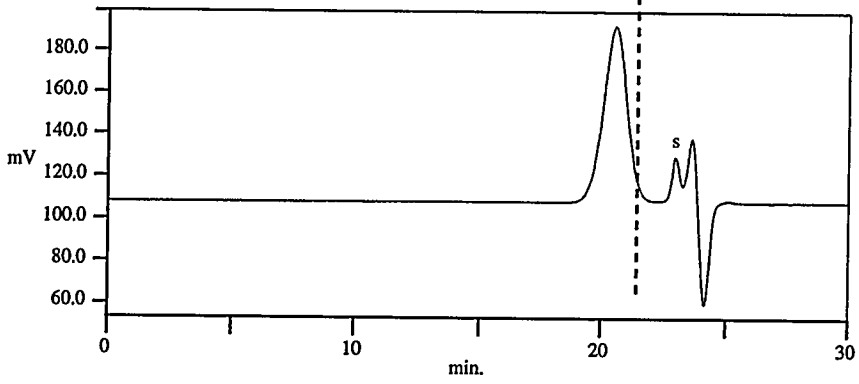
Waymouth *et. al.* have developed a methodology for free radical hydrosilation of unsaturated organic substrates (*J. Am. Chem. Soc.* **1994**, *116*, 9779). We have extended this approach to include the incorporation of latent siloxane groups via the hydrosilation of allyl(ethoxy)silanes.



$M_w/M_n = 4887/3971 = 1.23$

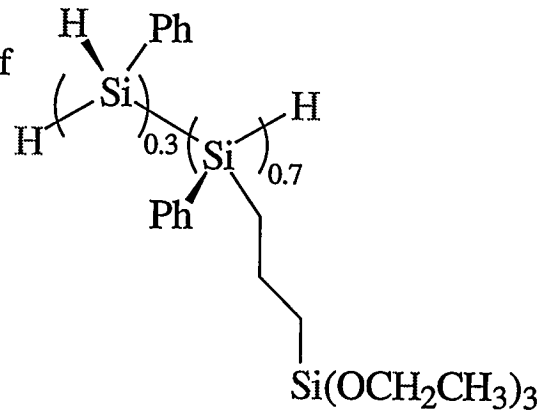


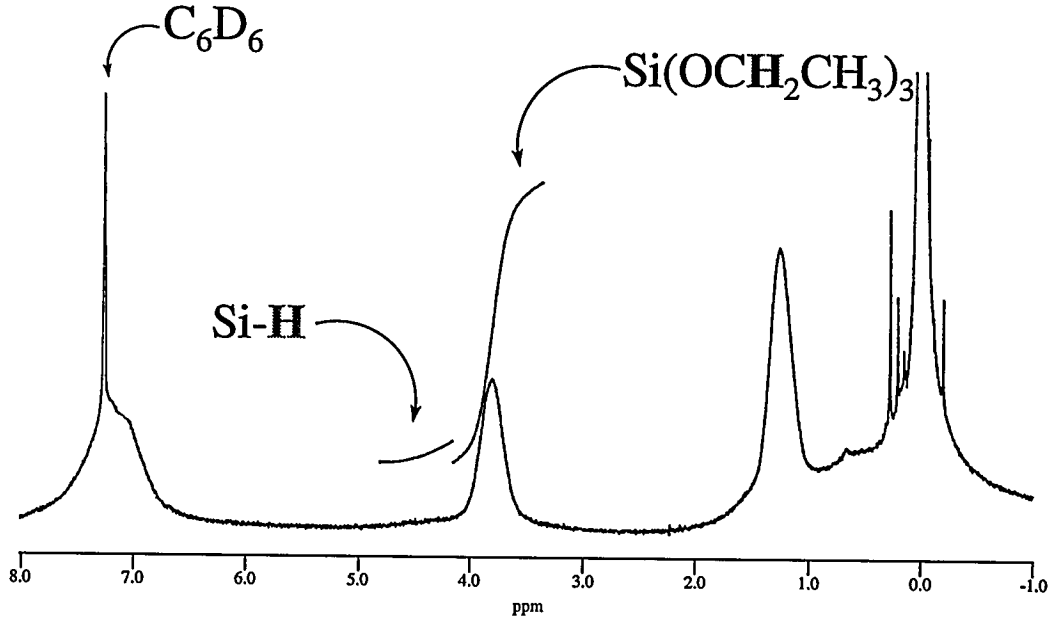
$M_w/M_n = 10{,}635/8636 = 1.23$

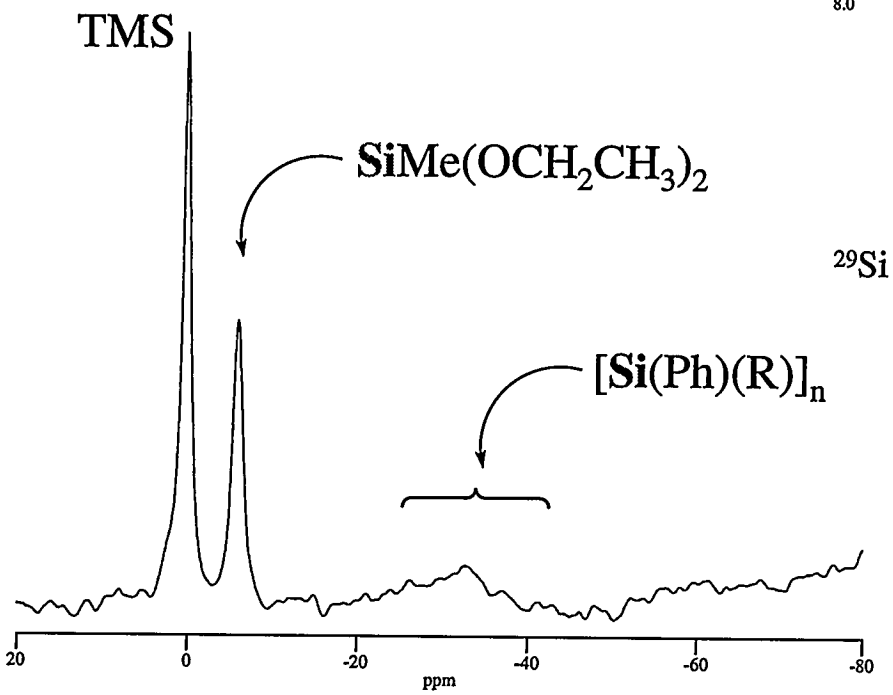


Characterization of Polysilane Sol-Gel Precursors by Multinuclear NMR Spectroscopy

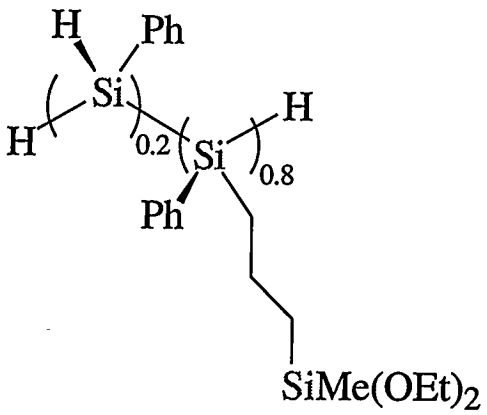
^{1}H NMR of



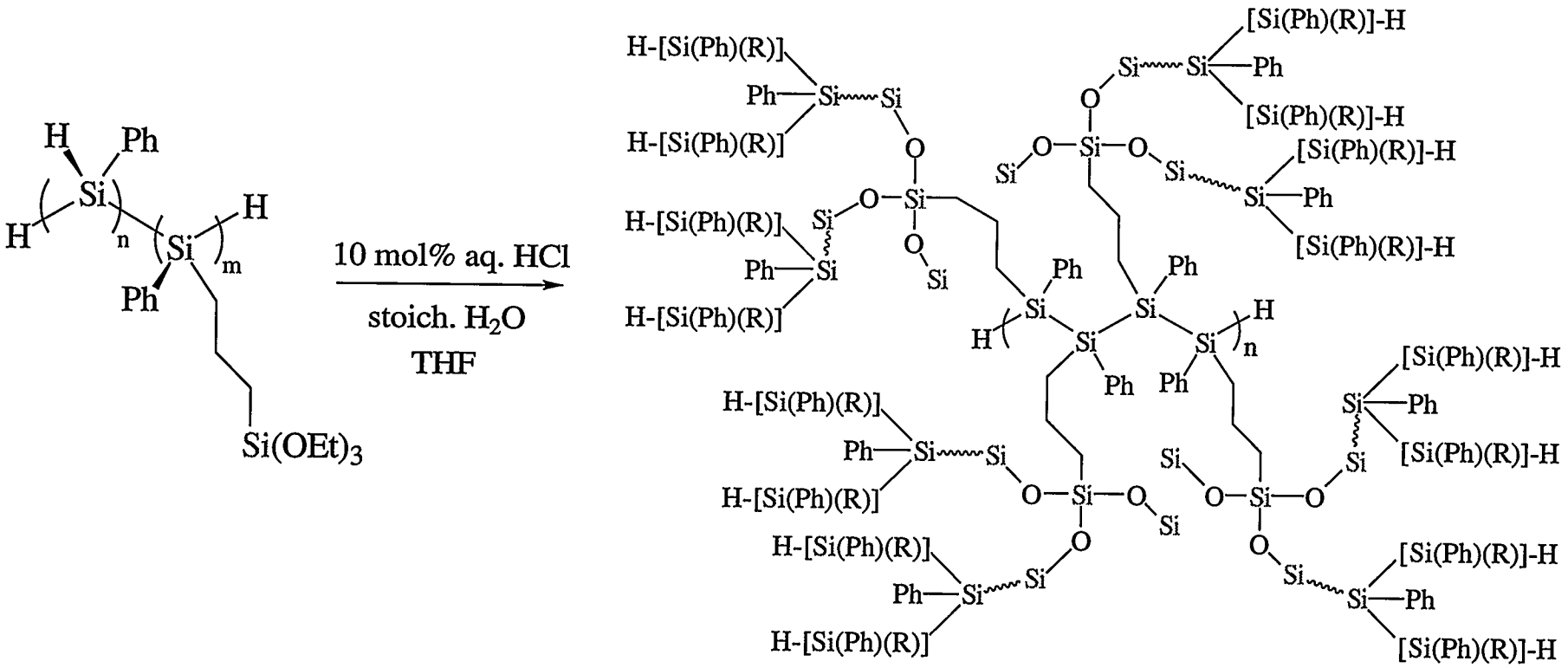




^{29}Si NMR of



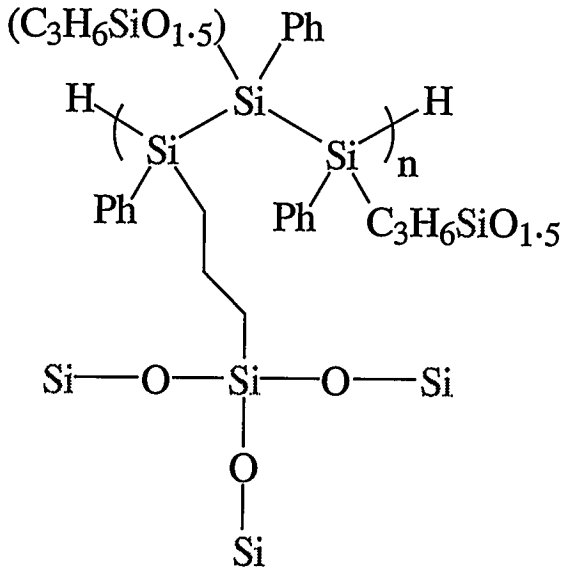
Acid-catalyzed sol-gel hydrolysis-condensation of the alkoxysilane residues leads to new oligosilane-siloxane hybrid materials.



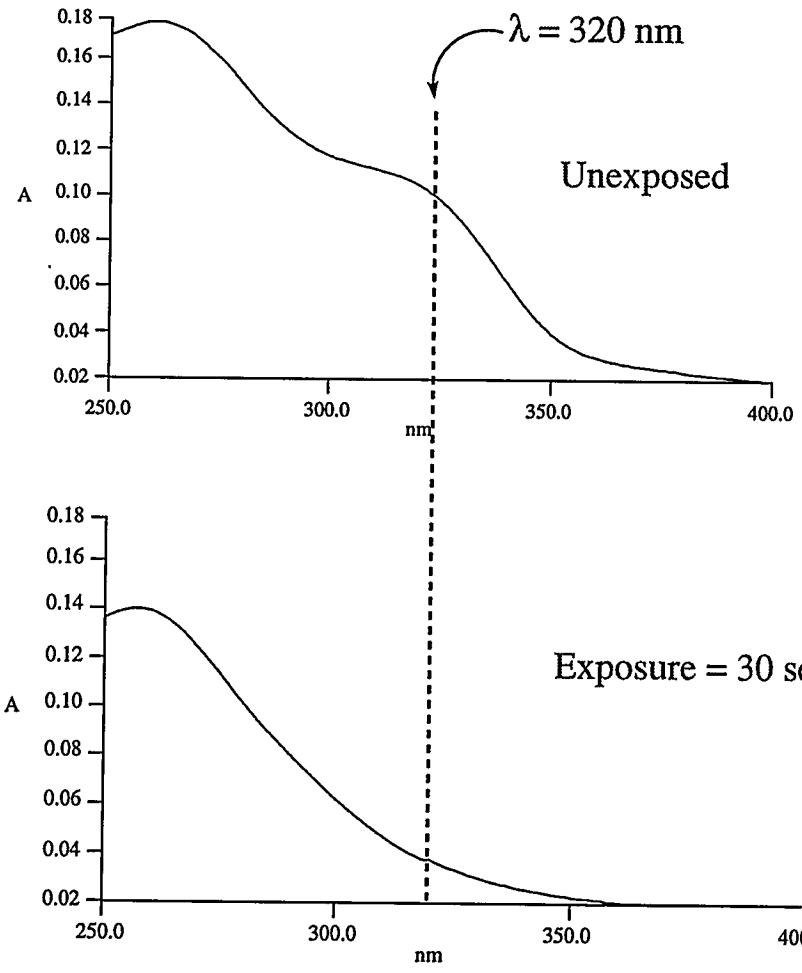
NOTE: Base-catalyzed sol-gel conditions lead to degradation of the polysilane backbone ⇒ NO GEL FORMS!!

The Oligosilane Chromophore Remains Intact and Displays Characteristic Photobleaching Behavior (Loy, Waymouth in *Microelectronics Technology*, ACS Symposium Series 614, p. 355 (1995)).

Solid State Photobleaching of

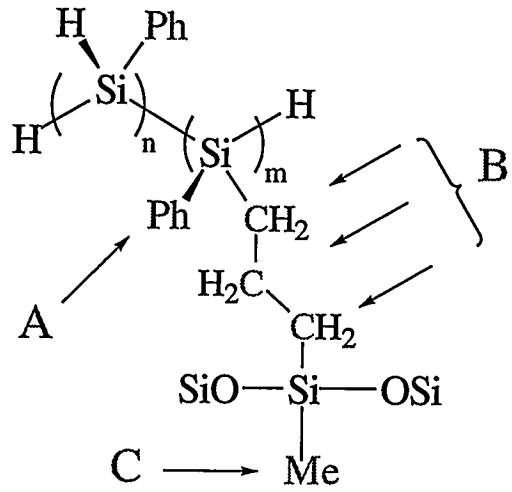


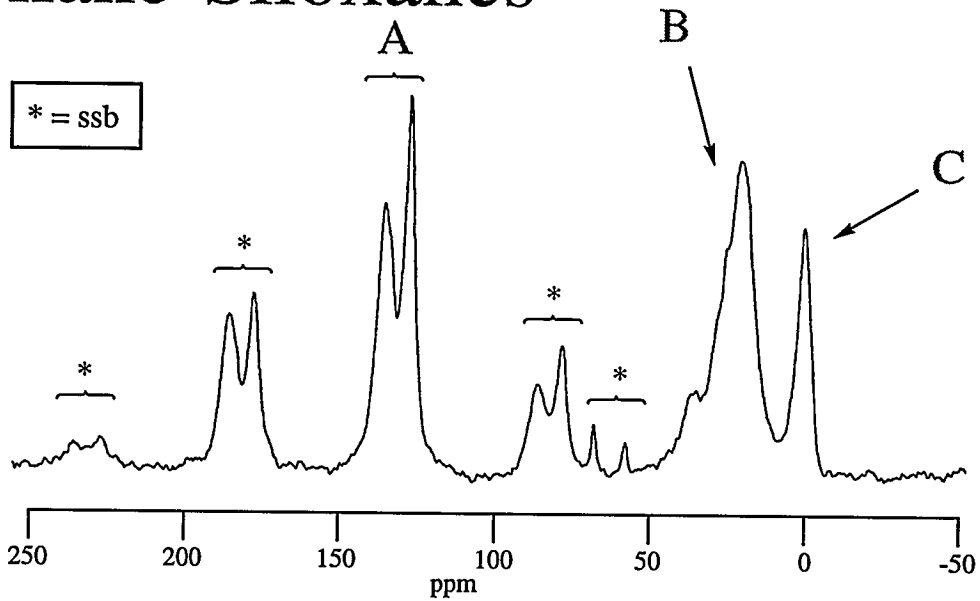
*UV exposure with 200W Hg/Xe lamp



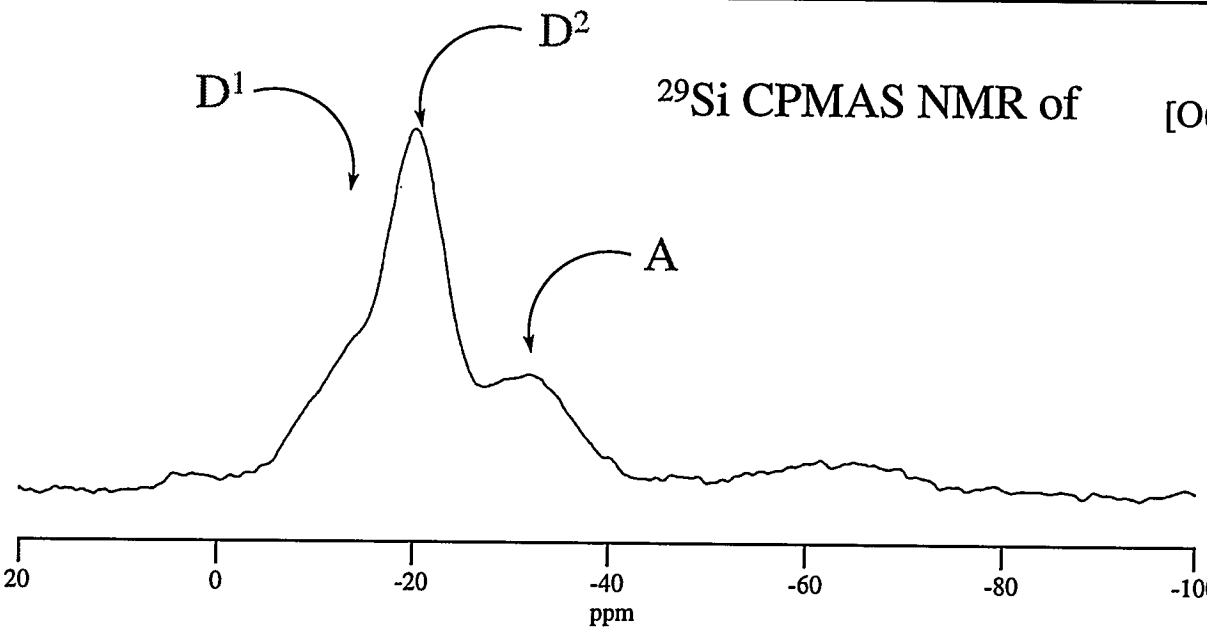
Multinuclear NMR Characterization of Oligosilane-Siloxanes

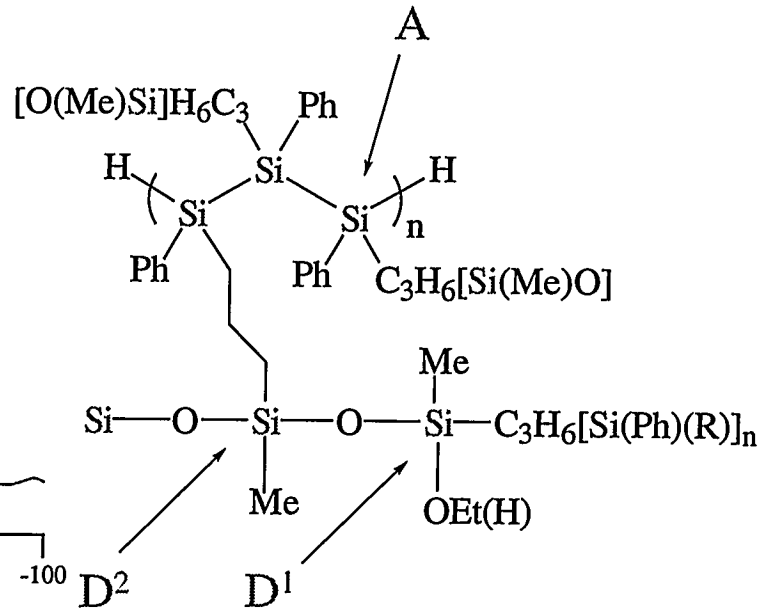
^{13}C CPMAS NMR of





^{29}Si CPMAS NMR of

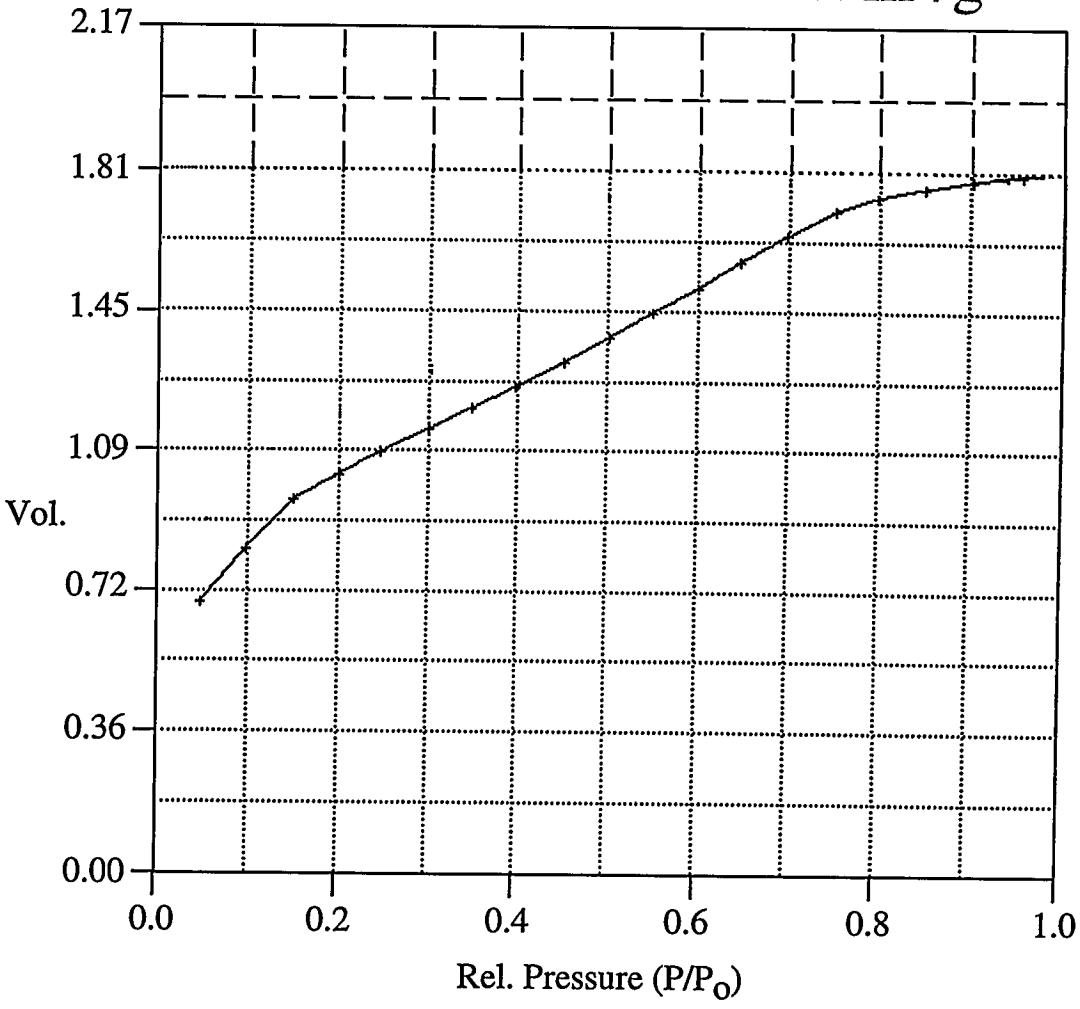


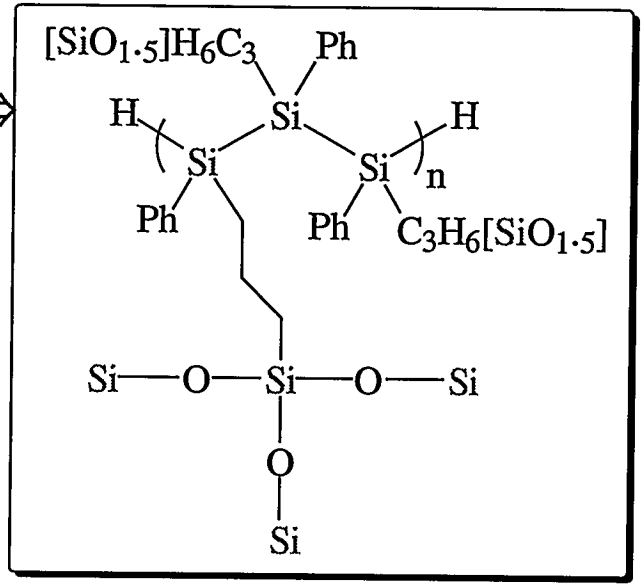


Surface Analysis

Type IV N_2 adsorption isotherm for polysilane aerogel ⇒ ⇒ ⇒ ⇒ ⇒ ⇒

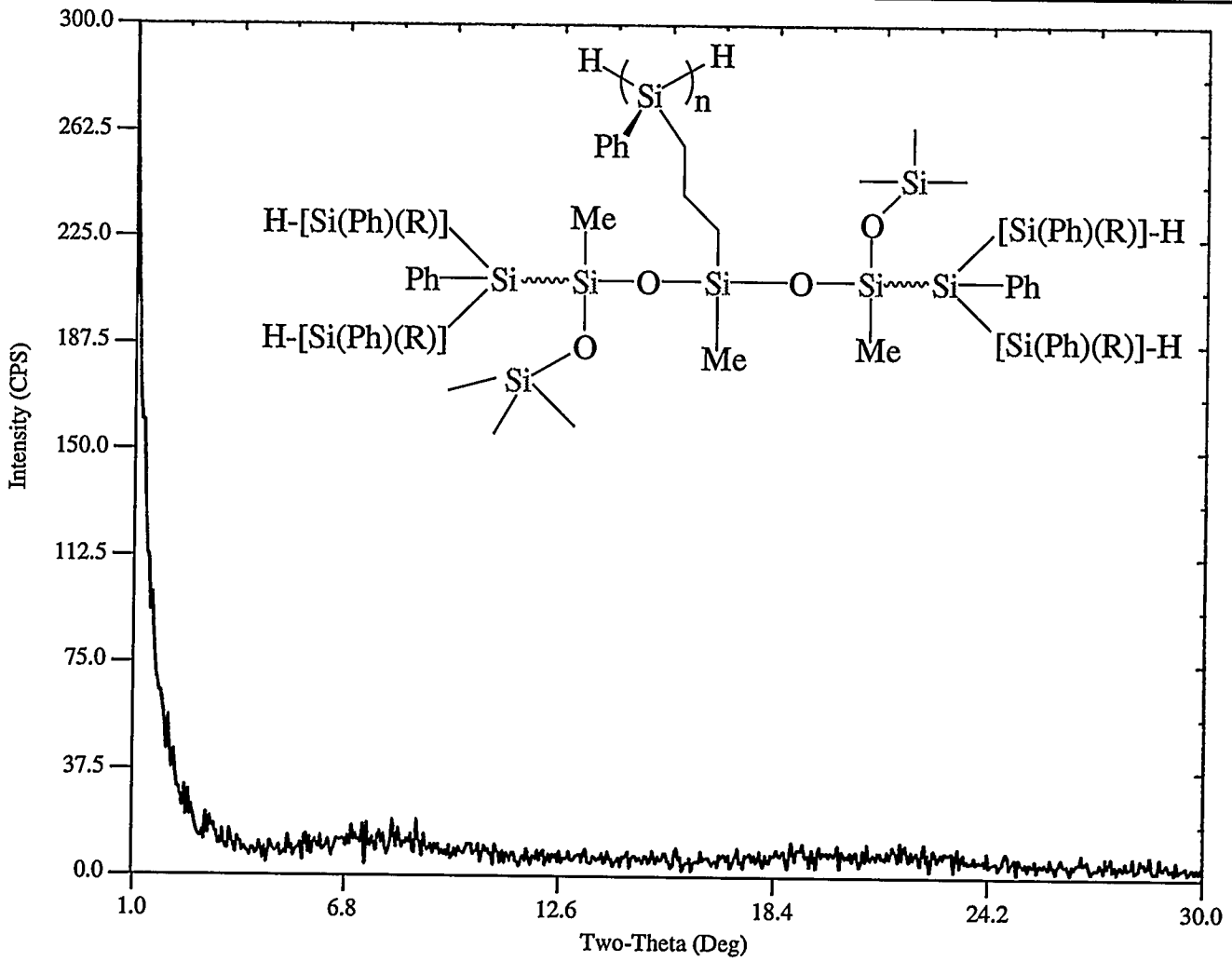
BET Surface area = 422 m^2/g





- Processing affects bulk properties.
- Xerogels - nonporous
- Supercritical CO_2-mesoporous aerogels.

None of the Oligosilane-Siloxane Materials Display Long Range Crystallinity; All Are Amorphous as Determined by XRD



SEM Micrographs Reveal Granular Fracture Surfaces, Confirming Mesoporosity

Summary

- Oligophenylsilane can be functionalized with sol-gel precursor side groups.
- Acid-catalyzed sol-gel polymerization leads to new hybrid oligosilane-siloxane network materials.
  - Base catalysis does not lead to gels, and degrades the oligosilane backbone.
- UV-Vis and multinuclear NMR spectroscopies verify that the oligosilane chromophore survives acid-catalyzed conditions.
  - Strong UV exposure leads to oligosilane photobleaching (thin film).
- The amorphous oligosilane-siloxane composites can be processed to nonporous xerogels or mesoporous aerogels of modest surface area (~ 400 m^2/g).

Acknowledgements

Solution ^{29}Si, CPMAS ^{13}C, ^{29}Si NMR

Todd Alam, Ralph Hunkins, SNL

XRD Analysis

Mary Gonzales, SNL

Nitrogen Sorption Porosimetry

Brigitta Baugher, SNL