

## NON-SHRINKING SOL-GEL TYPE POLYMERS BY RING OPENING POLYMERIZATION

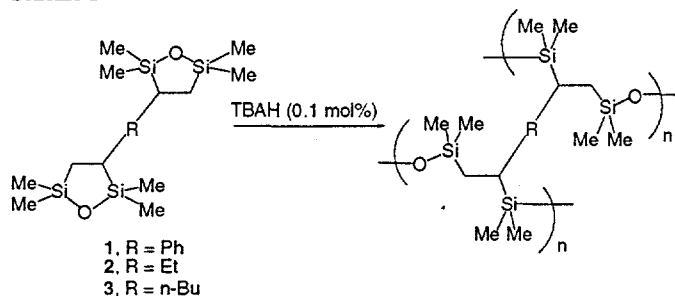
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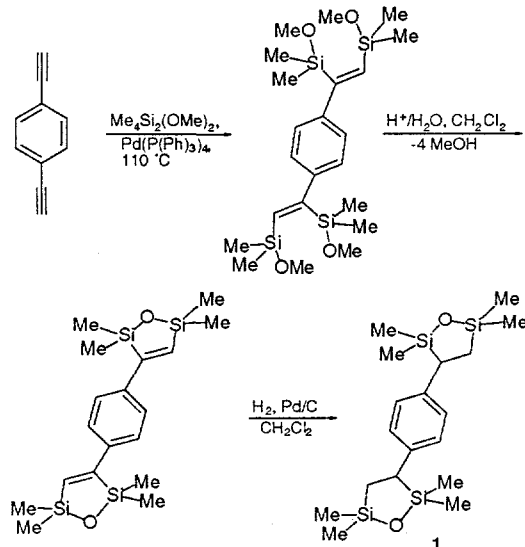
## Introduction

Hydrolysis and condensation of alkoxy silanes to form highly crosslinked siloxane gels has become synonymous with sol-gel polymerization.<sup>[1,2]</sup> However, application of these sol-gel systems has been limited by shrinkage associated with evaporation of the solvent needed for monomer/water miscibility and the resulting condensation products formed during polymerization. An attractive strategy for reducing shrinkage is to eliminate solvent<sup>[3]</sup> and condensation byproducts entirely by replacing the step growth polymerization used in sol-gel processing of alkoxy silanes with a chain growth polymerization, such as ring-opening polymerization (ROP). ROP is a chain growth process that has proven to be an effective means for reducing or, as with the polymerization of spiroorthocarbonates, completely eliminating shrinkage in linear, hydrocarbon polymers.<sup>[4]</sup> Here, we report on the ring opening polymerization (ROP) of arylene, **1**, and alkylene (ethylene, **2**, and butylene, **3**), bridged disilaoxacyclopentanes (scheme 1), as well as their copolymerization with the simple 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane (**4**), to make sol-gel type materials and their application in encapsulation of microelectronics.

Scheme 1



Scheme 2



## Experimental Section

**Monomer syntheses.** Scheme 2 shows the synthetic scheme for preparation of the phenylene-bridged disilaoxacyclopentane, **1**, which also applies to the preparation of the ethylene (**2**) and butylene (**3**) bridged

precursors. All compounds have been spectroscopically characterized and experimental details will be published in future publications.

**Polymer syntheses.** Polymerization of **1**, a white solid, can be achieved either neat as a melt polymerization using octadecylamine as catalyst, or as a solution in THF (**IM**) using Bu<sub>4</sub>NOH (TBAH) as catalyst. Rapid polymerization of all monomers can be achieved when polymerized as a copolymer system with **4**, using TBAH as catalyst.

## Results and Discussion

Monomer **1** can readily be polymerized either in THF or when dissolved in monomer **4** (used as a solvent/co-monomer) to give transparent, yellow-tinted gels which show no visible shrinkage during polymerization. Furthermore, because the copolymer is prepared without solvent, total shrinkage is kept to less than 5% compared with 50-90% for traditional sol-gels. Because the resulting gels are insoluble, solid state NMR and infrared spectroscopy are used in their characterization. <sup>29</sup>Si NMR confirmed the opening of the disilaoxacyclopentane rings with the pronounced upfield shift in the two observed resonances; 21.9 and 20.9 ppm for **1** in solution and 9.8 and 5.5 ppm for the homopolymer in the solid state. This upfield shift is consistent with the release of ring strain in the five membered ring with ROP.<sup>[5]</sup> This is further confirmed when comparing the IR spectra of **1** and its homopolymer; the resonance at 920.7 cm<sup>-1</sup> due to the cyclic SiOSi stretch in **1** is replaced by the broad resonance at 1061.8 cm<sup>-1</sup> due to acyclic SiOSi stretches in the homopolymer.

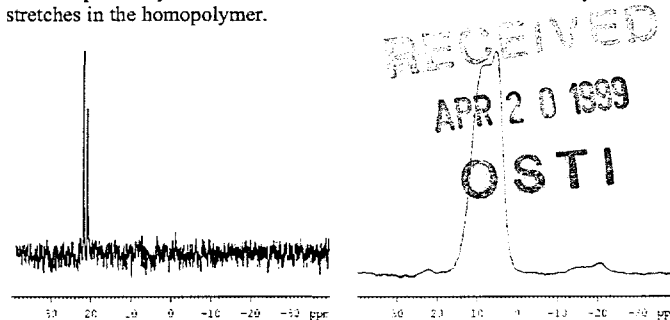


Figure 1. <sup>29</sup>Si NMR spectra for monomer **1** and its homopolymer. NMR resonances for **1** (left spectrum) are 21.9 and 20.9 ppm and those for the polymer (right spectrum) are 9.8 and 5.5 ppm.

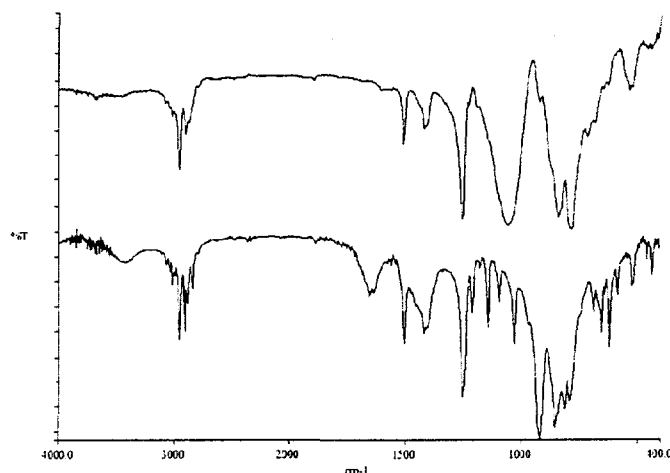


Figure 2. IR spectra of monomer **1** (bottom spectrum) and its homopolymer (top spectrum).

By using **4** as both a solvent and a reactive monomer in the polymerization, the entire solution is converted into a network polymer and shrinkage can be further reduced. Exothermic polymerization of a mixture of **4** and **1** (80:20 by weight) with TBAH (0.2 mol% based on **4**) gives rise to a transparent, crack-free gel within seconds of mixing. Higher catalyst concentration (1 mol% based on **4**) leads to generation of enough heat during polymerization to cause bubbles to form (presumably due to monomer

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volatilization) and become entrapped within the resulting gel. Solid state  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR reveal a polymer composition representative of starting comonomer ratio (80:20) and no detectable unreacted monomer in the final gel.

Thermal gravimetric analysis of the polymers (figure 3) revealed relatively robust materials in homopolymer of 1 and its copolymer with 4 compared to the linear polymer of 4, which begins to degrade at 250 °C and is completely depolymerized by 500 °C. In contrast, the homopolymer of 1 begins to decompose at 375 °C and leaves a ceramic residue (17.1%). The copolymer shows an initial weight loss of about 4% followed by complete degradation starting at 500 °C. The addition of the phenylene-bridged crosslinker to the polymer of 4 increases the thermal stability by over 150 °C.

Nitrogen sorption porosimetry and scanning electron microscopy of the homopolymer of 1, prepared in THF, and the copolymer of 1 and 4 revealed no significant micro- or mesoporosity (figure 4). This lack of porosity suggests that the gels are composed of network polymers that are compliant enough to permit collapse of the pores.<sup>[6]</sup>

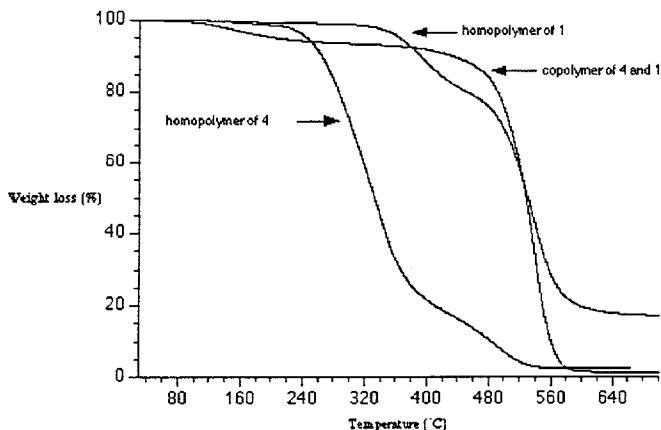


Figure 3. TGA plot comparing the weight loss of homopolymers of 1, 4, and 80:20 copolymer of 4 and 1.

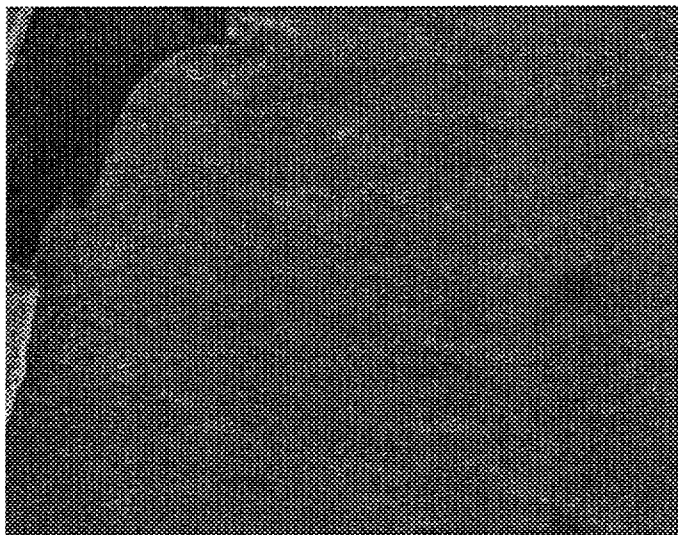


Figure 4. SEM photograph of 80:20 copolymer of 4 and 1.

A microelectronic test chip was successfully encapsulated using the ROP of the 80/20 mixture of 4 and 1. The copolymer formed quickly around the test chip as a transparent, slightly yellow resin with only few bubbles forming due to the heat of polymerization (figure 5). No visible cracks or shrinkage of the encapsulant were observed.

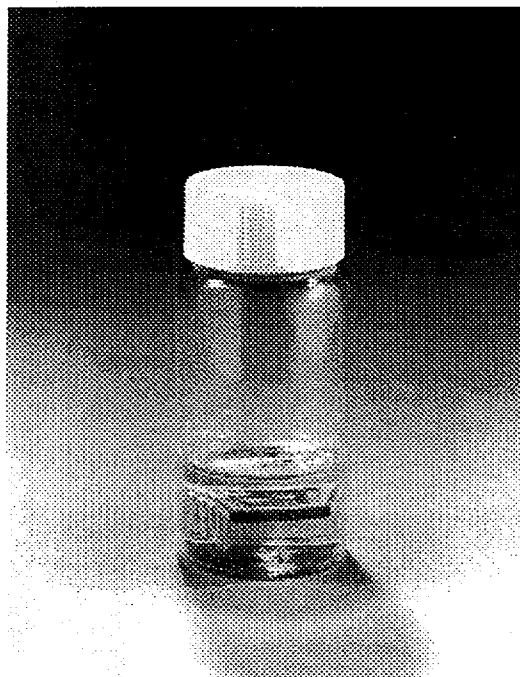


Figure 5.

## Conclusions

We have designed a new class of cyclic siloxane compounds that behave as sol-gel systems when ring open polymerized using a hydroxide base. These monomers polymerize through chain growth polymerization, unlike conventional alkoxysilane sol-gel precursors, to form sol-gel polymers. They do not require solvent or water for polymerization, show no visible shrinkage or cracking during polymerization and are thermally stable. We have successfully utilized these materials in encapsulation of microelectronics. Current efforts are focused toward expanding this family of ROP monomers and optimization of their mechanical properties.

## Acknowledgments

We would like to thank Duane Schneider and Brigitta Baugher for their unwavering technical support. We would also like to thank Dr. David R. Wheeler and Dr. Gregory M. Jamison for numerous technical discussions relating to this work, and Roger A. Assink and Todd M. Alam for NMR spectroscopy assistance. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

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