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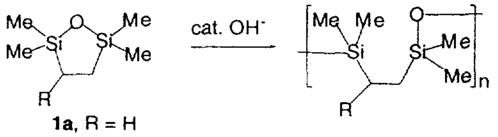
Arylene-Bridged 2,2,5,5-Tetramethyl-2,5- Disila-1-Oxacyclopentanes as Precursors to Non-Shrinking Polysiloxanes. A New Route to Sol-Gel Type Polymers

*Kamyar Rahimian and Douglas A. Loy**

Encapsulants and Foams Department, Sandia National Laboratories,
Albuquerque, NM 87185-1407

Introduction

Sol-gel chemistry has been the focus of much attention in the design and preparation of highly crosslinked polysiloxane gels. Preparation of sol-gel processed silica or polysilsesquioxane gels is carried out by the hydrolysis and condensation of alkoxysilyl monomers, usually in the presence of catalytic acid or base and an excess of water. Removal of the alcohol and water byproducts of the condensation reactions, in addition to the alcohol needed to co-dissolve the hydrophobic monomers with water, leads to substantial shrinkage during drying of the resulting gels. This limits the utility of sol-gel processing for applications requiring net-shape casting of artifacts, crack free coatings, or low vaporous organic contaminants (VOC's). It would be advantageous to have a sol-gel process based on an organosilicon monomer that would not require water as a reactant or produce water and alcohol condensation products and still result in siloxane network polymers capable of forming gels. Furthermore, it would be beneficial to eliminate solvents altogether to further minimize shrinkage and VOC's. Ring opening of cyclic monomers such as lactams, lactones, cyclic ethers, spiroorthocarbonates, and oligosiloxanes has proven to be an effective method in reducing shrinkage, even increasing volume, accompanying polymerization.[2] The organosilicon equivalent of the above, 2,2,5,5,-tetramethyl-2,5-disila-1-oxacyclopentane (R = H), was demonstrated to readily undergo anionically-catalyzed ring-opening polymerization to afford high molecular weight poly(1,2-ethylene-bis(dimethylsiloxane)).[2] Here, we show the synthesis and preparation of a novel sol-gel monomer which can easily be polymerized by ring opening polymerization to give highly crosslinked polysiloxane gels with no condensation byproducts.



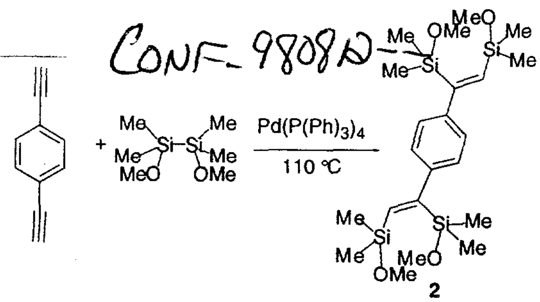
(1)

1a, R = H
1b, R = Ph

Results and Discussion

In order for a monomer to be a suitable sol-gel precursor it must be capable of forming a crosslinked polymer. Monomers **1a-b** are difunctional and can only form linear polymers. By connecting two or more of the 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentyl groups together, one has a crosslinking monomer analogous to divinyl benzene. The phenylene-bridged monomer (**4**) was prepared in three steps from p-diethynylbenzene; 3-phenyl-2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane (**1b**) was prepared as a model compound from ethynylbenzene by the same procedures.

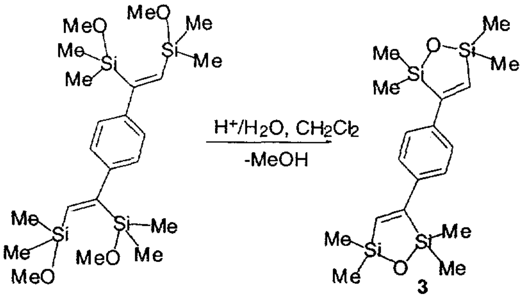
Compound **2**, a potential sol-gel monomer in its own right, was prepared in high yield (85% isolated) by disilylation of *p*-diethynylbenzene with 1,2-dimethoxy-tetramethyldisilane in the presence of a palladium catalyst (equation 2).[3] Disilylation results in formation of only the *cis* isomer. NMR spectroscopy provides an easy handle on the characterization of this compound; the ^1H NMR of the product shows only one vinylic proton and the ^{29}Si NMR shows the presence of two inequivalent silicons.



(2)

2

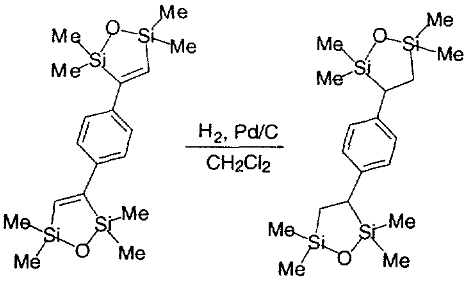
The corresponding phenylene-bridged 2,5-disila-1-oxacyclopentene **3** was prepared through the mild, acid-catalyzed condensation of compound **2** (equation 3). There was no intermolecular coupling during ring closure and compound **3** was isolated in quantitative yield. The NMR spectrum of **3** is very similar to that of compound **2** with only one vinylic proton and inequivalent silicons due to the *cis* geometry, but minus the methoxide resonances.



(3)

3

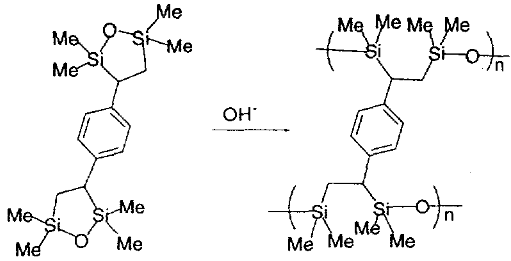
Attempts to polymerize the 2,5-disila-1-oxacyclopentene monomers **3** or the unsaturated precursor to **1b** were met with failure. The unsaturated cyclic compounds did not undergo ring-opening polymerization with a variety of anionic catalysts and conditions. Conversion of the monomers to their more reactive, hydrogenated forms (**1b** and **4**) was quantitative in the presence of hydrogen and Pd/C catalyst (equation 4).



(4)

4

Anionic ring-opening polymerization of **4** (1M) in tetrahydrofuran was easily achieved with catalytic Bu_4NOH at room temperature (equation 5). The resulting polymer formed a transparent gel and no shrinkage was observed during the polymerization.



(5)

DISCLAIMER

Conclusions

We have successfully prepared and characterized the first member of a new class of sol-gel monomers which can easily be ring-opening polymerized to give a highly crosslinked polymer. Monomer **4** reacted with catalytic tetrabutylammonium hydroxide to afford a transparent gel. The ring-opening polymerization reaction eliminates the problems associated with normal sol-gel condensation byproducts and since water is not required for hydrolyzing alkoxide groups, solvent can also be eliminated. Current efforts are directed at preparing copolymers of **4** with monomers **1a-b** and synthesis of additional bridged 2,5-disila-1-oxacyclopentane monomers.

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