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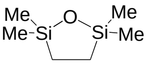
Phenylene-Bridged Cyclic Siloxanes as Precursors to Nonshrinking Sol–Gel Systems and Their Use as Encapsulants

Douglas A. Loy,* Kamyar Rahimian, and Michael Samara

Sol–gel polymerization has been the focus of much attention in the design and preparation of highly cross-linked polysiloxane gels.[1, 2] However, application of sol–gel systems has been limited by the shrinkage associated with the 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[3] and condensation byproducts entirely by replacing the step-growth polymerization used in the sol–gel processing of alkoxysilanes 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.[4] In this study, we have prepared a new class of sol–gel processed, hybrid organic–inorganic materials based on the ROP of monomers **1**–**3** bearing one or more 2,2,5,5-tetramethyl-2,5-disilaoxacyclopentane groups (Scheme 1).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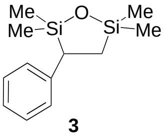
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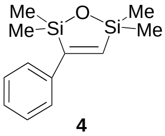
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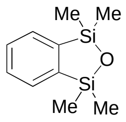
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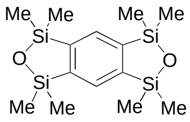
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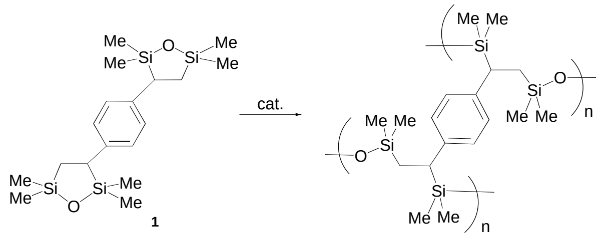
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Scheme 1. Ring-opening polymerization of **1** to the corresponding polymer.

Unlike the sol–gel chemistry of alkoxysilanes, which requires stoichiometric quantities of water, ROP of disilaoxacyclopentane groups only requires catalytic quantities of an anionic base, such as tetrabutylammonium hydroxide

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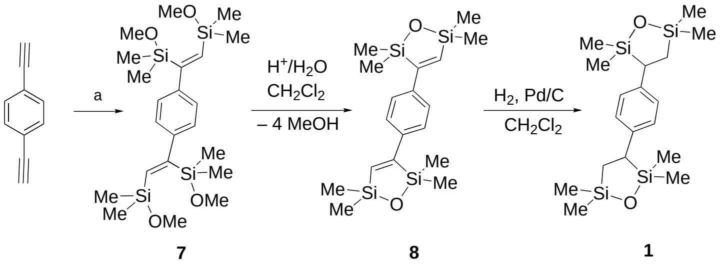
(TBAH). We showed previously that ROP of neat monomer **2** is accompanied by a shrinkage of less than 5%.[5] Likewise, ROP of **3** results in a similar loss of volume during the ROP reaction. Despite the structural similarity of **3** and **4**, disilaoxacyclopentene **4,** and the disilaindoles **5** and **6**,[6] do not undergo ROP with a variety of anionic catalysts and reaction conditions.

A monomer with two or more of the disilaoxacyclopentane groups is required to generate the cross-linked network necessary for forming sol–gels. Monomer **1**, readily prepared in three steps from diethynylbenzene (Scheme 2), possesses two of the strained rings bridged by a phenylene group. Fortuitously, the lower reactivity of the disilaoxacyclopentenes (see above) facilitated the preparation of **1** by allowing ring closure to provide the precursor **8** with two unsaturated five-membered rings without threat of polymerization. Palladium-catalyzed hydrogenation of **8** afforded **1** in quantitative yield.



Scheme 2. Synthesis of **1**. a) $Me_4Si_2(OMe)_2$, $[Pd(PPh_3)_4]$, 110 °C.

Monomer **1** can readily be polymerized either in THF or when dissolved in monomer **2** (used as a solvent/comonomer) to give transparent, yellow-tinted gels that showed no visible shrinkage during polymerization. The gels of both the homopolymer and copolymer with **2** were insoluble materials. The opening of the disilaoxacyclopentane rings was confirmed by an upfield shift in the ^{29}Si NMR spectrum (Figure 1), which is consistent with the release of ring strain in the five membered ring with ROP.[7]

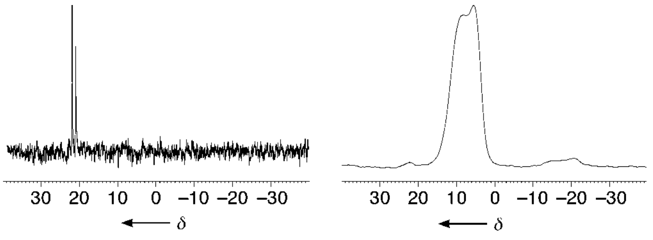


Figure 1. ^{29}Si NMR spectra of monomer **1** (left, $\delta = 21.9$ and 20.9) and its homopolymer (right, $\delta = 9.8$ and 5.5).

By using **2** as both a solvent and a comonomer in the polymerization the solvent is converted into part of the network polymer and shrinkage can be further reduced. The exothermic polymerization of a mixture of **2** and **1** (80:20 by weight) with TBAH (0.2 mol% based on **2**) gave rise to a transparent, crack-free gel within seconds of mixing. A higher concentration of the catalyst (1 mol% based on **2**) led to the generation of more heat during polymerization, which caused bubbles to form (presumably a result of volatilization of monomer **2**) and become entrapped within the gel. Solid state ^{13}C and ^{29}Si NMR spectroscopy revealed a polymer composition representative of the starting comonomer ratio (80:20) and with no detectable unreacted monomer in the final gel.

Thermal gravimetric analysis (TGA) of the polymers (Figure 2) revealed the homopolymer of **1** and its copolymer with **2** were relatively robust materials relative to the homopolymer of **2**, which begins to degrade at 250 °C and is completely depolymerized before 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, which starts at 500 °C. The addition of the phenylene-bridged cross-linker to the polymer of **2** 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 **2** revealed no significant micro- and mesoporosity. This lack of porosity suggests that the gels are composed of network polymers that are compliant enough to permit collapse of the pores.[8]

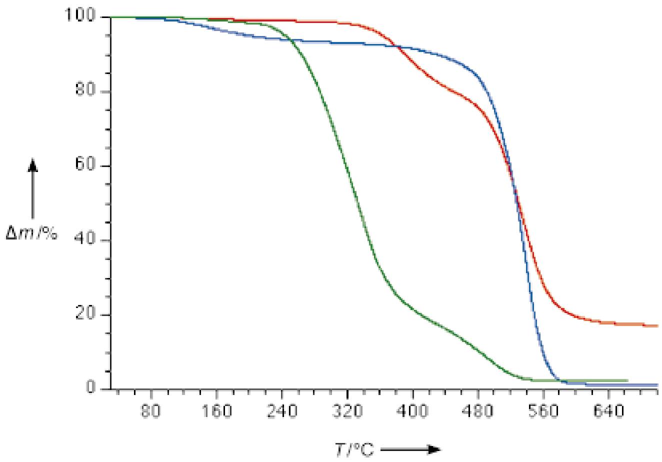


Figure 2. TGA data of the homopolymer of **1** (red), its copolymer with **2** (blue), and the homopolymer of **2** (green).

Encouraged by these results and by the lack of significant shrinkage in the copolymer of **1** and **2**, a microelectronic test chip was successfully encapsulated with the ROP of the 80:20 mixture of **2** and **1**. The copolymer formed quickly around the test chip as a transparent, slightly yellow resin with only a few bubbles formed because of the heat of polymerization (Figure 3). No visible cracks or shrinkage of the encapsulant were observed.

Figure 3. Encapsulated test microchip from a 80:20 copolymer mixture of **2** and **1**.

In summary, we have demonstrated that highly cross-linked sol–gel systems of siloxane gels can be prepared by a ring-opening polymerization process. The polymerization does not require water or solvent and does not generate condensation by-products. This discovery opens the way for application of sol–gel processing to encapsulation, coatings, or net-shape casting. Current efforts are being directed at expanding this family of ROP monomers and determination of the mechanical properties of the gels.

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Template-Directed Self-Recognition of Alkyl-Bridged Bis(catechol) Ligands in the Formation of Helicate-Type Complexes[**]

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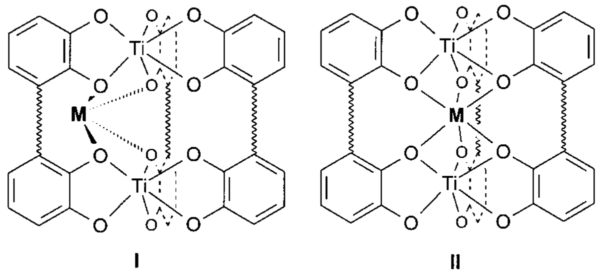
(Metallo-)supramolecular aggregates are formed in spontaneous self-assembly processes. Hereby the steric and electronic information that is embedded in each single molecular component often forces the system to follow a program which affords only one defined supramolecular species.[1–3] Self-recognition of linear ligand strands during the formation of double- or triple-stranded helicates from mixtures of different ligands leads to the self-assembly of structurally well-defined coordination compounds out of a number of different possibilities. Mixtures of complexes are formed that contain only one type of ligand per complex.[4–6] “Hetero”-recognition, on the other hand, leads to compounds that are composed of different ligands.[7, 8]

Lehn et al. described examples in which the self-recognition of ligands in the formation of helicates is influenced by 1) the number of binding sites of the ligands or 2) the preferred coordination geometry of the metal ions in combination with an appropriate structure of the ligands.[4] On the other hand, Raymond et al. performed a study in which the self-recognition during the self-assembly of triple-stranded homoleptic helicates from a mixture of ligands is based on the length of different rigid spacers which bridge two catecholamide moieties.[5] Self-recognition also can be controlled by the chirality of the organic ligands.[6, 7] Herein we describe investigations on the self-recognition of alkyl-bridged bis(catechol) ligands **1**-H_4 and **2**-H_4 on the formation of a mixture of dinuclear titanium(IV) complexes. During this process binding of the countercations to the tetraanionic complexes plays a crucial role in the selective formation of specific coordination compounds (Scheme 1).



Scheme 1. Possible binding modes of alkali metal cations **M** by which dinuclear helicate-type complexes are stabilized: “Outside” coordination (**I**)[9] or “inside” coordination (**II**).[10]

In principle, reaction of a 1:1 mixture of **1**-H_4 and **2**-H_4 (1.5 equiv of each) with two equivalents titanium(IV) ions ($Ti(OMe)_4$ or $(acac)_2TiO$) in the presence of alkali metal carbonate (2 equiv) as base could lead to the homoleptic dinuclear complexes **A1** and **A2**, the heteroleptic dinuclear complexes **B1** and **B2**, the homoleptic oligomeric complexes **C1** and **C2**, and/or the heteroleptic oligomeric complexes **D** (Scheme 2). In earlier investigations we already isolated and characterized the lithium and sodium salts of the *meso*-helicate **A1**. With potassium cations only the oligomeric (but still soluble!) complex **C1** was obtained.[9] The dinuclear helicate **A2** was formed in the presence of lithium, sodium, potassium as well as many other countercations.[10]

For entropic reasons the formation of the dinuclear complexes **A** and **B** should be favored over the oligonuclear species **C** and **D**.[5] However, the binding of the countercations to the anionic coordination compounds either stabilizes the dinuclear complexes or destabilizes them leading to the formation of the oligomers **C** or **D**.[9, 11]

A red soluble solid is obtained when a 1:1 mixture of **1**-H_4 and **2**-H_4 with $Ti(OMe)_4$ (methanol, reflux or $(acac)_2TiO$, methanol, room temperature) is treated with potassium carbonate as base and the solvent is removed. The ^1H and ^{13}C NMR spectra (in [D_4]methanol) of this red solid show only signals of the homoleptic helicate **A2** (positive-ion FAB MS (3-nitrobenzyl alcohol (3-NBA) matrix): m/z: 940 $\{K_3H[(\mathbf{2})_3Ti_2]\}^+$). Signals of a titanium complex of ligand **1** are not observed. This is attributed to the formation of the oligomeric species **C1**, which leads to very broad signals in the NMR spectrum, as described previously.[9] However, the presence of titanium complexes of **1** was shown by acidic hydrolysis (2 N HCl) of the red solid obtained. After extraction of the aqueous phase with diethyl ether, the

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