SOLVENTLESS SOL-GEL CHEMISTRY THROUGH RING-OPENING POLYMERIZATION OF BRIDGED DISILAOXACYCLOPENTANES

Kamyar Rahimian *
* Organic Materials Department, Sandia National Laboratories, Albuquerque, NM 87185-1407

Douglas A. Loy
Catalysis and Chemical Technologies Department, Sandia National Laboratories, Albuquerque, NM 87185-1407

Introduction

Disilaoxacyclopentanes have proven to be excellent precursors to sol-gel type materials.1 These materials have shown promise as precursors for encapsulation and microelectronics applications (Figure 1). The polymers are highly crosslinked and are structurally similar to traditional sol-gels, but unlike typical sol-gels they are prepared without the use of solvents and water, they have low VOC's and show little shrinkage during processing.

![Microelectronic test chip encapsulated with a mixture of 2/1.](image)

Figure 1. Microelectronic test chip encapsulated with a mixture of 2/1.

Our initial efforts were focused on the synthesis and utility of the phenylene-bridged disilaoxacyclopentane, 1, (Figure 2). This precursor is a white solid which can be polymerized either by itself, in a solvent such as THF, or as a copolymer system with 2 which is used as the solvent/co-monomer. In both cases, the polymerizations were performed using tetrabutylammonium hydroxide (TBAH) as the catalyst; earlier reports indicated that acids did not polymerize disilaoxacyclopentanes.2 The mechanical and thermal properties of the materials can be changed by simply varying the ratios of 1 to 2.

![Homo-polymerization of 1 and its copolymerization with 2.](image)

Figure 2. Homo-polymerization of 1 and its copolymerization with 2.

The following report discusses the synthesis of alkylene-bridged disilaoxacyclopentanes, which are high boiling liquids, as well as the ring-opening polymerization of disilaoxacyclopentanes using acids and photo-generated acids (PAG) and their use in thin films and coatings applications.

Experimental Section

The ethylene- and butylene-bridged disilaoxacyclopentanes are synthesized by the same methodology as the previously reported phenylene-bridged disilaoxacyclopentane, 1 (scheme 1), with one exception. The hydrogenation step is performed under higher pressure (~800 psi), in the presence of formic acid as a hydrogenation accelerator.

Results and Discussion

Synthesis of Base-Catalyzed ROP of Alkylene-Bridged Disilaoxacyclopentanes. The alkylene-bridged disilaoxacyclopentanes (3, R = Et; 4, R = n-Bu) are synthesized according to Scheme 1. This is the same methodology that was utilized for the synthesis of phenylene-bridged disilaoxacyclopentane with one exception. The hydrogenation of the disilaoxacyclopentanes is performed under higher H2 pressure (~800 psi) and in the presence of formic acid as hydrogenation accelerator.2 Monomers 3 and 4 are high boiling, colorless liquids/ils that display the same spectroscopic characteristics as 1.

Scheme 1.

![Scheme 1](image)

The monomers can be ring-open polymerized with catalytic TBAH. For example, monomer 3 produces a polymer which has a Tg of ~25 °C and a coefficient of thermal expansion (CTE) of 274 e-6°C. Its copolymer with 2 (2:3 ratio of 80:20 by weight), has a Tg of ~75 °C and CTE of 335 e-6°C (Table 1).

<table>
<thead>
<tr>
<th>Polymer composition</th>
<th>Tg (°C)</th>
<th>CTE (e-6°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homopolymer of 1</td>
<td>80</td>
<td>110</td>
</tr>
<tr>
<td>2:1 (80:20 by weight)</td>
<td>-81</td>
<td>352</td>
</tr>
<tr>
<td>2:2 (80:20 by weight)</td>
<td>-74</td>
<td>302</td>
</tr>
<tr>
<td>Homopolymer of 3</td>
<td>22</td>
<td>274</td>
</tr>
<tr>
<td>2:3 (60:20 by weight)</td>
<td>-75</td>
<td>335</td>
</tr>
</tbody>
</table>

These values compare well with those of the phenylene-bridged materials. The lower Tg value of the homopolymer of 3, relative to that of 1, is not unexpected since the ethylene linkage is more flexible than the phenylene spacer. This, in turn, should result in higher CTE values, which in fact it does: 110 for 1 compared to 274 for 3. The copolymers of both 1 and 3 with 2 are similar, which indicates that the co-monomer 2 dictates the properties of the materials in the ratios studied.

Acid Catalyzed Ring-Opening Polymerization. During the hydrogenation of the alkylene-bridged disilaoxacyclopentane, we discovered that catalytic amounts of formic acid, HCO2H, were needed for hydrogenation to occur; the use of acids as hydrogenation accelerators has been demonstrated before.2 Thus, we performed the hydrogenation of the phenylene-bridged analog under similar conditions, i.e. in the presence of HCO2H. Not only did hydrogenation occur, but also the solution gelled overnight. This was contrary to early reports which stated that disilaoxacyclopentanes do not undergo ROP under acidic conditions.2
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
Independent polymerizations of 1, 2, and 3 all confirmed that disilaaoxacyclopentanes do in fact undergo acid catalyzed ring-opening polymerization using organic acids such as HCO₂H and triflic acid. As expected, polymerization is much more rapid when the stronger triflic acid is used. Photo-acid generators such as PbH(O₂SCF₃) and UV9310C (available from GE-Silicones) also ring-open polymerize disilaaoxacyclopentanes upon exposure to short-wave ultraviolet light.

Thin Film Applications. Disilaaoxacyclopentanes make excellent candidates for thin film applications as they are easily processible (they do not shrink or crack during polymerization and do not produce unwanted by-products). We have been exploring their use in such applications as spray coatings and thin film applications. Figure 3 demonstrates some of the early results from these studies, a thin film of the copolymer mixture of 1/2 on an alumina substrate. The fluid monomer mixture was in situ polymerized on the substrate over a layer of TBAH, which was applied prior to spin coating of the mixture.

![Figure 3. SEM photographs of 1/2 copolymer system on 0.02 μM alumina disk.](image)

Conclusions

We have synthesized novel alkylene-bridged disilaaoxacyclopentanes through the same methodology utilized in the synthesis of phenylene-bridged disilaaoxacyclopentane, 1. These precursors can be ring-open polymerized in the same manner as 1. We have successfully polymerized disilaaoxacyclopentanes using organic acids, which has allowed us to use photo-acid generators to polymerize these compounds. Furthermore, we have also been able to apply thin films of these materials to different substrates. Successful ROP of these materials using photo-acid generators should allow us to use these materials for applications such as conformal coatings and microlithography, which we are currently pursuing.

Acknowledgement. We would like to thank Jeff Kawola for his assistance in the thin film application and Bonnie McKenzie for SEM work. 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.

References

(3) Rylander, P. N. Hydrogenation Methods, 1985, Academic press.

Polymer Preprints 2000, 41(1), xxxx