

Degradable Dendritic Template for Synthesis of Siloxane Catalyst Nanocages

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Introduction

Recently, our laboratory has reported the synthesis of micelle-directed 2 nm siloxane nanocages with interior amine functionality, which exhibited size selectivity for probe molecules [1]. The siloxane shell was prepared through hydrolysis and condensation of triethoxy head groups in a silicon-containing surfactant. This approach has certain advantages, including rapid micelle formation, and an operational similarity to the sol-gel process. However, in this method shell cross-linking must be performed under conditions that preserve micelle integrity. In particular, a high fraction of water is needed to stabilize the micelles, precluding the use of moisture-sensitive shell cross-linking monomers and oligomers.

Therefore, we have investigated dendritic macromolecules as degradable templates for siloxane nanocage synthesis. Previously, Lang and co-workers reported an alkoxy silane dendrimer which could be synthesized up to the second generation from a tetrahedral core, or up to the third and fourth generations from less hindered cores [2]. In principle, this type of structure could be hydrolyzed under acid or base catalysis to produce organosilanol fragments. We postulated that, under favorable conditions, these fragments could diffuse through a shell cross-linked siloxane network to produce an evacuated nanocage.

Here we report the synthesis and degradation properties of dendritic acyloxysilane macromolecules with tetrahedral cores. In order to hydrolyze alkoxy silanes at a useful rate, acidic conditions are generally required that jeopardize the integrity of the siloxane shell. Acyloxysilanes, on the other hand, hydrolyze rapidly under milder pH conditions. This serves to protect the siloxane shell from hydrolysis, and inhibits the silanol fragments from agglomerating before they have diffused out of the nanocage.

Materials and Methods

Dendritic poly(acyloxysilane)s were synthesized by an iterative self-terminating process, starting from an olefinic core molecule. Hydrosilylation of the olefins with excess Cl_2HSiR ($\text{R} = \text{Me}, \text{Et}$) produced chlorosilane-terminated CG0.5 (Figure 1). The excess chlorosilane monomer was removed under vacuum. Condensation of CG0.5 with excess alkenoic acid in the presence of pyridine produced CG1 with eight acyloxysilane linkages. By repeating these steps, higher-generation dendritic structures were prepared. The solvolytic degradation of these molecules was tested under a variety of solvent and pH conditions. Because the template must remain intact during shell cross-linking, the stability of these templates towards silanol and chlorosilane reagents was established.

Results and Discussion

Starting from a tetraallyloxysilane core molecule, the half-generation intermediate was prepared via hydrosilylation of ethyldichlorosilane. Condensation of the peripheral chlorosilane groups with alkenoic acids (e.g., vinylacetic acid) proceeds to completion at the first generation (CG1), as shown by ^1H , ^{13}C , and ^{29}Si NMR, and ESI-MS. Subsequent growth cycles resulted in spherical macromolecules. When handled under an inert atmosphere, CG1 was found to be stable at room temperature. As expected, the macromolecule degraded rapidly in aqueous-organic solvent systems.

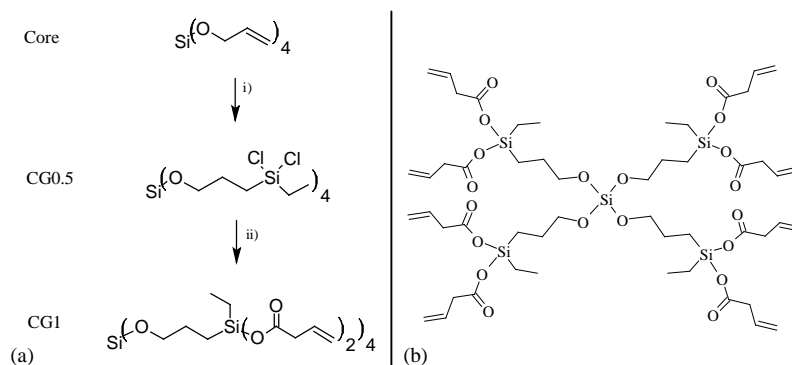


Figure 1. (a) Two-step reaction sequence for generation growth: i) core, Karstedt catalyst, dichlorosilanes; ii) CG0.5, pyridine, 3-butenic acid. (b) Structure of CG1 dendrimer.

Due to the enhanced reactivity of these structures, care must be taken to avoid degradation by dendrimer growth monomers and shell cross-linking reagents. Ligand exchange between chloride groups and acyloxysilane groups was observed; the rate of exchange decreased with increasing steric bulk at silicon. The effects of ligand exchange can be minimized by reducing the contact time between hydrochlorosilane monomers and the dendrimer substrate during hydrosilylation.

Significance

The acyloxysilane dendritic structures are ideal templates for siloxane shell cross-linking under anhydrous conditions. This enables functional siloxane oligomers to be incorporated into the nanocage with interior- or exterior-directed functionality. Simultaneous control of the active site configuration and the nanocage porosity is essential in the design of selective catalyst structures.

References

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2. Bruning, K. and Lang, H. *Synthesis* 11, 1931 (1999).