Synthesis of Oligosiloxane Molecular Catalyst Precursors on Solid Phase

Michael N. Missaghi, Mayfair C. Kung, and Harold H. Kung*
Chemical and Biological Engineering, Northwestern University, Evanston, IL 60208 USA
*hkung@northwestern.edu

Introduction

Recently, new synthesis methods have been reported for siloxane oligomers and nanostructures, such as an asymmetric [3,5,7]-bicyclosiloxane [1] and surfactant micelle-directed, 2 nm siloxane nanocages [2]. These structures are of interest as catalytic host materials, providing a controlled active site environment and regulating access to the active site. Traditional preparations employ solution-phase techniques, including the need for high-dilution conditions to suppress unwanted oligomerization, and the frequent necessity of distillation and column chromatography to separate the reaction product from unreacted reagents, byproducts, and side products.

Solid-phase synthesis is a well-known alternative to solution-phase techniques for peptide and nucleotide synthesis, and also for organic synthesis. In principle, immobilizing the synthetic intermediates on a solid support would promote site isolation and inhibit cross-linking of reactive groups, although this effect is support- and solvent-dependent [3]. Also, the intermediates could be separated from byproducts and excess reagents by simple procedures such as rinsing the support with solvent.

We have extended the solid-phase synthesis method to the preparation of siloxane oligomers and developed a protocol to synthesize structures with reactive functionality. Utilizing organoxysilane linkers, we were able to prepare siloxane oligomers by reacting alternately with dihalosilanes and sil(ox)anediols. Functional groups such as hydride, phenyl, alkoxy, and vinyl groups could be installed at designated positions in the macromolecule by varying the identity of the monomers used. Subsequent derivatization of the functional groups would produce novel molecular catalysts with acidic or basic sites, hydrophilic or hydrophobic interaction sites, or good ligands to bind transition metal centers.

Materials and Methods

Macroporous polystyrene resins, such as Amberlite XAD1600 (Rohm and Haas, 700 m^2/g), were functionalized with alcohol and carboxylic acid groups to anchor the siloxane intermediates through the corresponding organoxysilane linkers. The loading of surface sites could be controlled over a wide range, from 0.05 to 1 mmol/g. The linker was synthesized by reacting the thoroughly dried support with a diorganodichlorosilane in the presence of an uncharged tertiary amine, such as pyridine, imidazole, or triethylamine. After rinsing the support with anhydrous solvent, the siloxane chain was elongated by reacting the resin-bound organoxychlorosilane with a sil(ox)anediol, again in the presence of a tertiary amine. Condensation occurred preferentially at the chloride position to form a siloxane bond and amine-HCl complex. Generally, a three- to fivefold excess of monomers was used to drive the condensation reactions to completion in a reasonable time (usually less than 1 h). This process could be repeated to extend the siloxane chain. The linker was cleaved in a water-alcohol mixture (typically 5% water-95% isopropanol) at pH 2-7. This scheme is represented in Figure 1 for the preparation of a tetrasiloxane in three steps.

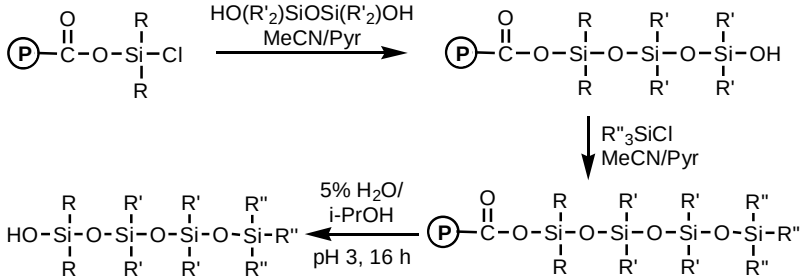

Figure 1. Three-step solid-phase synthesis of a model tetrasiloxane (P represents the polymeric support), starting from the linker residue. With R = ethyl and R´ = R´´ = methyl, the compound was isolated in 66 mol % purity from a support loading of 0.8 mmol/g. Crosslinking of the siloxanediol reagent with two surface sites accounted for most of the observed impurities.

Results and Discussion

The stabilities of alkoxy- and acyloxysilane linkers were controlled by varying the steric bulk at the linker silicon atom. It was observed that moderately hindered acyloxysilane linkers hydrolyzed easily at mild pH to produce stable siloxanols. Alkoxysilane linkers could also be employed, although hydrolysis was slower and required more acidic conditions. Because symmetric difunctional monomers were used in the synthesis, cross-linking of support-bound intermediates was observed as a side reaction. This could be suppressed by lowering the loading of surface sites, improving the homogeneity of functionalization, and utilizing solvents that minimize the mobility of the support polymer chains. Because the side products contain polar silanol groups at both of the chain ends, purification of the desired product by chromatographic methods is facile.

Significance

The method enables new functional siloxanes to be prepared much more efficiently in appreciable yields for use as molecular catalyst precursors. The ability to systematically vary the structure and functionality of the siloxane molecules is expected to facilitate structure-activity relationship studies. Eventually we aim to develop novel metal-oxide and hybrid organic-inorganic catalysts from these framework structures.

References

1. Xue, W., Kung, M.C., and Kung, H.H., *Chem. Commun*. 2164 (2005).
2. Suh, Y.-W., Kung, M.C., Wang, Y., and Kung, H.H., *J. Amer. Chem. Soc*. 128, 2776 (2006).
3. Regen, S.L., and Lee, D.P., *Macromolecules* 10, 6, 1418 (1977).