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Soluble, High Molecular Weight Polysilsesquioxanes with Carboxylate Functionalities

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Polysilsesquioxanes, $(RSiO_{1.5})_n$, have attracted increasing attention in the polymer and materials science fields in recent years because of the ease of their preparation as well as their excellent physical and chemical properties.[1] However, introduction of functionality into these materials has been limited to organic substituents, R, that do not react with the alkoxysilyl and silanol groups or the catalyst itself present under sol−gel polymerization conditions. Thus, reactive functionalities are introduced into polysilsesquioxanes through chemical modification, usually with hydrido-, vinyl-, and allyl-substituted polysilsesquioxanes, and a few examples of aminoalkyl, epoxy, isocyanato, and thiols are also known.[1] Alternatively, the organic group can be modified with a protecting group that is stable to the polymerization conditions and deprotected once the polymer has been formed. Organic carboxylates and carboxylic acids would be useful functionalities to attach to polysilsesquioxanes to provide chemically and thermally robust ion-exchange resins for scavenging heavy metals[2] and organic amines. There is only one reported case where acid functionality was introduced, in a random fashion, to an insoluble, bridged silsesquioxane polymer.[3] Here, we describe the synthesis and characterization of soluble and processable, high molecular weight polysilsesquioxanes in which every repeat unit bears the *tert*-butyl ester functionality as a masked or protected carboxylic acid group. The *tert*-butyl functionality in these polymers can be easily chemically eliminated to give carboxylic acid functionalized polysilsesquioxanes or methyltin carboxylatosilsesquioxane gels (Scheme 1), both of which are insoluble materials in common organic solvents unlike the starting *tert*-butyl ester-functionalized polysilsesquioxane.

Monomers of the type $(RO)_3Si(CH_2)_3COOC(CH_3)_3$ (**1**, R = Me; **2**, R = Et) are obtained from hydrosilylation of the olefin $CH_2CHCH_2COOBu^t$ with the corresponding $(RO)_3SiH$ (R = Me, Et) using H_2PtCl_6 as the catalyst, at room temperature and under an inert atmosphere. (For experimental details, see the Supporting Information.) The reaction is complete overnight and is quantitative by NMR spectroscopy and GC. The monomers are obtained in very high yield (95%) by fractional distillation and are easily characterized by conventional analytical techniques as the desired terminal silyl regioisomers. They are stable liquids and do not decompose when stored on the benchtop over a period of several weeks.

Compounds **1** and **2** can be polymerized under aqueous basic conditions (0.1 M KOH, 3 equiv. of H_2O) or acidic conditions (0.1 M HCl, 3 equiv. of H_2O) *without* deprotection of the *tert*-butyl ester functionality (vida infra). A typical polymerization reaction is shown in Scheme 2.

The polymerizations were performed with 3 equiv of water to ensure complete, or close to complete, condensation of all the alkoxy groups. After the water and catalyst were added to the neat monomer, the mixture was stirred for approximately 2 h, and the condensed alcohol and excess water were then removed in vacuo to leave a material that was too viscous to stir mechanically. This was allowed to stand and cure for 1 week to ensure complete loss of unreacted alkoxide groups. Any residual volatiles are removed periodically in vacuo. After 1 week, the solution ^1H NMR spectrum showed no alkoxide groups present, indicating complete condensation had occurred.

The polymers are white, tacky solids and are soluble in polar solvents such as THF, benzene, and $CHCl_3$. The nature of the alkoxide substituent on the monomer does not seem to affect molecular weights and thermal properties of the polymer. The polymers of **1** and **2**, prepared under identical sol−gel conditions, are spectroscopically similar.

Molecular weights of these highly branched polymers were determined by light scattering GPC to avoid erroneous results that would occur if linear polystyrene standards were used. Polymers produced using aqueous KOH as catalyst have higher molecular weights ($M_w = 2.18 \times 10^5$) and lower polydispersity ($M_w/M_n = 2.29$) than those produced using aqueous HCl as catalyst ($M_w = 5.24 \times 10^4$, $M_w/M_n = 2.94$). (These values are the averages from several experiments.) The molecular weight values are unusually high for soluble polysilsesquioxanes, with the base-catalyzed polymers having some of the highest reported molecular weights.[1]

Dynamic mechanical analysis of the *tert*-butyl functionalized polysilsesquioxane showed a T_g of about −85 °C. This is surprising in light of its high molecular weight and high degree of branching of the polymer suggested by the NMR and light scattering GPC analyses.

One attractive property of polysilsesquioxanes is their thermal stability, which in this case allows thermal liberation of the carboxylic acid groups without siloxane degradation. Thermal gravimetric analysis of the polymer showed an initial weight loss of approximately 30% starting at 270 °C, which corresponds to the loss of the *tert*-butyl fraction of the organic moiety in the polymer (calculated value = 29.3%). A second weight loss transition at 350 °C, followed by a third at 475 °C, corresponds to bulk decomposition, leaving a black residue with about 41% weight of the original sample remaining. Quantitative liberation of the carboxylic acid functionalized polysilsesquioxane can be effected either by heating the polymer to 300 °C for about 8 h or in solvent at room temperature, with catalytic *p*-toluenesulfonic acid overnight. The deprotected polymer does not show the initial weight loss transition observed with the *tert*-

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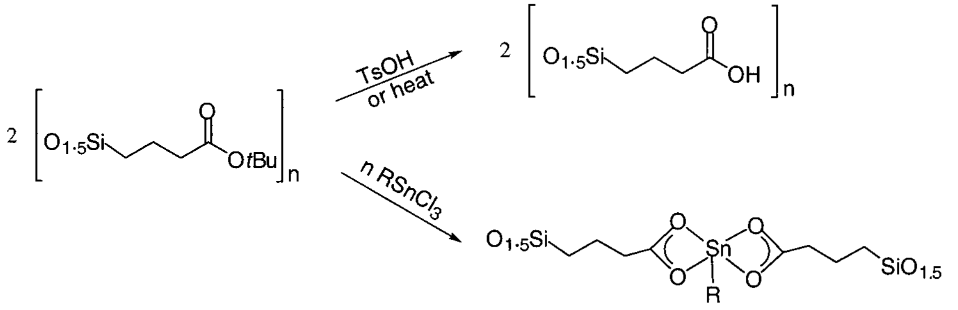
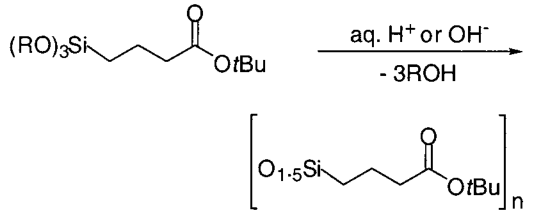
Scheme 1. Deprotection of the *tert*-Butoxy Functionality of the Polysilsesquioxane



Scheme 2. Aqueous Base (KOH) or Acid (HCl) Catalyzed Hydrolysis and Condensation Polymerization of Trialkoxysilyl Monomers 1 and 2



butyl ester polysilsesquioxane at 270 °C but does show the other decomposition temperatures, at 350 and 475 °C. Absence of the *tert*-butyl functionality was confirmed by IR and solid-state NMR spectroscopies. Although it is not soluble in most organic solvents, it is soluble in cyclohexanone.

Solid-state ^{13}C NMR spectroscopy of the *tert*-butyl ester polysilsesquioxanes revealed two resonances for the *tert*-butyl functionality as well as the remainder of the organic pendant group attached to the silicon. This suggests that the *tert*-butyl functionality is stable enough to survive mild acidic sol−gel conditions. The solid-state ^{29}Si NMR spectrum (Figure 1b) showed a single peak centered at −67 ppm due to fully condensed (T^3) silicons. This high degree of condensation suggests a substantial portion of cyclic structures are contributing to the polymer structure and eliminates the risk of changes in the polymer properties that would accompany continued condensation reactions.

Although these polymers are soluble in conventional organic solvents such as benzene, their solution ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies (Figure 1a) contained a plethora of cyclic and branched structures. This, along with the *high molecular weights* of the polymers, rules out the presence of any one species, such as low molecular weight, cagelike polyhedral oligosilsesquioxanes.[4] It also eliminates the possibility of isolating any one product in high yield. Furthermore, solution NMR spectra did not display any substantial resonances corresponding to other species than completely condensed T^3 polysilsesquioxane species, lending more proof that complete condensation of all the alkoxide groups was accomplished during the polymerization, even at such mild conditions.

Solubility of the *tert*-butyl ester functionalized polysilsesquioxane, and the fact that deprotection of the *tert*-butyl ester leads solely to the carboxylic acid substituted polysilsesquioxane, prompted us to study the use of this polymer for removal of heavy metals from solutions. When a 0.25 M benzene solution of the polymer (based on the molar mass of the monomer) is exposed to a solution of $MeSnCl_3$ (0.5 equiv. when compared to that of the *tert*-butoxide group) at room temperature, gelation of the mixture occurs overnight. Analysis of the dry gel, after washing with benzene, by solid-state NMR and IR spectroscopy revealed no remaining *tert*-butyl moiety. The solid-state ^{13}C NMR spectrum is similar to that of the deprotected polysilsesquioxane with an additional resonance present due to the methyl group from $MeSnCl_3$. ^{29}Si NMR is indicative of fully condensed, T^3, silicons with only one resonance centered at −67.0 ppm. ^{119}Sn resonances are shifted upfield of $MeSnCl_3$ ($\partial = -3.6$ ppm) by over 350 ppm to −364 and −367 ppm, indicating conversion of the SnCl groups to SnO(O)CR.[5,6c] The IR spectrum of the gel displays the presence of SnO(O)CR carbonyl stretching frequency at 1709 cm^{-1},[6] further indicating formation of a tin carboxylate species. This clearly demonstrates that the polysilsesquioxane binds and, through gelation, removes the tin from solution. Although there was no analysis of the benzene solubles, it is conceivable that not all of the $MeSnCl_3$ reacted with the gel since there were no Sn−Cl bond stretches present in the IR spectrum of the gel product. The scanning electron microscopy of the material revealed

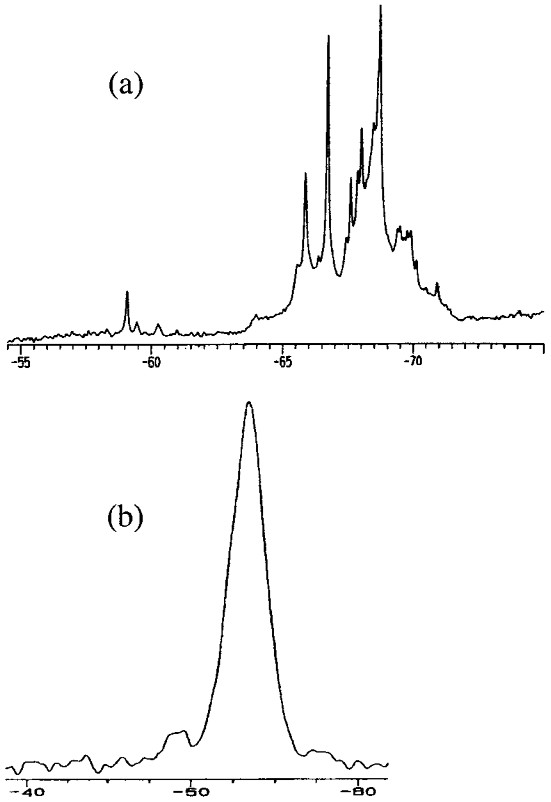


Figure 1. (a) Solution ^{29}Si NMR spectrum of polysilsesquioxane polymer. (b) Solid-state ^{29}Si NMR spectrum of polysilsesquioxane polymer.

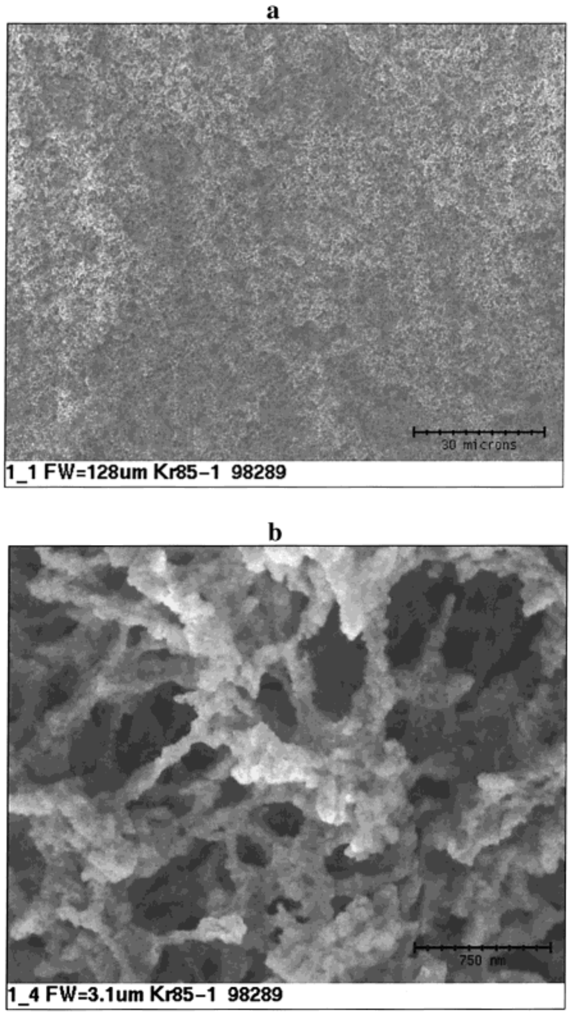


Figure 2. SEM photographs of the polysilsesquioxane gel treated with $MeSnCl_3$.

large pores on the order of about 1−2 μm in size (Figure 2), and porosimetry measurements revealed a surface area of 8.9 m^2/g.

In conclusion, by means of simple acid- or base-catalyzed sol−gel processing, we have prepared novel, soluble polysilesesquioxanes with high molecular weights and good thermal stability. These polymers have a *tert*-butyl ester functionality that can easily be removed to yield the carboxylic acid groups. Early results indicate that these soluble materials can also be useful for forming gels with other main group metal complexes such as methyltin trichloride. There is potential for these materials in the field of environmental chemistry for the removal of such heavy metals from contaminated solutions. Furthermore, their solubility and *tert*-butyl functionality should allow for the utility of these polymers in lithographic applications, which we are pursuing.

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Supporting Information Available: Detailed experimental information. This material is available free of charge via the Internet at http://pubs.acs.org.

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