SOLUBLE, HIGH MOLECULAR WEIGHT POLYSILSESQUOXANES WITH
CARBOXYLATE FUNCTIONALITIES

*Kamyar Rahimian*¹, Douglas A. Loy*² and David R. Wheeler¹*

RECEIVED

AUG 17 2000

OSTI

¹Organic Materials Department, Sandia National Laboratories, Albuquerque, NM 87185-1407.

²Catalysis and Chemical Technologies Department, Sandia National Laboratories, Albuquerque,
NM 87185-1407.

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.

Abstract

Trialkoxysilyl-containing monomers of the type $(\text{RO})_3\text{Si}(\text{CH}_2)_3\text{C}(\text{O})\text{OtBu}$ ($\text{R} = \text{Me, Et}$) were prepared by hydrosilation of the corresponding vinylic *tert*-butyl esters $\text{CH}_3\text{CHCH}_2\text{C}(\text{O})\text{OtBu}$. Acid- or base-catalyzed polymerization of the monomers leads to very high molecular weight polymers with relatively narrow polydispersities. The polymerization results in complete condensation of the alkoxy groups while the *tert*-butyl ester functionality remains fully intact. Partial or full deprotection of the *tert*-butyl group can easily be achieved to yield the corresponding carboxylic acid polymers. The ester and carboxylic acid functionalities of these new materials allow for their potential use in a variety of applications such as scavenging of heavy metals.

Polysilsesquioxanes, $(\text{RSiO}_{1.5})_n$, 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 metals² 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 processible, 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.

Scheme 1

Monomers of the type $(RO)_3Si(CH_2)_3COOC(CH_3)_3$ ($R = Me, Et$) are obtained from hydrosilation 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 inert atmosphere (Scheme 2; for experimental details see the supporting information).

Scheme 2

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. They are stable liquids and do not decompose when stored on the bench-top over a period of several weeks.

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

Scheme 3

After the water and catalyst were added to the neat monomer, the mixture was stirred for approximately two hours and the condensed alcohol and excess water were then removed *en vacuo* to leave a very viscous material. At this point, the mixture was too viscous to stir mechanically and was allowed to simply stand and cure for approximately one week to ensure complete loss of unreacted alkoxy groups. Any residual volatiles are removed periodically *en*

vacuo. After one 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 the molecular weight and the thermal properties of the polymer as the polymers obtained from both **1** and **2**, under identical catalytic conditions using acid or base, 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 ($M_w = 2.18\text{e}+5$) and lower polydispersity ($M_w/M_n = 2.29$) than those produced using aqueous HCl as catalyst ($M_w = 5.24\text{e}+4$, $M_w/M_n = 2.94$) (these values are the averages from several experiments). These 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 $-85\text{ }^\circ\text{C}$. 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 analysis.

One attractive property of polysilsesquioxanes is their thermal stability. The high molecular weight polymers made here show a similar behavior. Results of the thermal gravimetric analysis of a sample polymer of compound **1** showed an initial weight loss of approximately 30% starting at $270\text{ }^\circ\text{C}$, 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 $350\text{ }^\circ\text{C}$, followed by a third at $475\text{ }^\circ\text{C}$, correspond to bulk decomposition, leaving a black

residue with about 41% weight of the original sample remaining. Quantitative deprotection of the *tert*-butyl ester functionality, and its conversion to the carboxylic acid functionalized polysilsesquioxane, can be affected by heating the polymer to 300 °C for about 8 hours or in solvent, at room temperature, with catalytic amount of *p*-toluenesulfonic acid overnight. This material does not show the initial weight loss transition observed with the *tert*-butyl ester polysilsesquioxane at 270 °C but does show the other decomposition temperatures, at 350 °C 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 one resonance 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 even mild acidic conditions. Solid state ^{29}Si NMR spectrum also showed a single peak centered at -67 ppm, which is due to fully condensed (T^3) silicones. 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.

Solubility of the *tert*-butyl ester functionalized polysilsesquioxane, and the fact that deprotection of the *tert*-butyl ester leads solely to the insoluble carboxylic acid substituted polysilsesquioxane, prompted us to study the use of this polymer for removal of heavy metals from solutions. When a benzene solution of the polymer is exposed to a solution of MeSnCl_3 (0.25M in benzene) at room temperature, gelation of the mixture occurs overnight. Analysis of the dry gel by solid state NMR and IR spectroscopy showed absence of the *tert*-butyl moiety.

The solid state ^{13}C spectrum is similar to that of the deprotected polysilsesquioxane with an additional resonance present due to the methyl group from MeSnCl_3 . Solid state ^{29}Si and ^{119}Sn NMR spectra have one and two resonances, respectively (-67.0 ppm for ^{29}Si and -364 and -367 ppm for ^{119}Sn). The ^{29}Si resonance is indicative of fully condensed, T^3 , silicons. The ^{119}Sn resonances are shifted upfield of MeSnCl_3 ($\delta = -3.6$ ppm) by over 350 ppm, indicating conversion of the SnCl groups to SnO(O)CR .^{4, 5c} IR spectrum of the gel, when compared to those of MeSnCl_3 and the starting polysilsesquioxane, clearly shows the absence of the carbonyl stretching frequency of the starting silsesquioxane at 1733 cm^{-1} , and at the same time the presence of SnO(O)CR carbonyl stretching frequency at 1709 cm^{-1} ,⁵ further indicating formation of a tin carboxylate species. This clearly demonstrates that the polysilsesquioxane binds, and through gelation, removes the tin from solution. The Scanning Electron Microscopy of the material revealed large pores on the order of about 1-2 microns in size (figure 1) and porosimetry measurements revealed surface area of $8.86\text{ m}^2/\text{g}$.

Figure 1

In conclusion, by means of simple aqueous acid and base catalysis, we have prepared novel, soluble polysilsesquioxanes with high molecular weights and good thermal stability. These polymers have a *tert*-butyl ester functionality that can easily be modified, through chemical means, to the carboxylic acid and 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.

ACKNOWLEDGEMENTS

The authors would like to thank Todd Alam and Roger A. Assink for their assistance in obtaining the solid state NMR spectra, and Bonnie McKenzie for SEM's. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-ACO4-94AL85000.

REFERENCES

1. Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev.* **1995**, *95*, 1409-1430, and referenced therein.
2. Caraher Jr., C. E.; He, F.; Sterling, D. *Synthesis, Characterization and Theory of Polymeric Networks and Gels*; Plenum Press, New York, 1992.
3. Brandvold, T. A.; Holmgren, J. S.; Malloy, T. P. (UOP Inc., USA) U.S. 7 pp. Cont.-in-part of U.S. 5371154. CODEN: USXXAM US 5475162 A 951212.
4. Mokal, V. B.; Jain, V. K.; Tiekink, E. R. T. *J. Organomet. Chem.* **1991**, *407*, 173-180.
5. (a) Plazzogna, G.; Peruzzo, V.; Tagliavini, G. *J. Organomet. Chem.* **1969**, *16*, 500-502. (b) Maeda, Y.; Okawara, R. *J. Organomet. Chem.* **1967**, *10*, 247-256. (c) Lockhart, T. P.; Calabrese, J. C.; Davidson, F. *Organometallics* **1987**, *6*, 2479-2483. (d) Deacon, P. R.; Mahon, M. F.; Molloy, K. C.; Waterfield, P. C. *J. Chem. Soc., Dalton Trans.* **1997**, 3705-3712.
6. Ozeki, T.; Kusaka, M. *Bull. Chem. Soc. Japan*, 1966, *39*, 1995-1998.

Scheme 1.

Reduce to 75% of current size for publication.

Scheme 2. General synthetic scheme for the preparation of trialkoxysilanes, **1** and **2**.

Reduce to 75% of current size for publication.

Scheme 3. Aqueous base (KOH) or acid (HCl) catalyzed hydrolysis and condensation polymerization of trialkoxysilyl monomers **1** and **2**.

Reduce to 75% of current size for publication.

Figure 1. SEM photographs of the polysilsesquioxane gel treated with MeSnCl₃.

Supporting Information

Experimental section

1-propenyl-*tert*-butyl ester was prepared according to published results.¹ All other reagents and solvents (in Sure Seal® bottles) were purchased from Aldrich Chemical Co. and used as received. All reactions and distillations were performed under an Argon atmosphere unless stated otherwise. Solution NMR spectra were performed on a Bruker DRX400 spectrometer (¹H, 400.16 MHz; ¹³C 100.04 MHz; ²⁹Si, 80.03 MHz) and were referenced against residual solvent peaks or external TMS. Solid state ¹³C, ²⁹Si and ¹¹⁹Sn CP MAS NMR spectra were obtained with a Bruker AMX-400 MHz spectrometer at 100.63 MHz, 79.5 MHz and 149.2 MHz, respectively, and were acquired with magic angle spinning (MAS) speeds of ~5 kHz and ~3-5 kHz, respectively. ¹³C NMR spectra were acquired using cross polarization (CP) with a relaxation delay of 1 sec and a cross polarization time of 2 msec. ¹³C referencing was performed on the carbonyl resonance of solid glycine ($\delta = 176.0$). ²⁹Si NMR spectra were acquired using single pulse excitation with a relaxation delay of 480 sec. With ²⁹Si T₁ values ranging from 19 to 135 sec, the relaxation delay is $\geq 3T_1$ which is sufficient for quantitative interpretation of spectra. ²⁹Si CP MAS NMR spectra were deconvoluted using a Lorentz-Gaussian (50:50) fit. High resolution mass spectra (CI, isobutane) were obtained on a Micromass 70-70E instrument from Altrincham, U.K. Monomer purity was determined either by solution NMR spectroscopy or by GC with an HP Series II 5890 and a packed column with HP-1 (crosslinked methyl siloxane), 15m x 0.32mm. Infrared spectra were obtained on a Perkin-Elmer 1750 Fourier

Transform Infrared spectrophotometer. Thermal gravimetric studies were performed on a Perkin Elmer TGA7, using N₂ as the carrier gas and a sample heating rate of 10 °C/min.

Synthesis of 1. To a solution of 1-propenyl-*tert*-butyl ester (20.00 g, 0.141 mol) and H₂PtCl₆ (57 mg, 0.0141 mmol) in benzene (100 mL) was added (MeO)₃SiH (18.91 g, 0.155 mol) dropwise. The solution was stirred at room temperature overnight after which the product was distilled to leave analytically pure **1** (95 % yield). IR for **1**: 2943.3, 2841.4, 1732.4, 1458.4, 1392.9, 1367.9, 1158.3, 1088.4, 819.0, 681.6, cm⁻¹. NMR for **1**: ¹H (400.1 MHz, C₆D₆), δ = 3.39 (s, 9H), 2.15 (t, 2H), 1.82 (m, 2H), 1.34 (s, 9H), 0.64 (m, 2H); ¹³C (100.05 MHz, C₆D₆), δ = 172.2, 79.3, 50.2, 38.3, 28.1, 19.0, 9.2; ²⁹Si (80.5 MHz, C₆D₆), δ = -42.3. HRMS (CI, isobutane) calcd. 265.1471, found 265.1468.

Synthesis of 2. To a solution of 1-propenyl-*tert*-butyl ester (20.00 g, 0.141 mmol) and H₂PtCl₆ (57 mg, 0.0141 mmol) in benzene (100 mL) was added (EtO)₃SiH (25.48 g, 0.155 mol) dropwise. The solution was stirred at room temperature overnight after which the product was distilled to leave analytically pure **2** (95 % yield). IR for **2**: 2975.9, 2929.6, 1732.9, 1456.6, 1391.9, 1367.4, 1220.4, 1104.5, 956.5, 848.8, 785.4, cm⁻¹. NMR for **2**: ¹H (400.1 MHz, C₆D₆), δ = 3.74 (q, 6H), 2.20 (t, 2H), 1.84 (m, 2H), 1.34 (s, 9H), 1.13 (t, 9H), 0.68 (m, 2H); ¹³C (100.05 MHz, C₆D₆), δ = 172.3, 79.3, 58.4, 38.4, 28.1, 19.3, 18.5, 10.5; ²⁹Si (80.5 MHz, C₆D₆), δ = -45.8. HRMS (CI, isobutane) calcd. 307.1940, found 307.1936.

Polymerization reactions. In a typical polymerization, to either neat **1** or **2** (0.040 mol) was added either aq. HCl or KOH (0.1 M solution, 2.16 mL) and the mixture was stirred vigorously for about 1.5 hours. The mixture becomes viscous and the volatiles were removed *en vacuo* (0.01 Torr) at room temperature. The tacky product was let stand for one week during which any residual volatiles were periodically removed. The polymers generated by base and acid catalysis had identical analytical data. ^{13}C CP MAS NMR, $\delta = 171.6, 79.0, 38.0, 28.2, 18.9, 13.1$. ^{29}Si CP MAS NMR, $\delta = -67.5$. IR: 2980.0, 2928.6, 1732.9, 1558.3, 1460.2, 1368.4, 1254.9, 1223.7, 1147.7, 1125.5, 1034.0, 849.1, 754.7, 697.2 cm^{-1} .

Polysilsesquioxane derotation. In a typical experiment, TsOH (10 % by weight) was added to a benzene solution of the polysilsesquioxane and the mixture stirred for at least two days. The volatiles were then removed *en vacuo* (25 °C, 0.01 Torr). Alternatively, the polymer was heated to 300 °C overnight in a vacuum oven. Both methods resulted in the formation of analytically similar solids. ^{13}C CP MAS NMR, $\delta = 178.4, 44.7, 17.5, 13.5$. ^{29}Si CP MAS NMR, $\delta = -66.2$. IR: 2939.9, 2883.9, 1718.0, 1576.2, 1411.1, 1125.5, 1034.5, 772.6, 688.3 cm^{-1} .

Polysilsesquioxane reaction with MeSnCl_3 . To a benzene solution of the polysilsesquioxane (0.50 g in 2.50 mL) was added MeSnCl_3 (0.307 g, 1.28 mmol), the mixture stirred for 5 minutes and let stand overnight. The gel was broken apart, washed with benzene and dried. ^{13}C CP MAS NMR, $\delta = 181.6, 37.4, 18.9, 13.1$. ^{29}Si

CP MAS NMR, $\delta = -67.0$. ^{119}Sn CP MAS NMR, $\delta = -364, -367$. IR: 2938.1, 1709.0, 1585.4, 1435.6, 1232.6, 1137.1, 1038.5, 788.0, 701.7 cm^{-1} .

References

1. Ozeki, T.; Kusaka, M. *Bull. Chem. Soc. Japan*, 1966, 39, 1995-1998.