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PREPARATION AND CHARACTERIZATION OF ARYL-SUBSTITUTED POLYSILSESQUIOXANES

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ABSTRACT

Polymerizations of aryltrialkoxysilanes generally afford soluble oligomeric or polymeric aryl-substituted silsesquioxanes. This is in spite of being based on trifunctional precursors capable of forming highly crosslinked and insoluble network polymers. In this study, soluble phenyl, benzyl, and phenethyl-substituted silsesquioxane oligomers and polymers were prepared by hydrolyzing their respective triethoxysilyl precursor with water or aqueous acid. Additional samples of the polymers were prepared by heating the materials at 100 °C or 200 °C under vacuum in order to drive the condensation chemistry. One sample of polybenzylsilsesquioxane was heated at 200 °C with catalytic NaOH. The resulting materials were characterized using solution ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, gel permeation chromatography, and differential scanning calorimetry. Of particular interest was the effect of the aryl substituent, and processing conditions on the molecular weight and glass transition temperatures of the polysilsesquioxanes.

INTRODUCTION

Polysilsesquioxanes are a class of siloxane polymers commonly prepared by the hydrolysis and condensation of trialkoxysilanes or trichlorosilanes [1]. From a trifunctional monomer one would expect the organically-modified polymers to be highly crosslinked and insoluble resins. However, while some silsesquioxane monomers with R = H, CH_3, or vinyl do form crosslinked polymers capable of forming gels, the majority react to form soluble oligosilsesquioxanes, including discrete polyhedral oligomers, and polymers. Because of their solubility, ladder structures have been proposed [2]. However, viscosity studies by Frye [3] indicate that the polyphenylsilsesquioxane is more likely best represented by a polymer rich in both cyclic structures and branches, but without any regular stereochemistry.

$$n\mathrm{Ar{-}Si(OR)_3} \quad + \quad 1.5n\,\mathrm{H_2O} \quad \xrightarrow{\mathrm{H+\ or\ OH-}} \quad \left[\mathrm{Ar{-}SiO_{1.5}}\right]_n \quad + \quad 3n\,\mathrm{ROH}$$

Ar = Phenyl (**1**), Benzyl (**2**), Phenethyl (**3**)

R = Me (**1-3a**); Et (**1-3b**)

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In this study, we have examined the hydrolysis and condensation polymerizations of phenyltrialkoxysilane, benzyltrialkoxysilane, and 2-phenethyltrialkoxysilane monomers under both acidic and basic conditions. The resulting phenyl, benzyl, and phenethyl-substituted polysilsesquioxanes were characterized by ^{1}H, ^{13}C, ^{29}Si NMR, gel permeation chromatography, and differential scanning calorimetry. The effects of the organic substituent (phenyl, benzyl, phenethyl), alkoxide group (OMe, OEt), catalyst (HCl, NaOH), monomer concentration, and polymer processing on polymer molecular weight, glass transition temperature were determined.

EXPERIMENTAL

Materials

Phenyltrimethoxysilane (**1a**) and phenyltriethoxysilane (**1b**) were purchased from Aldrich. Benzyltrimethoxysilane (**2a**) and benzyltriethoxysilane (**2b**) were purchased from Geleste. Phenethyltrimethoxysilane (**3a**) and phenethyltriethoxysilane (**3b**) were prepared by esterification of phenethyltrichlorosilane (Geleste) with methylorthoformate and ethylortho-formate, respectively. Monomers' purity was checked by GC and ^{1}H, ^{13}C, and ^{29}Si NMR and monomers were distilled until purity was greater than 96% (GC). Ethanol was distilled from magnesium ethoxide. Anhydrous methanol was purchased from Aldrich. Aqueous acid and base solutions (0.1M and 1M) were purchased from Aldrich.

Polymerizations

Polymerizations were carried out at 1M, 3.5M and neat monomer concentration in ethanol or methanol with 1.5-3 equivalents water with 1 M HCl or NaOH as catalysts to determine if monomers would gel under these conditions. Solution ^{29}Si NMR studies of the polymerizations of the monomers were carried out under these conditions.

Once, it was determined that the monomers would not gel, monomers **1b**-**3b** were allowed to react with aqueous catalyst (0.1 M HCl or NaOH) to prepare polymers for characterization and to provide materials with which to study the effects of processing. The mixtures were stirred until homogeneous solutions were formed. The viscous solutions were then heated (100 °C) under vacuum to remove hydrolysis products and help drive polymerizations to higher molecular weights. The effect of heating/curing time on molecular weight was determined by heating polymers between 1-185 hours at 100 °C. Alternatively, samples were heated at 200 °C under vacuum for 1 hour. Soluble polymers were characterized by gel permeation chromatography using light scattering detectors, differential scanning calorimetry to determine glass transition temperatures (T_g) and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy for structural information at the molecular level.

RESULTS

All six monomers (**1a**-**3a**, **1b**-**3b**) reacted under acidic and basic conditions to give aryl-substituted oligo- and polysilsesquioxanes. However, unlike tetraethoxysilane or other trialkoxysilanes known to form gels, these aryl monomers reacted to form oligomeric oils or gummy resins. Polymerizations were carried out with 1M, 3.5M and neat monomer, 1.5-3.0 equivalents of water, and an acid (HCl) or base (NaOH) catalyst. Reactions with NaOH catalyst took longer than the identical reactions with HCl as catalyst. In both cases, materials would often phase separate into a dense oily polymer or hard resin on the bottom of the vessel and a lighter alcohol phase. No gels were obtained from the polymerizations under any of the conditions examined-even with neat monomer. Nor were significant quantities of polyhedral oligosilsesquioxanes observed by NMR.

Solution NMR Studies

^{29}Si NMR has proven to be an invaluable technique for investigating the hydrolysis and condensation reactions required to polymerize alkoxysilane monomers [4]. The monomers all exhibit a single resonance in the ^{29}Si NMR spectra (**1a**: δ = -55.4; **1b**: δ = -58.9; **2b**: δ = -51.4; **3a**: δ = -43.8; **3b**: δ = -46.5).. Hydrolysis experiments performed at 1M monomer concentration with one equivalent of H_2O revealed no major differences in the early hydrolysis and condensation chemistry between these trialkoxysilanes and other alkoxysilanes. Under acidic conditions, it is possible to see the hydrolysis products of the monomer (T^0) and the early condensation products (T^1). Under basic conditions, no hydrolysis and early condensation products were observed; the monomer peak would slowly be replaced with T^3 resonances from fully condensed silsesquioxanes.

Molecular Weights

The oily resins isolated from the room temperature polymerizations of monomers **1b**-**3b** were found to be oligomeric (Table 1) with molecular weights under 1.6-3.2K under acidic conditions and 2.8-9.6K under basic conditions. All of the molecular weight data shown were determined using a light scattering detector; analyses run with polystyrene standards gave molecular weights that were typically a factor of two lower. The disparity between light scattering weights and those determined using polystyrene standards is characteristic for highly branched polymers. Condensation reactions continued with heating at 100 °C allowing the molecular weight to be driven to as high as 4.3K for the phenyl silsesquioxane, 3.5K for the benzyl silsesquioxane and 14K for the phenethyl silsesquioxane after 185 hours. Heating the samples at 200 °C under vacuum for 1 hour [5] also gave brittle, hard resins in most cases with molecular weights still under 10K. Heating the benzylsilsesquioxane at 200 °C in the presence of catalytic solid NaOH [6] also increased the molecular weight to 7K. Longer heat treatments at 200 °C with NaOH led to insoluble resins.

Table 1. Molecular weight and glass transition temperature data for phenyl-, benzyl, and phenethylsilsesquioxane polymers.

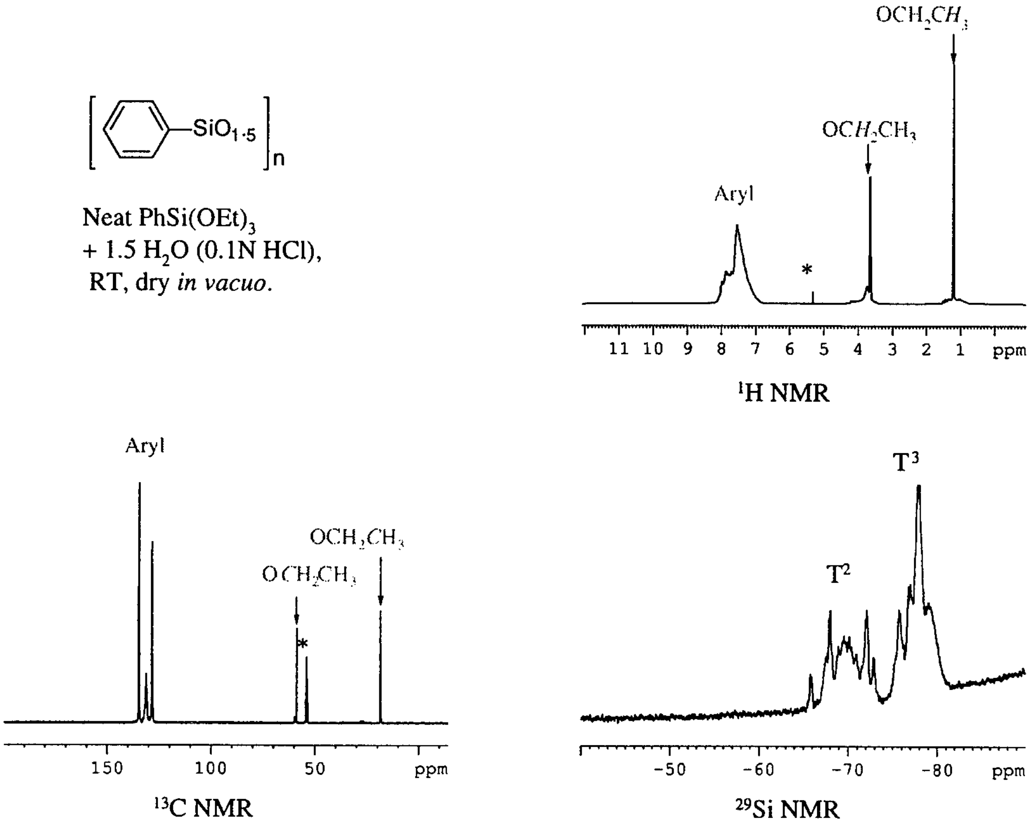
Monomer	Polymerization Conditions	Molecular Weight (M_w)	Polydispersity (M_w/M_n)	Glass Transition Temperature (°C)
1	neat, 3 H_2O, HCl, RT	2780	1.35	45.0
1	neat, 3 H_2O, NaOH, RT	2895	1.52	68.7
1	neat, 3 H_2O, HCl, 200 °C	6677	2.52	75.9
2	neat, 3 H_2O, HCl, RT	2294	1.22	4.0
2	neat, 3 H_2O, NaOH, RT	2894	1.35	29.3
2	neat, 3 H_2O, HCl, 200 °C	3140	1.27	20.2
2	1) $6H_2O$, 1N HCl, -EtOH	1) 3071	1) 1.31	1) 27.3
	2) NaOH/200 °C	2) 7030	2) 1.62	2) 39.6
3	neat, 3 H_2O, HCl, RT	2702	1.31	< -25.0
3	neat, 3 H_2O, NaOH, RT	9420	2.68	< -25.0
3	neat, 3 H_2O, HCl, 200 °C	9045	1.85	-10.6

Glass Transition Temperatures

The low molecular weight polysilsesquioxanes prepared and dried without heating exhibited the lowest glass transition temperatures (Table 1). Heat treating the polymers at 100 °C or 200 °C significantly increased the T_g's to near room temperature or above. Moreover, it was possible to see the effect of the different aryl groups (phenyl, benzyl, phenethyl) on the Tg's. The phenyl group produced materials with the highest T_g's ranging from 45-76 °C. The polybenzylsilsesquioxanes, with a single methylene spacer between the phenyl ring and the silicon, exhibited T_g's between 4-40 °C and the polyphenethylsilsesquioxanes, with an ethylene spacer between the phenyl and the silicon, had the lowest T_g, at -10 °C or below. Materials prepared with base catalysts exhibited higher T_g's than those prepared with acid.

NMR Characterization

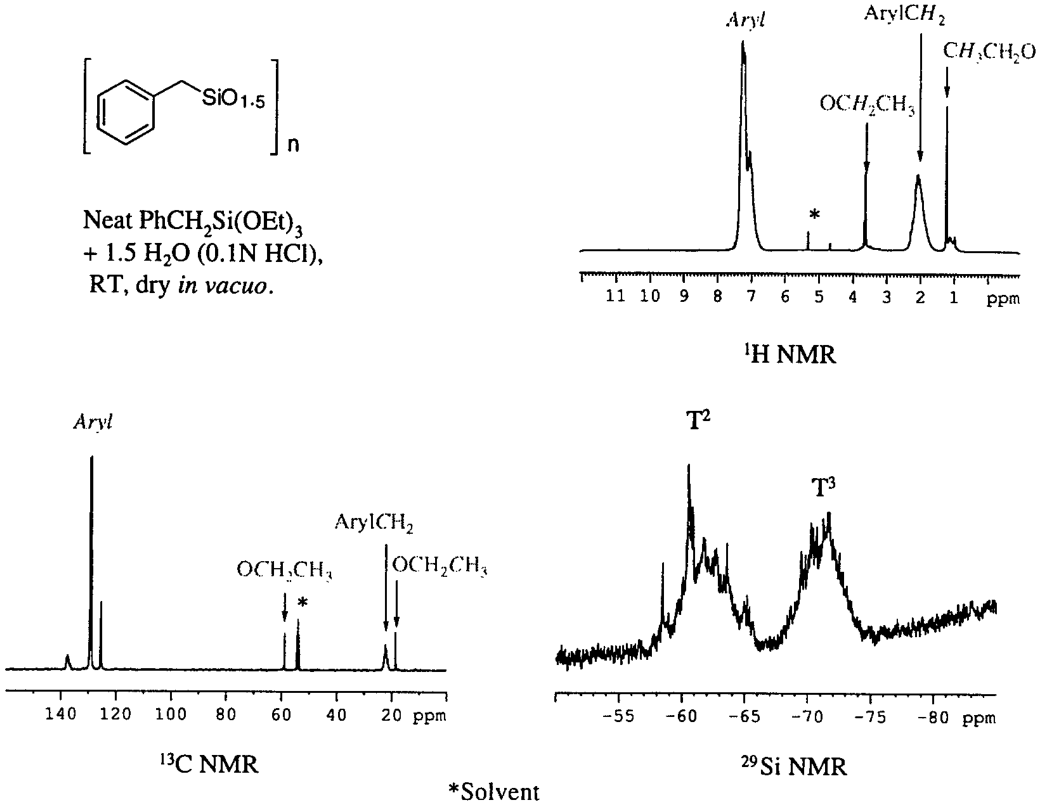
In addition to molecular weight and glass transition temperature determinations, the polysilsesquioxanes were also characterized by solution ^{1}H, ^{13}C, and ^{29}Si NMR (Figures 1-3). Proton and ^{13}C NMR provide structural details and information of the degree of hydrolysis of the alkoxide groups. In all cases, the expected aryl and aliphatic resonances were found in ^{1}H and ^{13}C spectra. Both the proton and ^{13}C NMR spectra revealed both residual ethoxide attached to the polymer and some ethanol in the polymers processed without heating. Heating the polymers to 200 °C under vacuum eliminated all of the residual solvent and much of the residual ethoxide.



*Solvent

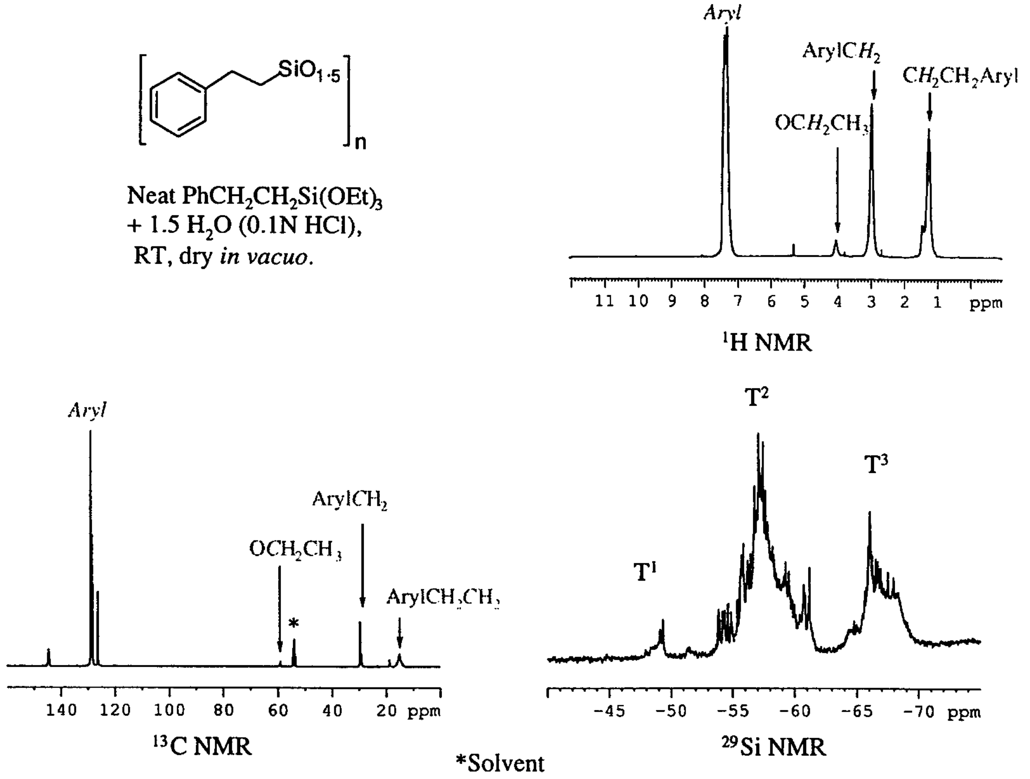
Figure 1. ^{1}H, ^{13}C, and ^{29}Si NMR spectra of phenylsilsesquioxane oligomer ($M_w = 2780$).

^{29}Si NMR provides not only structural information concerning the type of silicons present in the material [6], but the integrity of the silicon-carbon bond through which the aryl group is attached, as well. The aryl-substituted polysilsesquioxanes (Figures 1-3) all exhibited similar distributions of T^2 and T^3 silicons, though the phenethyl-substituted polysilsesquioxane appears to have the greatest contribution from T^2 silicons of the three. Heating the polymers at 200 °C failed to significantly reduce the contribution from T^2 silicons, despite the observed increase in molecular weights. Only after heating the benzyl polysilsesquioxane at 200 °C in the presence of catalytic NaOH did the T^2 peak disappear (Figure 4) leaving a fully condensed polysilsesquioxane. In all of these cases, there must be a significant contribution of cyclic structures to account for the solubility of these polymers with such high degrees of condensation. The ^{29}Si NMR spectra of the polysilsesquioxanes have too great a contribution of T^2 silicons and too broad a distribution of chemical environments for the materials to be ladder polymers. The x-ray diffraction pattern of the fully condensed polybenzylsilsesquioxane has some of the characteristics that have been attributed to ladder polymers [7], but there is insufficient evidence to confirm the structural assignment.



Neat $PhCH_2Si(OEt)_3$
+ 1.5 H_2O (0.1N HCl),
RT, dry *in vacuo.*

Figure 2. ^{1}H, ^{13}C, and ^{29}Si NMR spectra of benzylsilsesquioxane oligomer (M_w = 2294).



Neat $PhCH_2CH_2Si(OEt)_3$
+ 1.5 H_2O (0.1N HCl),
RT, dry *in vacuo.*

Figure 3. ^{1}H, ^{13}C, and ^{29}Si NMR spectra of phenethylsilsesquioxane oligomer (M_w = 2702).

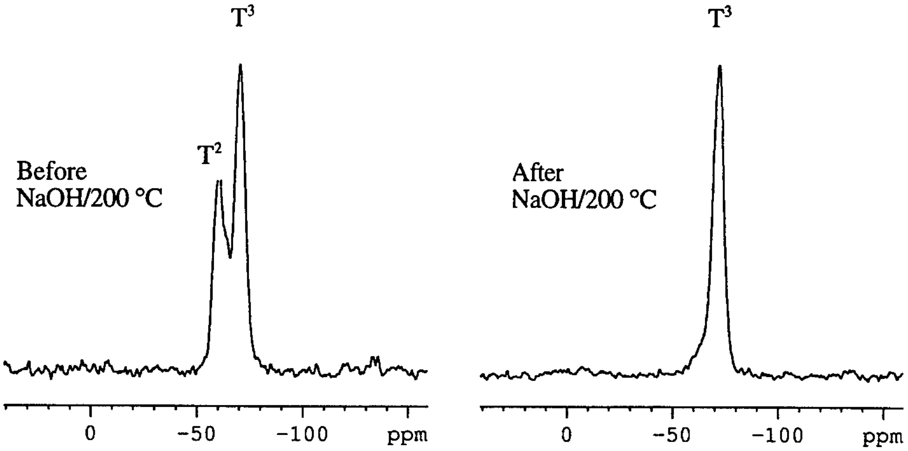


Figure 4. Solid state ^{29}Si NMR spectra of polybenzylsilsesquioxane before and after heating with catalytic NaOH at 200 °C for 1 hour.

CONCLUSIONS

Phenyl-,benzyl-, and phenethyltrialkoxysilanes polymerize to form *soluble* oligo- and polysilsesquioxanes. No gels of any of the monomers were observed to form. The molecular weights of the materials prepared and dried at room temperature were near 2K, but would continuously increase with heating at 100 °C to between 5-15K. The highest molecular weight were obtained from the phenethyl-substituted monomer. The glass transition temperatures for the polymers increased as the organic group was changed in the order: phenethyl<benzyl<phenyl. The glass transition temperature also increased with molecular weight . The polymers were structurally characterized by ^{1}H, ^{13}C, and ^{29}Si NMR. ^{29}Si NMR revealed substantial contributions from partially condensed silicons (T^2) even with heat treatments at 200 °C. A fully condensed polybenzylsilsesquioxane was obtained only after heating at 200 °C with catalytic base. The inability of these monomers to form crosslinked gels under mild conditions and the difficulty encountered in increasing the molecular weight of the soluble oligomers appears to be related to the steric bulk of the aryl substituents.

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