Surfactant and pH-Mediated Control over the Molecular Structure of Poly(phenylsilsesquioxane) Resins

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Control over the macromolecular structural characteristics of poly(phenylsilsesquioxane) resin materials was obtained by combining the effects of surfactant addition with dynamic pH modification in aqueous condensation media. Average molecular weight, polydispersity, and the degree of condensation in the resulting polymer were adjusted over a wide range by tuning the pH and by the selective use of alkylammonium-based surfactants. The average intermolecular spacing of condensate exhibits a linear dependency on the pH of the polymerization medium during condensation. A 14% increase in spacing occurs as pH is increased from 1.7 through neutrality to 11. The addition of cetyltrimethylammonium surfactant acts to either promote or inhibit the growth of the polymer, depending on the pH range of condensation. Under acid conditions (pH 3−4), 14 wt % alkylammonium surfactant increases the average molecular weight of condensate by over 4 times from 2700 amu. Near neutral conditions (pH 8), the molecular weight of resin product decreases 6-fold from 18900 amu with the same concentration of surfactant. The interruption of siloxane growth is tunable by selecting different alkylammonium components and is stronger using smaller cations. Dynamic mechanical thermal analyses were used to identify preliminary structure−property correlations for selected resin products.

Introduction

Poly(phenylsilsesquioxane) (PPSQ) is an important member of the poly(organosilsesquioxane) class of materials that has especially interesting properties for applications as dielectric, electro-optical, and thermal coatings.[1] PPSQ resins are generally obtained by hydrolysis and polycondensation of trifunctional phenylsilane monomers.[1−3] The resulting products are composed of a branching siloxane backbone where the phenyl group modifies the network at each silicon atom. Since the pioneering efforts in PPSQ chemical synthesis by Sprung and Guenther[4] and by Brown et al.,[5−7] a wide range of materials have been obtained in phenylsilsesquioxane systems such as branched polymer resins of various morphologies,[8−10] complete polyhedral cage compounds,[11,12] and oligomeric intermediates.[13−15]

Although many siloxane network configurations are available in silsesquioxane materials, improved synthetic approaches are still needed for directing the formation and resultant properties of PPSQ and other organosiloxane resin systems. Physical properties such as solubility, thermal and thermomechanical stability, mechanical strength and toughness, optical transparency, and dielectric constant may be designed into poly(organosilsesquioxane) products once new chemical methods have been developed for controlling the local and long-range structure of their molecular components.

In the present paper, we demonstrate chemical methods that can be used to direct the macromolecular characteristics in phenylsilsesquioxane resins synthesized from aqueous solutions. The relative kinetics of hydrolysis and condensation reactions may be manipu-

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lated by controlling the pH of the reaction medium, and these factors are known to strongly influence the morphology of the product in sol−gel-derived silicate systems.[16−18] Another successful approach for the structural control of siloxane network materials has been the incorporation of alkylammonium ions[19,20] and surfactants.[21] The independent and combined influences of pH and ammonium-based additives on directing the formation and structure of PPSQ resin materials are described.

Experimental Section

Base-Catalyzed Hydrolysis and Condensation. The initial set of experiments was performed by allowing hydrolysis and condensation of phenyltriethoxysilane (PhTES) monomer to occur under entirely basic conditions. PhTES was added to a stirring basic solution and the reaction product was obtained as precipitate. The basic agent used was tetramethylammonium hydroxide (TMAOH), octylamine, or a combination of both. The molar ratios of three representative reaction solutions were the following: 1.0:6.6:5.7:0.010 PhTES:EtOH:H_2O:TMAOH; 1.0:6.6:5.7:0.004:3.2 PhTES:EtOH:H_2O:TMAOH:octylamine; and 1.0:5.7:2.4 PhTES:H_2O:octylamine. The pH of each solution remained at 12.1 ± 0.2 from the time of monomer addition to that of precipitation. Precipitated condensate was collected by decantation of the clear supernatant, washed by vacuum filtration with deionized water/ethanol (1/3 by volume) until neutral by pH paper, and then washed again in pure ethanol. The rinsed powder was dried thoroughly under vacuum at room temperature.

Base-Mediated Condensation of Acid-Hydrolyzed Monomer. PhTES was prehydrolyzed for 60 min in a stirring solution of aqueous HCl and ethanol (1:5.2:13:0.014 molar ratio of PhTES:EtOH:H_2O:HCl). The solution pH prior to the addition of phenylsilane monomer was 1.8, and the initial pH of the complete reaction mixture was 1.7. After the prehydrolysis step, cetyltrimethylammonium bromide surfactant (CTAB, Aldrich) was added to a final concentration between 0 and 14 wt %. A base (NaOH, TMAOH, or one of various specified alkylamines) was added to adjust the pH of the solution to a value between 1.7 and 12. Precipitate obtained by condensation below a pH of 7 was collected by decantation and washed with a solution of deionized water/ethanol (1/1 by volume). In cases where no precipitate was obtained after 10 days, precipitation was induced by the addition of an equivalent volume of deionized water to the original solution. The resulting solid product was washed in pure deionized water. Condensate obtained above pH 7 began to precipitate within 5 min. After 24 h, the solid was collected by vacuum filtration, washed with a solution of deionized water/ethanol (1/1 by volume), and dried thoroughly under vacuum at room temperature. Characterized materials synthesized in the presence of octylamine without surfactant are designated as "OA*x*", where "*x*" is the sample number. The designation of those synthesized in octylamine with CTAB added are appended with the suffix "-C*y*", where "*y*" increases with the surfactant concentration. Characterized materials synthesize in the presence of dimethyloctylamine (without surfactant) are designated as "DMOAz", where "*z*" is the sample number.

Molecular weight fractions of polymer product obtained by condensation at pH 10 (without the addition of CTAB) were separated by solvent-selective precipitation from various mixtures of methanol and tetrahydrofuran. A known quantity of polymer was dissolved completely in tetrahydrofuran and then methanol was added to the stirring solution until the final polymer concentration was 10 wt % at the same time that the desired mass ratio of MeOH:THF was reached.

Characterization Methods. Washed condensate was examined using a complementary array of chemical structure characterization techniques. Molecular weight distribution (MWD), radius of gyration (R_g), and intrinsic viscosity (η) data of THF-soluble products were obtained from triple-detection gel permeation chromatography (GPC) measurements. The triple-detection GPC system employed includes a Waters Alliance 2690 Separation Module equipped with a Waters 2410 Differential Refractometer and a Viscotek T60A Dual Detection system with differential viscosimetry and laser light scattering detectors. The size-exclusion gel column set consisted of a PLgel 5-μm Guard and two PLgel 5-μm Mixed-C columns (Polymer Laboratories) arranged in series. Detector calibration, data acquisition, and data processing were performed through the Viscotek TriSEC software package. Solutions for GPC characterization were prepared by dissolving polymer product into THF to concentrations of $\approx$10 wt % and filtering the solution through a 0.2-μm polypropylene filter using a glass syringe. Sample volumes of 100 μL were measured at 30 °C and in THF flowing at 1.00 mL/min. Polystyrene standards with molecular mass of 90 100 amu (Viscotek) were measured at the beginning of each sample set to calibrate the light-scattering detector.

X-ray diffraction data were collected from powder samples using a Scintag X2 diffractometer. Infrared absorption spectra of pure powder samples were measured using a Nicolet Magna 850 IR Spectrometer with a PAC300 Photoacoustic detector (MTEC Photoacoustics).

Solution ^{29}Si NMR data were collected from condensates dissolved in $CDCl_3$ and from hydrolysates dissolved in acetone-d_6 solutions. Solution samples were placed in a 10-mm probe and measured in a Bruker AVANCE 200-MHz spectrometer. $Cr(acac)_3$ was added (0.02 M) to the test samples as a spin-relaxing agent. Solid-state samples were measured in a 4-mm zirconia rotor spinning at 10 000 rpm using a silicon-free probe and a Bruker AVANCE 500-MHz spectrometer. A single 30° rf pulse was applied on the ^{29}Si channel with a 45-s pulse delay and a proton-decoupling composite pulse. All ^{29}Si shifts are referenced to tetramethylsilane (TMS). Chemical shifts of silicon atoms in silsesquioxane compounds are referred to using the traditional terminology T^n where the superscript corresponds to the number of oxygen bridges to other silicon atoms. Thus, an uncondensed monomer is designated T^0, and a fully condensed polymer with no residual silanols would be comprised of T^3 silicon atoms.

Thermogravimetric and differential thermal analyses were performed using a Netzsch STA 409 simultaneous thermal analyzer under flowing oxygen at a heating rate of 5 °C/min. Dynamic mechanical thermal analysis (DMTA) was used to differentiate the physical properties between selected resin products. Samples were cast into glass filters (Advantec GA100) from toluene solutions of 20 wt % and left to dry for 2 days at room temperature. Each measurement was conducted isochronally at a heating rate of 3 °C/min and a frequency of 1 Hz. The first DMTA run was conducted from room temperature to 200 °C and kept for 10 min before cooling back to room temperature. The second run was conducted up to 250 °C and kept for 10 min. After these cycles, the sample was again cooled to room temperature and subjected to a third run up to 300 °C.

Results

Polymer from Base-Catalyzed Hydrolysis and Condensation. PPSQ condensates derived from water/ethanol/amine solutions at pH 12 show a clear trend of increasing molecular weights as TMAOH is gradually

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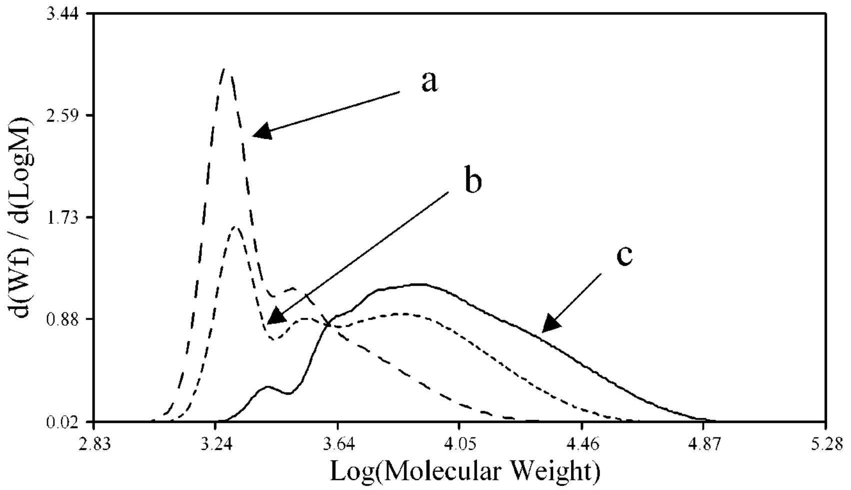

Figure 1. Molecular weight distribution of condensate products from base-catalyzed hydrolysis and condensation reactions where the catalyst employed was (a) TMAOH only, (b) a mixture of TMAOH and octylamine, and (c) octylamine only.

replaced by octylamine as the amine component (Figure 1). The data from GPC analyses demonstrate clearly that this synthesis procedure provides a very simple method of tuning the MWD of polymer product by varying only the ratio of primary:quaternary amine additive.

At pH 12, TMAOH solutions produced a high yield of PPSQ condensate in <1 day. The product was primarily composed of a narrow MWD centered at ≈2000 amu and contained another small population centered at ≈3000 amu. Washed samples of this material were dissolved to 10 wt % in THF and left to equilibrate, resulting in the crystal growth of the dodecameric polyhedral cage compound $(PhSiO_{3/2})_{12}$ over the course of several days at 30 °C. Identification of this compound was verified by matching the lattice parameters from single-crystal XRD measurements with the published values[12] and by comparison to powder XRD traces of commercially obtained samples of $(PhSiO_{3/2})_{12}$ and $(PhSiO_{3/2})_8$ (Hybrid Plastics). The population of soluble PPSQ centered at around 2000 amu presumably contained a significant portion of partial cage molecules that were able to undergo intramolecular condensation and form the completely condensed and insoluble polyhedral compound.

When octylamine was used as the base instead of TMAOH, the precipitation of polymer product was much slower. The yield of polymer precipitate from octylamine solutions increased steadily with time between 1 and 16 days (from 6 to 50% yield, respectively). The material obtained from this reaction was composed of a very broad distribution of molecular weights (Figure 1) centered at around 6000 amu. No significant fraction of product as low as 2000 amu was detected, which is consistent with the observation that no insoluble compounds evolved from THF solutions. The MWD of the condensate products remained constant regardless of the amount of incubation time prior to washing, indicating that the initial precipitate did not equilibrate to lower molecular weights in the basic polymerization medium.

Acid/Base-Catalyzed Polymerization Products. Aqueous HCl (pH 1.2) was added to ethanol, resulting in a pH increase to 1.8. PhTES was added, bringing the mass ratio to 1:1:1 H_2O:EtOH:PhTES, and the initial pH value was 1.7. After 5 min of stirring, the solution became a single phase as the monomer became hydrolyzed. If the pH is not increased, the solution is stable for over 1 week before polycondensation induces phase separation. The hydrolysis reaction was determined to be complete after 60 min by comparing the ^1H NMR chemical shifts of a sample hydrolyzed in HCl/EtOH to a control solution consisting of fresh monomer mixed with the same water and ethanol content but without the acid catalyst (Figure 2 a, b). At this time and pH value condensation is primarily limited to the formation of dimers (T^1) with a very low content of chains (T^2) or residual monomers (T^0) as indicated by the corresponding ^{29}Si NMR data (Figure 2 c). The completely hydrolyzed triol monomer was synthesized and isolated by Taylor,[22] and the most likely chain compound is expected to be the cyclic tetramer tetrol synthesized by Brown et al.[5] and studied in greater detail by Feher et al..[15] After this prehydrolysis step, a base was added dropwise to bring the pH up to the selected value. As the pH was slowly increased, each of the solutions remained clear and single phase until it reached pH 7−8 at which point it became opaque white with the precipitation of condensate.

Polymeric condensate that was formed at pH 8 using dimethyloctylamine (DMOA) had a greater than 3-fold higher M_w than that which was formed with octylamine. This was largely due to the appearance of an additional polymer population having a log molecular weight centered at ≈5.2. This result suggests that the replacement of octylamine with DMOA in the base-catalyzed hydrolysis and condensation method (described in the previous section) could significantly increase the range in which the molecular weight may be controlled. However, the MWD of the PPSQ product obtained in the presence of the other primary, secondary, and tertiary amines tested (tetraethylamine, diethylamine, methylheptylamine, trimethylamine, and tetramethylmethylenediamine) had essentially the same profile as that of the polymer formed in octylamine solution.

Octylamine was chosen as a representative alkylamine base to study in more detail the influence of pH on the molecular structure of condensate from PhTES hydrolysate. The MWD of the resulting products exhibited a strong pH dependency in the range of 1.7−8 (Table 1). A relatively monodisperse molecular weight

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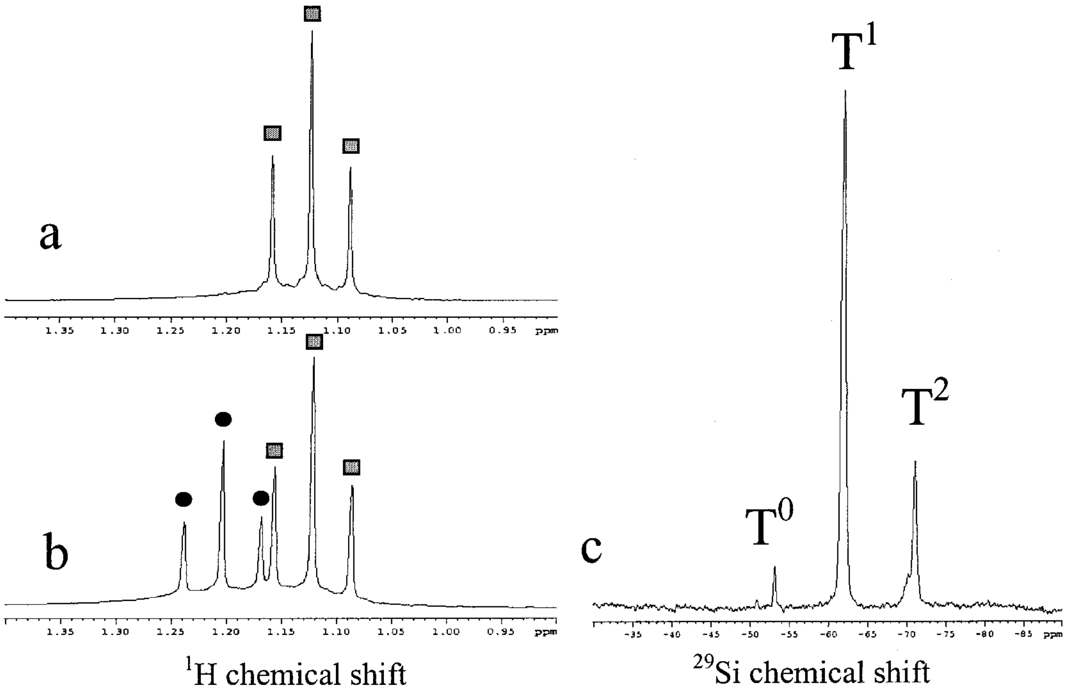

Figure 2. NMR chemical shift data of prehydrolysis product after 60 min. ^{1}H NMR data (a) show the completion of acid-catalyzed hydrolysis reactions after 60 min in water/EtOH solution compared to (b) a control at 1 min with no acid. The methyl groups of ethoxysilanes (corresponding to peaks designated with black circles) are totally absent in the prehydrolyzed sample relative to the methyl groups of ethanol (gray squares). ^{29}Si NMR data (c) indicate that the 60-min prehydrolyzed solution consists primarily of dimers (T^1) and relatively few chains or cyclics (T^2) or residual monomer (T^0).

Table 1. pH Dependency of Some Parameters Related to Polymer Structure by Octylamine-Catalyzed Condensation of Prehydrolyzed Monomer (PD = Polydispersity Index, a_{MH} = Mark−Houwink Parameter, d_{XRD} = Spacing Corresponding to First XRD Reflection, t_{ppt} = Time between Setting pH and Observation of Precipitation of Insoluble Product)

PhTES:EtOH:H_2O:HCl = 1:5.2:13:0.014

sample	pH	M_w (amu)	PD	η_w (dL/g)	R_{gw} (nm)	a_{MH}	d_{XRD} (Å)	polymer yield (%)	t_{ppt}
OA1	1.7	1780	1.1	0.023	1.1	1	10.4	17	4 days
OA2	4.2	4410	1.5	0.041	1.5	0.5	10.8	35	5 days
OA3	8.1	13700	2.5	0.033	2.3	0.4	11.0	90	0 min
OA4	10.8	14600	2.0	0.039	2.6	0.5	11.9	98	0 min
OA5	11.3	14900	1.9	0.040	2.6	0.5	11.8	88	0 min

Table 2. pH Dependency of Some Parameters Related to Polymer Structure Synthesized by DMOA-Catalyzed Condensation of Prehydrolyzed Monomer

sample	pH	M_w (amu)	PD	η_w (dL/g)	R_{gw} (nm)	a_{MH}	d_{XRD} (Å)
DMOA1	1.7	1780	1.1	0.023	1.1	1	10.4
DMOA2	2.0	2360	1.3	0.025	1.2	0.6	10.5
DMOA3	7.0	273000	31	0.063	6.0	0.4	11.2
DMOA4	8.8	120000	12	0.063	5.1	0.5	11.5
DMOA5	9.5	10200	1.9	0.032	2.1	0.6	11.6

population was exhibited by sample OA1, which was condensed without the addition of base. The M_w of sample OA1 is consistent with oligomers composed of ≈10−11 monomer residues. Polymer obtained at and above pH 8 had a much higher M_w and polydispersity index.

Because DMOA promoted the formation of substantially higher molecular weight resin material at pH 8, this base was used to prepare an additional set of PPSQ polymers at several other pH values. The dependency of polymer structure on pH was quite dramatic as evidenced by the GPC data summarized in Table 2. For example, sample DMOA3 (from pH of 7.0) exhibited a M_w value of a quarter million with a polydispersity of over 30.

The primary X-ray reflection exhibited by materials prepared using this two step acid−base polymerization method correlated well with the pH imposed in the polymerization medium during condensation (Figure 3 A,B). This relationship is approximately linear and continuous within the pH range probed and is not altered across either the titration point of the HCl/silanol/alkylamine system (pH 5−6) or the point of pH neutrality. Moreover, the correlation between *d* spacing and pH from samples obtained by either octylamine or DMOA occurred on the same line. It was also discovered that a similar increase in intermolecular spacing was affected by thermally curing the resin (Figure 3C). The shift in the XRD reflection occurs concurrently with a loss of silanol groups as the material becomes cross-linked and insoluble.

Spectroscopic studies were performed to further investigate the correlation between pH-dependent structural changes and the residual silanol content in the resin. FTIR data from polymers obtained at higher pH values show an increase in the intensity of the siloxane "cage" vibrational band (1130 cm^{-1}) relative to the antisymmetric stretch from "branching" siloxane (≈1035 cm^{-1}). Additionally, the cage vibration was confirmed to be a characteristic mode of the $(PhSiO_{3/2})_{12}$ cage compound. The increased presence of cage vibrations is attributed to the more complete degree of condensation in the polymer. Condensation was also observed by the disappearance of the SiOH stretching band between 920 and 860 cm^{-1} as the pH of the polymerization reaction is increased. Quantitative determination of the residual silanol content was obtained by measuring the relative fractions of T^0, T^1, T^2, and T^3 in the material using ^{29}Si

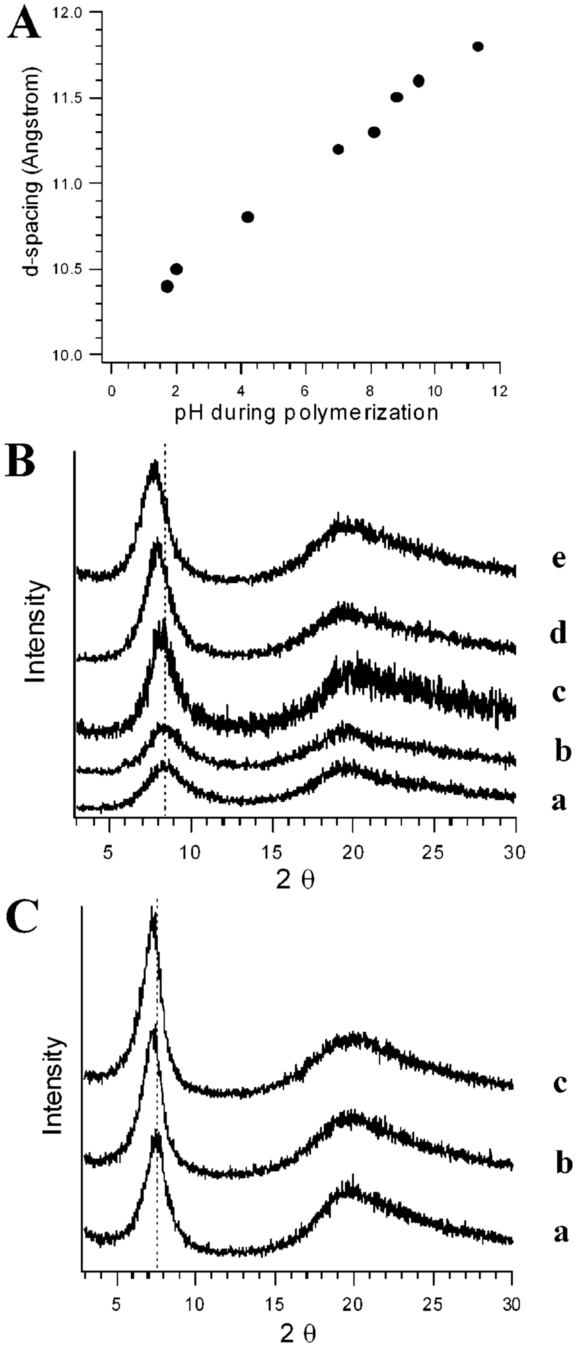

Figure 3. The first two plots present the relationship between the pH at which precipitation of condensate is induced and the XRD characteristics of the corresponding resin product. (A) The linear correlation between pH and position of the primary X-ray reflection; (B) XRD traces of resin products obtained at a pH of (a) 1.7, (b) 4.2, (c) 8.1, (d) 10.8, and (e) 11.3, showing a shift of the primary reflection to higher *d* spacings with increasing pH. The primary X-ray reflection is attributed to intermolecular spacing of the resin components and the very broad reflection at higher angles is caused by the intramolecular siloxane structure. Plot (C) shows a shift to higher intermolecular spacing in a resin (from pH 10.8) that is thermally cured from (a) 25 °C to (b) 240 °C to (c) 300 °C.

NMR characterization. Samples precipitated from acidic, neutral, and basic solutions were analyzed and condensation was confirmed to be greater for higher values of pH (Figure 4).

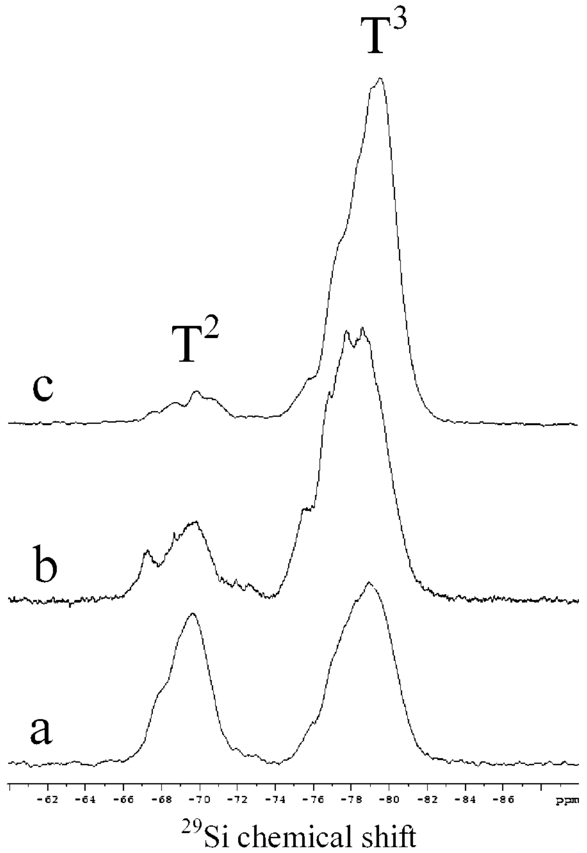

Figure 4. The ^{29}Si spectra of PPSQ resin products obtained at a pH of (a) 4.2, (b) 8.1, and (c) 11.3, indicating that the degree of condensation increases progressively (89, 94, and 97%, respectively) with increasing pH.

Two probable explanations for the pH-dependent changes in the XRD data are (1) that the polymers are composed of linked cages of changing average sizes and/or (2) that the conformations selected at different pH values have progressively different packing characteristics. Whatever is the reason for the shifting XRD peak, it is not believed to be significantly influenced by molecular weight of the product. The periodicity correlates well with the pH during condensation but not with the MWD of the product. That is, the *d* spacing increased continuously across the point of pH neutrality, whereas the M_w was at a maximum using a pH between 7 and 10. Additionally, octylamine and DMOA promoted the growth of PPSQ to a very different MWD at a given pH value; however, the XRD patterns and *d* spacings of the corresponding polymers were nearly identical.

To identify structural differences as a function of molecular weight in PPSQ resin material condensed at a fixed pH, several molecular weight fractions were isolated. The complete resin was synthesized by octylamine titration of prehydrolysate to pH 10. Individual molecular weight fractions were separated by solvent-selective precipitation from various mixtures of methanol and tetrahydrofuran. The GPC data show that the selective precipitation method was successful in isolating separate molecular weight populations from the original polymer mixture (Figure 5). The polydispersity increased and the Mark−Houwink *a* parameter decreased at a higher value of M_w, indicating a more densely branched structure. Within the total polymer each fraction was found to have a *d* spacing in the range of 11.5−11.8 Å and these distances did not correlate with the respective fraction's M_w (ranging from 4.9 to 25 k).

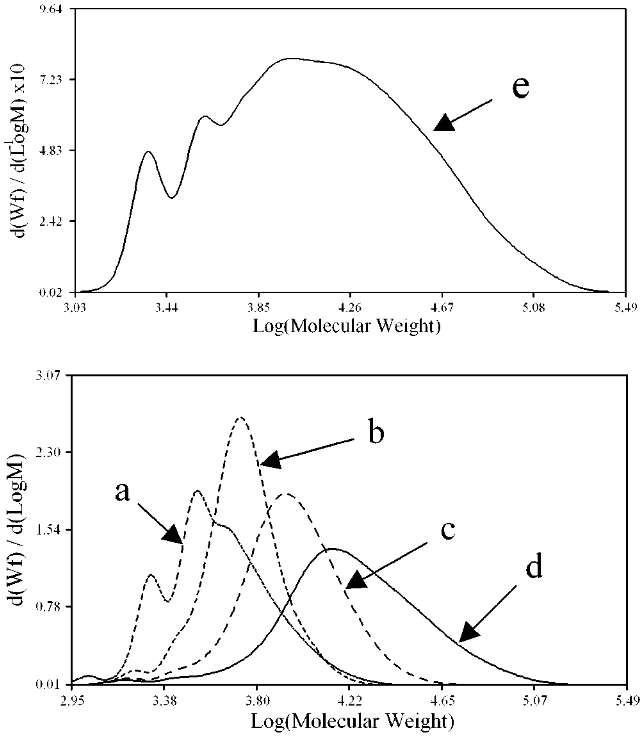

Figure 5. Molecular weight distributions from isolated molecular weight fractions of PPSQ resin synthesized at pH 10 without surfactant. Fractions were collected by precipitation between MeOH:THF ratios of (a) 100:0 to 80:20, (b) 80:20 to 70:30, (c) 70:30 to 60:40, and (d) 60:40 to 50:50. The molecular weight distribution of total product (e) prior to fractionation is also presented.

The physical transitions of silsesquioxane resins, such as the glass transition (T_g), cross-linking, and chemical decomposition events, can be easily identified by comparing the results from TGA, FTIR, and DMTA analyses. Curing of the as-synthesized resin and the decomposition of organic groups were observed by TGA analysis in flowing oxygen for high and low molecular weight resins. A gradual mass loss occurred from room temperature to around 400 °C and was attributed to the decrease in silanol content as condensation reactions occur during thermal curing. This assignment is consistent with FTIR studies and with the corresponding transition from a soluble to an insoluble resin. The decomposition temperature of phenyl groups in oxygen were identified by a sharp exothermic DTA peak observed at 560 °C for the low molecular weight material and at 530 °C for the higher molecular weight material.

The resin cure and decomposition processes were studied further using DMTA by monitoring the dynamic mechanical shear properties. In a typical measurement, a resin sample in solution was adsorbed onto a porous glass filter substrate and dried in air first under ambient pressure and then under vacuum. Normalized DMTA profiles are presented for uncured resin during the first run (Figure 6 A,B) and cured resins during the third run (Figure 6C,D). A peak in the viscous modulus (or imaginary component, G'') occurring with a drop in the elastic modulus (or real component, G') is assigned to the T_g. Prior to thermal curing, sample OA5 exhibited a T_g of 60 °C, compared with a much lower T_g of 30 °C for sample OA1. After curing, however, these materials show no significant difference in T_g ($\approx$100 °C). The increase in G' from 80 to 200 °C is attributed to the curing of the resin into a higher molecular weight polymer or a more cross-linked network. As would be expected in the case of irreversible condensative polymerization reactions, the T_g response of the first thermal cycle was not repeated in the second and third cycles. The thermomechanical behavior of the sample synthesized under higher pH conditions was relatively uniform for the three tests; however, the T_g did increase after the initial thermal cycle.

Addition of CTAB Surfactant to Prehydrolysis Polymerization Solutions. CTAB was added to the prehydrolyzed monomer solution prior to setting the final pH with octylamine. In the previously described base-catalyzed hydrolysis and condensation experiments, the presence of tetramethylammonium headgroups was shown to limit the growth of the polymer. A similar effect was observed by the addition of tetramethylammonium salts to octylamine-catalyzed hydrolysis and condensation reactions of PhTES at pH 12. Although an acid prehydrolysis step had not been used in these previous examples, the same size-limiting trend was observed. Furthermore, the substitution of "softer" cationic salts such as tetrapropyl- and tetrabutylammonium for tetramethylammonium resulted in products having intermediate MWD profiles between those measured when tetramethylammonium or no additive was used (Figure 7).

The data from the acid/base-catalysis studies demonstrated that the pH imposed during condensation of prehydrolyzed monomer controls various structural aspects of the polymer precipitate. Having defined several of these relationships, the addition of surfactant additives was investigated for the purpose of modifying the pH-dependent trends. Two experiments were designed to explore the interacting influences of surfactant concentration and pH. In one study, CTAB was added to the prehydrolyzed monomer solution (0.17, 1.6, or 14 wt % of the total mixture) prior to titration with octylamine to a final pH range of 3.4−4.2 or 8.1−8.5. In a second study, 14 wt % CTAB was added to the prehydrolyzed monomer solution followed by the addition of octylamine to a final pH varied between 1.7 and 10.5.

The addition of various amounts of CTAB presented a surprising degree of control over the previously observed trend toward increasing M_w with pH 1.7−8.5. As seen from the data presented in Table 3, the concentration of CTAB controls polymer MWD within roughly the same range whether condensed under either acidic (pH 3−4) or slightly basic (pH 8) conditions. Furthermore, the MWD of sample OA1 is very similar to that exhibited by sample OA3−3C, although there are significant pH-dependent differences in structure as indicated by the measured values of η_w and R_{wg}. Conversely, the MWD of sample OA2−C3 is very similar to that of sample OA3. With use of surfactant additives to overcome the pH dependency of MWD, the average molecular weight and intermolecular spacing may be significantly decoupled. This ability enhances the power to synthetically control and design the structural characteristics of PPSQ resins using aqueous media.

An additional experiment was performed by holding the CTAB concentration constant at 14 wt % and varying the pH at which condensation was induced. The

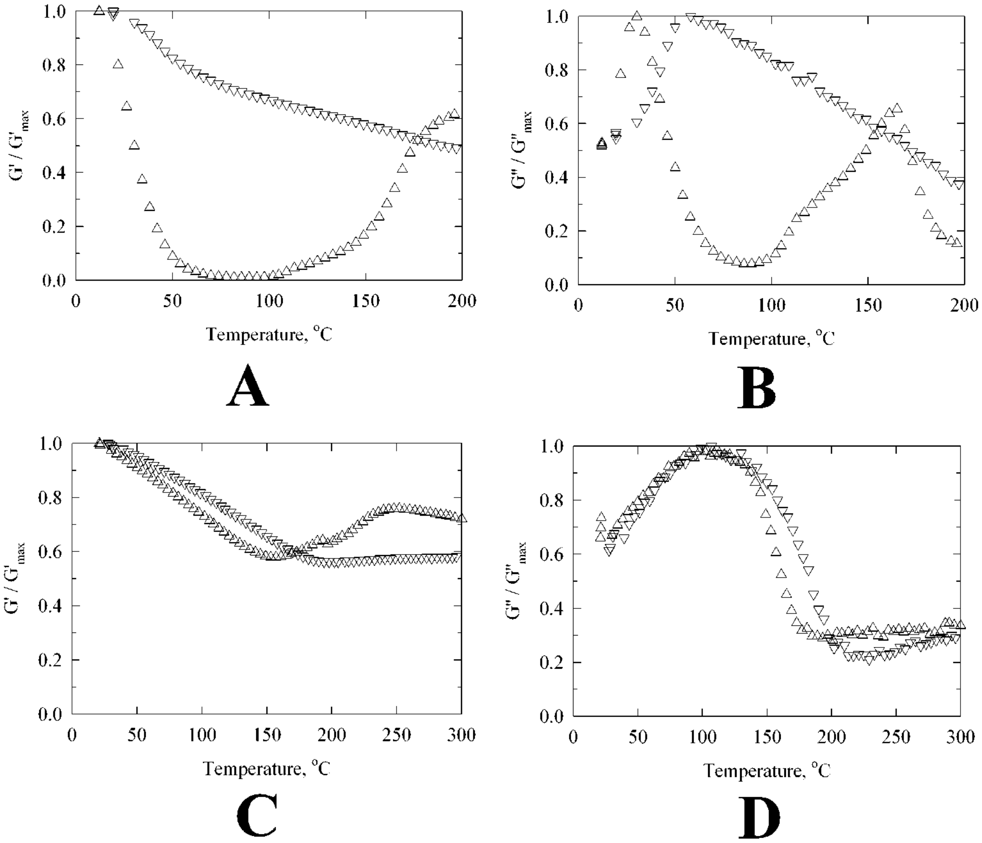

Figure 6. Normalized DMTA profiles from (A, B) uncured resin during first run and (C, D) cured resins during third run. Upright triangles correspond to resin product obtained at pH 1.7, and inverted triangles correspond to resin product obtained at pH 11.3.

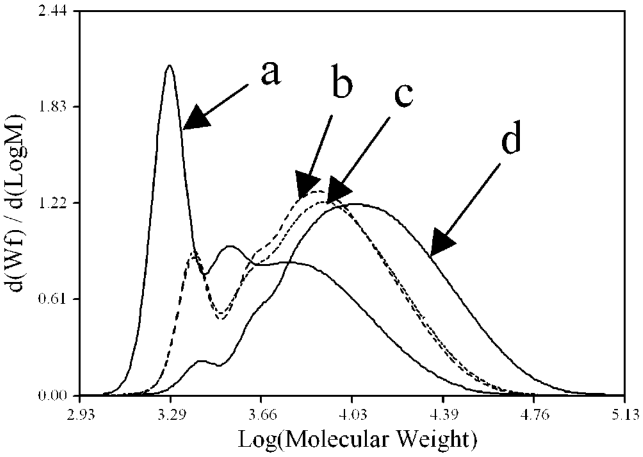

Figure 7. Molecular weight distributions of condensate products from octylamine base-catalyzed hydrolysis and condensation reactions in which the following tetraalkylammonium salts were included in the polymerization medium: (a) tetramethylammonium bromide; (b) tetrapropylammonium bromide; and (c) tetrabutylammonium iodide. The molecular weight distribution of the product obtained by octylamine base catalysis without dissolved alkylammonium salts is included for comparison (d).

Table 3. CTAB Concentration Dependency of Some Parameters Related to Polymer Structure Synthesized by Octylamine-Catalyzed Condensation of Prehydrolyzed Monomer

sample	pH range	CTAB concn (%)	M_w (amu)	PD	η_w (dL/g)	R_{gw} (nm)
OA2	3.4−4.2	0	2730	1.5	0.041	1.5
OA2−C1		0.17	6360	1.8	0.027	1.7
OA2−C2		1.6	6500	1.8	0.027	1.7
OA2−C3		14	12600	2.6	0.033	2.2
OA3	8.1−8.5	0	18900	2.7	0.033	2.3
OA3−C1		0.17	4150	1.4	0.024	1.5
OA3−C2		1.6	3520	1.3	0.023	1.4
OA3−C3		14	2920	1.2	0.022	1.3

Table 4. pH Dependency of Some Parameters Related to Polymer Structure Synthesized by Octylamine-Catalyzed Condensation of Prehydrolyzed Monomer in the Presence of 14 wt % CTAB Surfactant

sample	pH	M_w (amu)	PD	η_w (dL/g)	R_{gw} (nm)
OA1−C3	1.7	2970	1.5	0.023	1.3
OA2−C3	3.2	12600	1.8	0.033	2.2
(OA5−C3)	7.3	3620	1.3	0.023	1.4
OA3−C3	8.5	2920	1.2	0.022	1.3
OA4−C3	10.5	1950	1.2	0.022	1.2

high CTAB content caused a strong influence on the MWD of polymer products (Table 4). Under acidic conditions, the polymer products exhibited significantly higher M_w than the corresponding samples made without CTAB. However, under near neutral and basic conditions the polymer growth was severely limited in the presence of the ammonium headgroup.

Although surfactant concentration causes a dramatic effect on the MWD of PPSQ products, FTIR and ^{29}Si NMR analyses indicated that the final silanol content and the degree of condensation were not changed significantly by the addition of CTAB. Moreover, the XRD traces were unaltered by changes in CTAB concentration at a given pH. The IR vibrational bands corresponding to silanol and siloxane groups between 1300 and 800 cm^{-1} were nearly identical for PPSQ products synthesized near pH 11 with or without the addition of CTAB. The ^{29}Si NMR data from sample OA4−3C exhibited a T^0:T^1:T^2:T^3 ratio corresponding to

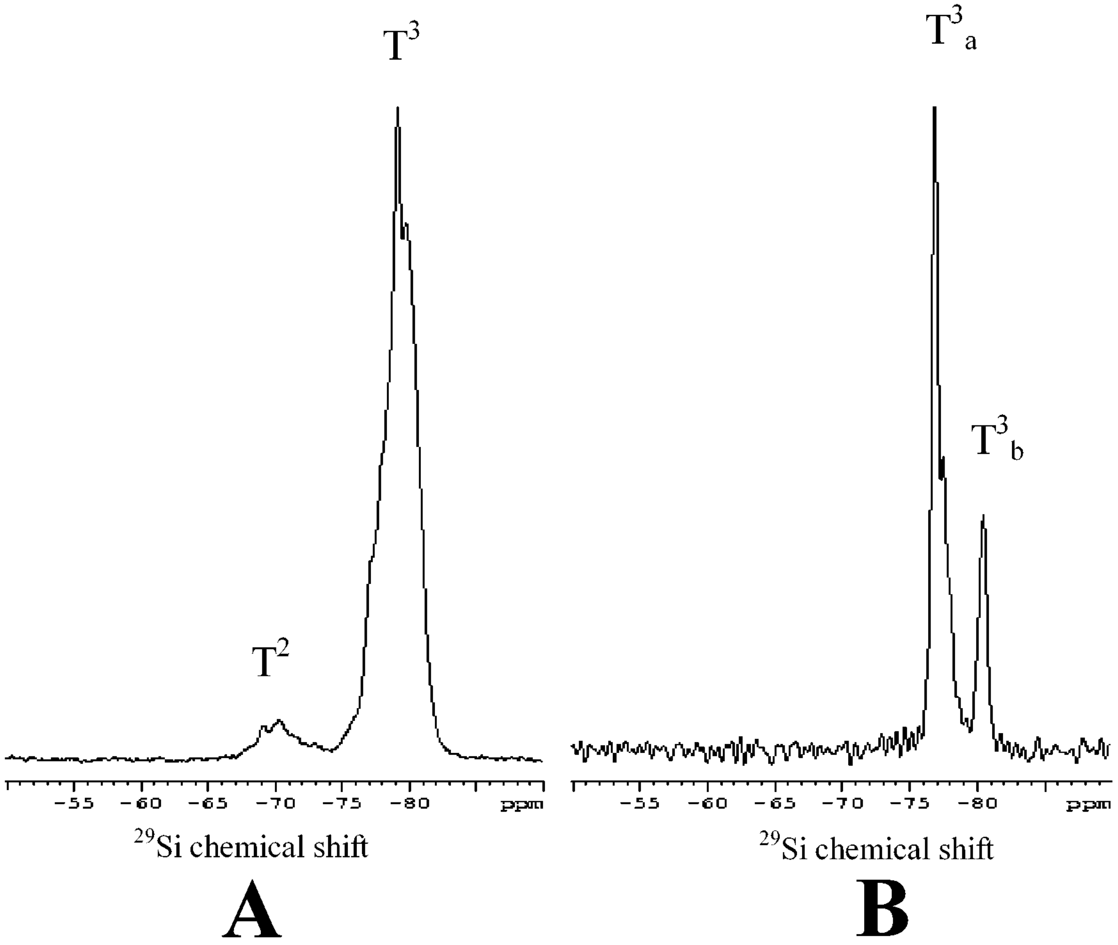

Figure 8. The ^{29}Si spectrum of (A) PPSQ resin product obtained at a pH of 11.3 in the presence of 14 wt % CTAB surfactant, indicating the degree of condensation to be 97% and the presence of a preferred Si bonding environment appearing at −79.2 ppm. As a reference of a known chemical structure, the ^{29}Si NMR spectrum was also measured for (B) the crystalline $(PhSiO_{3/2})_{12}$ compound which has only two sharp bands at −76.9 and −80.5 ppm representing two structurally unique Si sites, labeled T^3_a and T^3_b, respectively.

a 97% degree of condensation (Figure 8 A). Although condensation occurred near pH 11 for both syntheses, the chemical shift line shapes from sample OA4−3C are very different than those of sample OA5 (Figure 4C). Specifically, a sharp feature appears above the broad T^3 envelope at −79.2 ppm that is absent in the resin made without surfactant.

This peak is indicative of a unique structural component that has not yet been conclusively identified. The authors postulate the existence of preferentially formed ring structures which are qualitatively similar to those present in the crystalline $(PhSiO_{3/2})_{12}$ compound. The dodecameric cage molecule has only two sharp bands corresponding to two structurally unique Si sites, labeled T^3_a (−76.9 ppm) and T^3_b (−80.5 ppm) in Figure 8B. In each cage molecule, eight Si atoms (T^3_a) are joined in one four-member and two five-member SiO rings, and the other four Si atoms (T^3_b) are joined in two four-member and one five-member SiO rings.[10] The chemical shift splitting of two distinct species has been described for several dodecameric polyhedral alkylsilsesquioxanes.[23] The positions of chemical shifts in silicate structures are correlated to the degree of strain in Si−O bond angles such that increasing bond strain moves the corresponding chemical shift downfield.[24,25] This line of reasoning would suggest that CTAB surfactant promotes a preferred bonding configuration in the resin having a bonding energy that is intermediate between the T^3_a and T^3_b configurations.

Discussion

In situ modification of the pH during the polymerization of PhTES monomer provides control over many important factors, including the relative rates of hydrolysis and condensation, average molecular weight and polydispersity, intermolecular spacing, and the concentration of residual silanol groups. Acid conditions can be used initially to prehydrolyze organosilane oligomers, and condensative polymerization may be induced in the presence of surfactants or other structure-directing agents by subsequently increasing the pH to a given final value.

At a pH value between 0 and 3, hydrolysis rates of alkoxysilane monomers are much greater than their respective condensation rates.[15,16] Under these conditions, such monomers can be reacted with water to obtain a relatively stable prehydrolyzed starting solu-

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tion. Benefits to the prehydrolysis step are that the reaction kinetics and chemical composition of the monomer and oligomeric intermediates are greatly simplified because the competition between hydrolysis and condensation reactions is minimized or eliminated. The pH at which condensation is induced strongly influences the structure and composition of the PPSQ resin product and also changes the interaction between the growing siloxane and cationic surfactants. The addition of a base such as metal hydroxide, tetraalkylammonium hydroxide, amine (primary, secondary, or tertiary), or buffer solution increases the pH of the solution and induces precipitation of condensate. Another important effect of increasing the pH is that it causes a corresponding increase in intermolecular spacing.

An additional and independent method of controlling the structure of PPSQ resin components is by incorporating cationic or amphiphilic molecular additives into the polymerization medium. The presence of cations such as sodium or tetraalkylammonium causes a disruption in the chain extension of silsesquioxane polymers and thereby lowers the M_w of the product. Near the isoelectric point of siloxane networks (ca. pH 1−2) the net charge associated with the growing siloxane interface is low and the ionic interaction with counterions will be correspondingly low. However, at higher values of pH (i.e., farther from the isoelectric point) the negative charge of the siloxane is increased and the effect of cations limiting the polymeric growth of the silsesquioxane becomes more prominent. The selection and concentration of cations can be used to adjust the M_w and the MWD profile of the resulting polymeric materials. The size of organic groups on a tetraalkylammonium additive may be chosen to modify the strength of interactions between the cation and the charged siloxane. Larger ammonium ions such as tetrabutylammonium are relatively “soft” and interact less with charged siloxanes compared with smaller and “harder” ions such as tetramethylammonium.

In cases where the cationic additive is part of an amphiphilic molecule (such as ammonium-based surfactants) a contrary influence can be exerted on the growth of PPSQ resins. As mentioned above, at pH values nearer to the isoelectric point of siloxane networks, the growing siloxane interface has a relatively low charge associated with it and the resulting association with charged cations is weaker. However, hydrophobic oligomers and polymers are solubilized in an aqueous or alcoholic solution by the presence of amphiphiles. The increased solubility of polymer subunits apparently promotes intermolecular condensation and chain growth over termination or premature precipitation.

Hydrophobic and electrostatic interactions between surfactant additives and organosiloxane oligomers provide synthetic handles to control macromolecular resin properties such as molecular size and density. Another component of the present structural-control methodology is to use the ammonium headgroup of the surfactant to create order in the bonding structures of polymer subunits by the preferential selection of intermediate siloxane structures from among the many available conformations. The ^{29}Si NMR data of the resin synthesized in the presence of CTAB does, in fact, indicate a preferred local bonding configuration relative to those in the polymer made at the same pH without surfactant. This configuration is believed to be energetically intermediate between those found in the two Si atom sites in the dodecameric phenylsilsesquioxane cage compound.

Conclusions

New chemical routes have been developed for introducing structural control into an aqueous-based synthesis of POSQ resin materials from prehydrolyzed organoalkoxysilane precursors. Average molecular weight, intermolecular spacing, and the degree of condensation in the resulting polymer may be adjusted by tuning the pH and by selecting the concentration of alkylammonium-based surfactants. Intermolecular spacing of condensate was probed by low-angle XRD and exhibits a linear dependency on the pH of the polymerization medium during condensation. A 14% increase in spacing prior to thermal curing is affected by changing the pH from 1.7 to 11. The intermolecular spacing appears to be directly related to the content of residual silanol groups in the resin and expands further as the material is thermally cured to an insoluble cross-linked network.

The addition of CTAB surfactant to the polymerization medium acts to either limit or promote the growth of the resin components. At a pH near the isoelectric point of silica, the presence of CTAB promotes an increase in the molecular weight of the resin product, whereas at higher pH values (e.g., above neutral) the positively charged CTAB headgroup frustrates intermolecular condensation of the negatively charged siloxane network. Apparently similar interactions are demonstrated by the addition of tetraalkylammonium halide salts in which the strength of the interaction is correlated to the size of the cation. “Harder” cations such as the CTAB headgroup or tetramethylammonium inhibit polycondensation in basic solution more than do “softer” cations such as tetrabutylammonium.

The ability to selectively synthesize different structural arrangements facilitates the study of structure−property relations that are necessary to improve the resin’s performance in various technological applications. Some preliminary structure−property correlations defined by DMTA analyses illustrated significant differences in the thermo-mechanical behavior of resins synthesized under high and low pH conditions.

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Supporting Information Available: Tabulated GPC numerical data from resins obtained by (1) hydrolysis and condensation by a single-step base catalysis, (2) base-catalyzed condensation of acid-hydrolyzed monomer for the various amines tested, and (3) molecular weight fractionation by solvent-selective precipitation. Powder XRD traces of $(PhSiO_{3/2})_{12}$ reference compound compared to those of commercially obtained $(PhSiO_{3/2})_{12}$ and $(PhSiO_{3/2})_8$, and an image of the single-crystal specimen. Photoacoustic infrared spectra of resin materials (1) obtained by condensation at varying pH values, (1) heated from 25 to 260 °C, and (3) synthesized with and without CTAB. TGA mass loss data for resins formed by condensation under acid and base pH values (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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