

Colloidal Silica-Bearing Hydrosilane Groups

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Stöber silica was functionalized with three silyl coupling agents: triethoxysilane (TES), dimethylethoxysilane (DMES), and vinyltrimethoxysilane (VTM). Microelectrophoresis, dynamic light scattering, and elemental analysis were used to study the degree of interaction between the silyl coupling agents and the silica surface. Small changes in the electrophoretic mobilities and particle diameters between the unmodified (Si–OH) and DMES silica (Si–DMES) showed that Si–DMES coupled to the surface through a single point of attachment. In contrast, the surface coupling reaction with TES (Si–TES) led to multilayered, oligomeric species bound to the surface. The electrophoretic mobilities in acetone decreased from $-4.47 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ for Si–OH to $-3.87 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ for Si–TES and the particle diameter of Si–TES was 13 nm larger than the bare silica. Although VTM has three alkoxy groups capable of forming large cross-linked oligomeric species, the mobility of the VTM-modified silica (Si–VTM) decreased to only $-4.41 \times 10^{-8} \text{ m}^2 \text{ V}^{-1}$ and the particle diameter increased by only 4 nm. The surface reaction with VTM showed that the nature of the functional group on the silyl coupling agent played an important role in determining the reactivity of alkoxy groups with the silica surface. Using the Pt-catalyzed hydrosilation reaction, Si–TES was reacted with vinyl naphthalene (Si–TES–VN), styrene (Si–TES–ST), and vinyl-terminated poly(dimethylsiloxanes) (Si–TES–PDMS). These reactions demonstrated that Stöber silica modified with TES can lead to a variety of colloiddally stable model dispersions in solvents varying in polarity from water to hexane. The modified silica systems were characterized by ¹³C and ²⁹Si solid-state NMR, diffuse reflectance infrared spectroscopy (DRIFTS), elemental analysis, transmission electron microscopy, fluorescence and UV–vis absorption spectroscopy.

Introduction

The study of colloidal materials is motivated by the remarkably interesting properties that they possess. It is further driven by the wide variety of industrial applications which exploit these species in fields including sol–gel science, adhesion and lubrication technology, chromatography, colloid science, and catalysis.¹ To better understand these materials, there remains the need for well-defined model colloidal systems. It would be of particular interest to develop model systems which are colloiddally stable in a variety of solvents of differing polarity and whose stability could originate from electrostatic, steric, or electrosteric forces.

The ideal model colloid would be monodisperse, have a regular surface with functional groups that can be freely interconverted between charged and nonpolar species, have a surface to which other moieties can be attached, have a core with no porosity, and be readily prepared and modified. There are very few chemical systems that can satisfy all of these requirements. We have begun a general exploration of the use of silica particles in this context because they possess many of the necessary properties.

One well-studied colloidal system, which has found widespread use as a model system in several areas, is silica prepared by the Stöber process.² The silica

synthesis involves the ammonia-catalyzed hydrolysis and condensation of tetraethyl orthosilicate (TEOS). There are several characteristic features of this process: (i) the particles can conveniently be grown to diameters in the colloidal range between 20 nm to 1 μm ,³ (ii) colloiddally stable spherical particles having a narrow size distribution can be readily prepared for particle diameters greater than 50 nm, (iii) the silica particles have a limited porosity, and (iv) the surface properties of the particles can be chemically modified.⁴

Stöber silica prepared in the manner just described is electrostatically stabilized by the electrical double layer formed from the ionization of silanol groups, a process facilitated by the presence of the aqueous NH₃ mixture.⁴ A series of centrifugation/redispersion cycles allows one to change the solvent while maintaining colloidal stability, providing that the permittivity of the continuous medium is sufficiently high.⁵

For investigations in nonpolar media, colloidal particles are usually stabilized with polymers.⁶ Although many techniques have been developed to prepare sterically stabilized dispersions, problems such as, swelling of the polymer lattices, irreproducibility in the synthesis, particularly if the process involves dry stages,⁷ and

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(1) Brinker, C. J.; Scherer, G. W. *Sol-Gel Science*; Academic Press: Boston, 1990; pp 839–870.

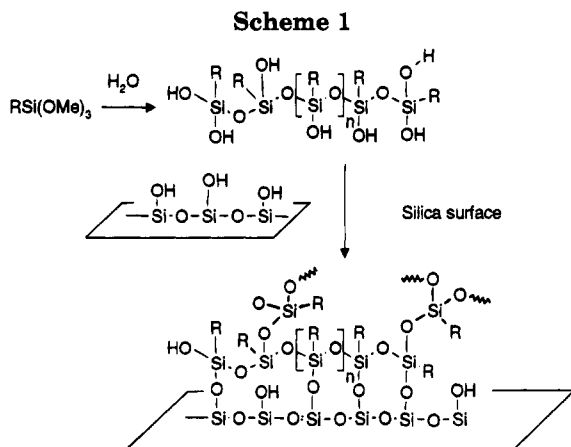
(2) Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62.

(3) Bogush, G. H.; Tracy, M. A.; Zukoski IV, C. F. *J. Non-Cryst. Solids* **1988**, *104*, 95.

(4) Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979.

(5) Philipse, A. P.; Vrij, A. *J. Colloid Interface Sci.* **1989**, *128*, 121.

(6) Napper, D. H. *Polymeric Stabilisation of Colloidal Dispersions*; Academic Press: London, 1983.



controlling the nature of the polymer attachment at the liquid/solid interface have been encountered.⁸

In the case of silica, problems associated with the particle core, such as swelling, do not arise. The modification of the surface is facilitated by the presence of reactive silanol groups. One approach developed to permit the use of mineral fillers in polymers, utilizes the strength of the Si–O bond. Organosilanes (RSi(OR')₃, coupling agents) are grafted to the mineral, rendering the inorganic surface much more hydrophobic (Si–OSiR', Scheme 1).⁹ Examples of this approach have already been reported for Stöber silica. For example, condensation reactions between colloidal silica and conventional alkoxy bearing silane coupling agents having aminopropyl (silica–O–SiCH₂CH₂CH₂NH₂), mercaptopropyl (silica–O–SiCH₂CH₂CH₂SH), or methacryloxypropyl (silica–O–SiCH₂CH₂CH₂OCO–CH(Me)=CH₂) functionalities have been described.^{5,10} Stöber silica has also been coated with fluorescent dyes.^{11,12}

There are several other methods by which polymers can be grafted onto a particle surface. As one example, the coupling process just described has been utilized to attach radical initiators to the surface. Upon radical initiation in the presence of a reactive monomer, steric groups are attached to the surface.¹³ Poly(stearic acid), poly(isobutene) derivatives,¹⁴ and hydroxy-terminated poly(dimethylsiloxanes) (PDMS) have been grafted to the surfaces of the particles using condensation reactions.^{7,15} Finally, vinyl- and methacrylate-modified silica spheres have been used to carry out the radical grafting of PMMA onto particle surfaces or the attachment of a hydrosilane terminated silicone (HMe₂Si(OSiMe₂)_nOSiMe₂H) through a hydrosilation reaction.¹⁶

(7) Edwards, J.; Lenon, S.; Toussaint, A. F.; Vincent, B. *ACS Symp. Ser.*, No. 240 **1984**, 281–296.

(8) Ryan, K. *Chem. Ind.* **1988**, 6 June, 359.

(9) Plueddemann, E. P. *Silane Coupling Agents*; Plenum Press: New York, 1982.

(10) Badley, R. D.; Ford, W. T.; McEnroe, F. J.; Assink, R. A. *Langmuir* **1990**, 6, 792.

(11) van Blaaderen, A.; Vrij, A. *J. Colloid Interface Sci.* **1992**, 8, 2921.

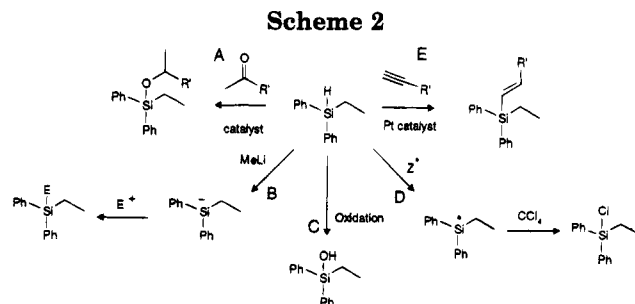
(12) Verhaegh, N. A. M.; van Blaaderen, A. *Langmuir* **1994**, 10, 1427.

(13) Tsubokawa, N.; Kimoto, T.; Koyama, K. *Colloid Polym. Sci.* **1993**, 271, 940. Sunkara, H. B.; Jethmalani, J. M.; Ford, W. T. *Chem. Mater.* **1994**, 6, 362.

(14) Pathmanoharan, C. *Colloids Surf.* **1988**, 50, 1. Pathmanoharan, C. *Colloids Surf.* **1988**, 34, 81.

(15) Auroy, P.; Auvray, L.; Leger, L. *J. Colloid. Interface Sci.* **1992**, 150, 187.

(16) Ketelson, H. A.; Brook, M. A.; Pelton, R. H. *Polym. Adv. Tech.*, in press.



Preparing a model colloidal system requires a generic, surface functional group that will allow the attachment of a wide variety of groups under ionic, transition-metal-catalyzed, or radical conditions.¹⁷ None of the systems described above is generic in this sense. Hydrosilane functionalities (Si–H), however, are remarkably versatile in that they serve as convenient precursors for the introduction of organic moieties under a wide range of conditions, taking advantage of the relatively weak Si–H bond (Scheme 2).¹⁷

Given the beneficial properties of silica already alluded to, we were interested in determining if Si–H modification of the silica surface would provide a general route to well-defined colloidal systems that could be readily modified in analogy to the reactions shown in Scheme 2. Although the modification of Stöber silica with Si–H groups has not been reported in the literature, there are a few studies which have attached Si–H groups to high surface area porous silica for applications in biomaterials,¹⁸ chromatography,¹⁹ and catalysis.²⁰

Our exploration to date of the use of hydrosilanes as surface functional groups for model colloidal systems is given below. We have examined the preparation of silica particles modified with Si–H groups derived from triethoxysilane and dimethylethoxysilane, characterized the materials spectroscopically and physically, and used them in the preparation of derivatized materials through the hydrosilation reaction.

Experimental Section

Instrumentation and Analytical Procedures. *Solid-State ¹³C and ²⁹Si Nuclear Magnetic Resonance Spectroscopy.* A Bruker-100 spectrometer operating at 25.2 MHz for carbon was used to obtain ¹³C cross polarization (CP)/magic angle spinning (MAS) solid-state spectra. Direct-polarization ²⁹Si spectra were obtained using a Bruker AM 500 spectrometer equipped with a solid-state accessory operating at 99.3 MHz for silicon. Adamantane was used as the internal reference in the ¹³C CP-MAS experiments, SiMe₄ was used as an internal standard for ²⁹Si NMR MAS experiments. The MAS spectra were run with long delay times (18 s) to allow essentially complete relaxation of the T and Q units.

Electron Microscopy. The transmission electron micrographs (TEM) of the colloids were acquired using a

(17) Eaborn, C.; Bott, R. W. In *Organometallic Compounds of the Group IV Elements*; MacDairmid, A. G., Ed.; Dekker: New York, 1968; Vol. 1. Pawlenko, S. In *Organosilicon Chemistry*; Walter de Gruyter & Co.: New York, 1986.

(18) Bräuer, L.; Gruber, H.; Greber, G. *Angew. Makromol. Chem.* **1990**, 180, 209.

(19) Sandoval, J. E.; Pesek, J. *J. Anal. Chem.* **1991**, 63, 2634.

(20) Le Déoré, C.; Révillon, A.; Hamaide, T.; Guyot, A. *Polymer* **1993**, 34, 3048.

Table 1. Characterization of Silica Particles before and after Treatment with Silanes

	Si-OH	Si-TES	Si-DMES	Si-VTM	Si-TES-PDMS
DLS (d_{av} , nm) ^a	179 ± 2	192 ± 3	178 ± 2	173 ± 2 ^b	242 ± 5
electrophoretic mobility (m ² V ⁻¹ s ⁻¹ × 10 ⁻⁸)	-4.79 ± 0.12	-3.87 ± 0.10	-5.35 ± 0.29	-4.41 ± 0.11	0
weight % C ^c	2.04	4.12	2.14	4.83	
weight % Si	40.53				
weight % H	1.25	1.55	1.36	1.37	
titration Si-H wt %		0.5-0.7	0.15-0.2		
no. of Si-H/nm ²		6-8	2-3		

^a The relative particle size changes upon functionalization were similar irrespective of whether TEM or DLS was used. The absolute sizes of the particles were somewhat smaller by TEM (average diameter, d_{av}). ^b New particle batch; $d_H = 169 ± 1$ nm. ^c No nitrogen was detected by combustion analysis in this sample; detection limit = 0.01%

JEOL JEM-1200EX microscope. Carbon-coated Formvar grids were used as sample grids.

Dynamic Light Scattering (DLS). DLS experiments were performed at 25 °C, and the colloid samples were prepared for analysis by filtering the dispersions through 0.8 μm Millipore filters to remove dust particles. Particle size measurements were carried out using a Brookhaven Model BI-9000AT correlator and a Lexel (25 mW) argon ion laser operating at 514.5 nm. All data were collected for 15-30 min at a scattering angle of 90°. Samples were diluted manually to achieve an optimum signal output. The intensity-averaged particle sizes were reported as the mean diameter using Version 4.0 of the Brookhaven BI-2P software. The viscosity and refractive index used for acetone at 25 °C were 0.316 cP and 1.359, respectively. The data for all compounds is summarized in Table 1.

Laser Doppler Microelectrophoresis. The electrophoretic mobilities for colloid samples in water and acetone were measured using a Coulter DELSA. Details of the experimental procedure have been published elsewhere.²¹

Diffuse Reflectance FTIR (DRIFTS). DRIFTS spectra were recorded on a Nicolet 20DX spectrometer using a Spectra Tech diffuse reflectance accessory. All spectra were measured from approximately 4000 to 400 cm⁻¹, and the number of scans was typically 100 with a resolution of 4 cm⁻¹. The samples were analyzed after washing with absolute ethanol and acetone, respectively, followed by precipitation of the particles in diethyl ether and drying in a vacuum oven at 60 °C/0.01 mmHg for 24 h. All samples were run neat, and fine KBr (FTIR grade, Aldrich) was used as the background file. The solids were approximately 2 mm deep in the sample (cup) holder.

UV-Vis Spectroscopy. The UV-vis spectra were recorded using a Hewlett-Packard 8452A UV-vis diode array spectrophotometer at 25 °C equipped with a quartz cuvette.

Elemental Analyses. Combustion analyses (C, H, N, and Si) of the unmodified and modified silica products were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada.

General Procedures. The glassware used for the silica synthesis and surface modifications was cleaned by rinsing several times with acetone followed by a 2% HF solution and finally with several rinses using Milli-Q water once again to remove traces of HF. The glassware was subsequently dried and stored in a vacuum oven for 24 h before each use. A Lauda Series RMS-6

refrigerating circulator bath was used to control reaction temperatures. A Beckman L7-55 ultracentrifuge with a type 60 Ti rotor operating at 3500 rpm and at 25 °C was used to carry out all the sedimentation/redispersion cycles on the unmodified and modified silica samples.

Materials. Ethanol solution (2.0 M NH₃, Aldrich), toluene (Caledon, reagent grade), carbon tetrachloride (BDH, reagent grade), chloroform (BDH, reagent grade), diethyl ether (BDH, reagent grade), hexane (Fisher Scientific, HPLC grade), acetone (Caledon, dried (95.5 wt %) and glass distilled), potassium iodide (Aldrich, 99%), sodium thiosulfate, volumetric standard solution in water (Aldrich, 0.0998 N), *N*-bromosuccinimide (Aldrich, 99%), vinyl-terminated poly(dimethylsiloxane) (PDMS-Vi, United Chemicals, $M_w = 62$ 700), Karstedt's Pt catalyst²² (2-3 wt % Pt concentration in xylene, [(Pt)₂(H₂C=CHSiMe₂OSiMe₂CH=CH₂)₄], United Chemicals), and 2-vinylnaphthalene (Aldrich, 98%) were used as received. Tetraethyl orthosilicate (TEOS, Aldrich, 99.999+%), triethoxysilane (TES, Aldrich, 95%), dimethylethoxysilane (DMES, United Chemical Technologies, 98%), and vinyltrimethoxysilane (VTM, Aldrich, 98%) were distilled prior to use.

Syntheses. **Preparation of Stöber Silica Si-OH.** H₂O (4.3 mL, 0.24 mol), NH₃ (50.7 mL, 0.1 mol) and absolute ethanol (73 mL) were mixed in a glass vessel inserted in a 30 °C water bath fitted with a submerged magnetic stirrer. The mixture was stirred for 30 min to allow the liquids to come to thermal equilibrium. TEOS (6 mL, 27 mmol) was quickly added. A sonicating probe was inserted through a specially fitted hole through the top of the vessel and positioned 5 cm below the liquid level.²³ The mixture turned cloudy after approximately 20 min and was left stirring with sonication for 10 h. At that time, TEOS (12 mL, 54 mmol) and H₂O (1.9 mL, 0.1 mol) were added to the alcohol mixture. Following a further 10 h mixing period, a third addition of TEOS (12 mL, 54 mmol) and water (1.9 mL, 0.1 mol) were added to the dispersion. Centrifugation and redispersion cycles with 5 × EtOH followed by 5 × fresh acetone (glass distilled) were employed to clean the products of unreacted material. The sedimented solids were redispersed in fresh solvent using a sonicator following each centrifugation cycle. Using this procedure, about 7 wt % solid content was obtained.^{13C}

(22) Karstedt, B. D. General Electric Co. Ger. Offen., DE 2307085 730823 1973; Chem. Abstr. 1973, 80, 16134.

(23) Although sonication is not necessary for the particle synthesis, we have found that in some samples a small amount of silica gel precipitated at bottom of reaction vessel due to mixing problems. It was observed that a sonicating probe helped to reduce this gel formation.

(21) Pelton, R.; Miller, P.; McPhee, W.; Rajaram, S. *Colloids Surf.* 1993, 80, 181.

NMR (CP-MAS) δ 60.59, 17.24. ^{29}Si NMR (MAS) δ -103, -110, -96.

Modified Colloidal Silica. $\text{HSi}(\text{OEt})_3$ -Modified Silica Si-*TES*. To a clean and colloidal stable acetone/silica dispersion containing 0.5 g of solid/200 mL of solvent was added TES (1.4 mL, 7.5 mmol). The mixture was stirred under reflux and a stream of nitrogen under positive pressure for 36 h. The silica Si-*TES* was subsequently cleaned free of unreacted silane coupling agent using centrifugation/redispersion cycles, $5 \times$ acetone. IR (DRIFTS) ν Si-H 2251 cm^{-1} v strong; this peak was not observed in Si-OH. This peak is found at 2225 cm^{-1} in TES.

HMe_2SiOEt -Modified Silica Si-*DMES*. As above, but with DMES (1.0 mL, 7.5 mmol). IR (DRIFTS) ν Si-H 2147 cm^{-1} v strong; this peak was not observed in Si-OH. This peak is found at 2147 cm^{-1} in DMES.

Oxidative Titration. The following procedure was used to determine the number of Si-H groups attached to the TES- or DMES-modified silica surface Si-*TES* and Si-*DMES*, respectively.²⁵ A general description follows: the modified particles (at least 0.5 g) were introduced into a 250 mL flask followed by carbon tetrachloride (25 mL) and a freshly prepared *N*-bromosuccinimide solution (15 mL, 0.1 M in acetic acid, 1.5 mmol). The mixture was sonicated at room temperature for 30 min. Immediately following this period, KI (2 g, 12 mmol) dissolved in water (50 mL) was added to the dispersion giving a reddish brown color. Titration with 0.0998 N sodium thiosulfate led to a violet color which became a clear, colorless solution at the endpoint. Blank titrations were done in the same manner except that the solids were excluded from the titration vessel and the mixture was not left to stand for 30 min. Two blanks were titrated for each analysis of a modified silica sample. The concentration of Si-H surface groups was determined from the difference in volumes of $\text{Na}_2\text{S}_2\text{O}_3$ needed to obtain the end point between the blank and silica compounds. See Table 1.

$\text{H}_2\text{C}=\text{CHSi}(\text{OMe})_3$ (VTM) Modified Silica Si-*VTM*. As above, but with $\text{H}_2\text{C}=\text{CHMe}_2\text{SiOEt}$ (1.0 mL, 7.5 mmol). ^{13}C NMR (CP-MAS) δ 137.14, 128.16, 51.41, 17.79.

Grafting to Surface Functionalized Silica. Hydro-silylation of TES Particles with Vinyl-naphthalene (VN) Si-*TES*-*VN*. To a colloidal dispersion of Si-*TES* containing 0.2 g of solid/10 mL of THF was added vinyl-naphthalene (VN, 0.95 g, 6.2 mmol). After this was stirred for 30 min at room temperature, Karstedt's catalyst (100 μL) was injected into the reaction mixture. The mixture was stirred at reflux for 24 h. The mixture was cleaned free of unreacted VN by washing with THF using $3 \times$ centrifugation/redispersion cycles. UV-Vis: The superposition of the starting material and Si-*TES*-*VN* is shown in Figure 5. IR (DRIFTS): An attenuation of the peak at 2251 cm^{-1} could clearly be seen to that shown in Figure 1. Combustion analysis: % C 4.85 % H 1.84.

Hydrosilylation of TES Particles with Styrene (ST) Si-*TES*-*ST*. As above: 7 (0.2 g of solid/10 mL THF); St (0.95 g, 6.2 mmol). IR (DRIFTS): An attenuation of the peak at 2251 cm^{-1} could clearly be seen similar to that shown in Figure 1. Combustion analysis: % C 4.47 % H 1.65.

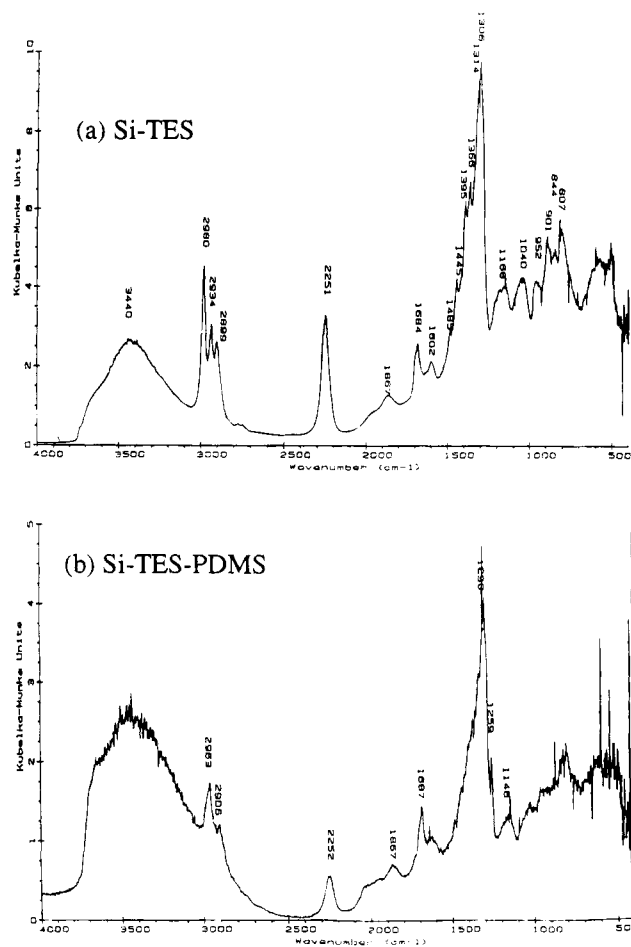


Figure 1. DRIFT spectra of Stöber silica: (a) modified with TES (Si-*TES*); (b) modified with silicone by the Pt-catalyzed hydrosilylation between Si-*TES* and VT-PDMS ($M_w = 62\,700$, Si-*TES*-PDMS).

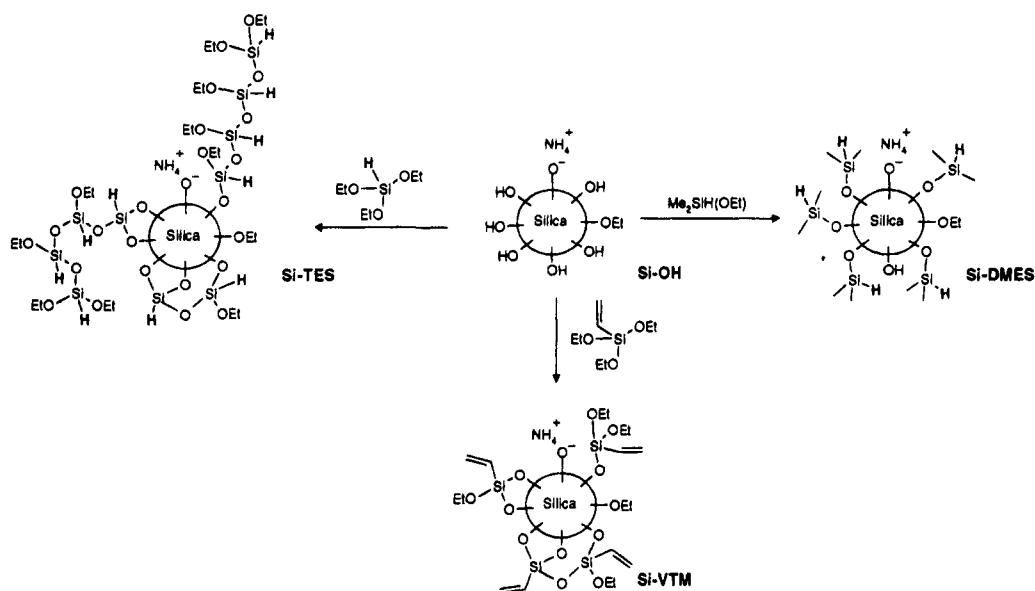
Hydrosilylation of TES Particles with Vinyl-Terminated Silicones (VT-PDMS). Si-*TES*-PDMS. Si-*TES* (ca. 1 g) was transferred to acetone (60 mL) and added to VT-PDMS ($M_w = 62\,700$, 10 g) dissolved in hexane (60 mL). The reaction vessel was charged with Karstedt's catalyst (100 μL). The mixture was stirred under an open atmosphere for 10 h at 80 $^\circ\text{C}$. The silica was cleaned of unreacted PDMS with fresh hexane using at least $5 \times$ centrifugation/redispersion cycles at 7000 rpm for 30 min. IR (DRIFTS): ν attenuation of the Si-H peak at 2251 cm^{-1} , 1259 cm^{-1} . ^{29}Si NMR (MAS) δ -111, -101, -92, -22.

Results and Discussion

Particle Surface Properties. DLS Measurements. The particle sizes as measured by DLS for Stöber silica (Si-OH) in acetone before and after the chemical modification reactions are given in Table 1. In the case of DMES surface functionalization, no significant differences were observed between the diameters obtained for the unfunctionalized and DMES functionalized spheres. For example, the average particle diameters obtained for Si-OH and Si-*DMES* in acetone were 179 and 178 nm, respectively. By contrast, the thickness of the surface layer of TES on the particles was different. For example, the particle diameter of Si-*TES* was 192 nm, which is 13 nm greater than that observed for Si-OH.

Since Si-*DMES* bears only one alkoxy group that can participate in a surface reaction, it is expected that the

Scheme 3



maximum surface coverage would be a monolayer assuming the DMES molecules are not physically adsorbed onto the particle surface. In contrast, Si-TES may oligomerize prior to or following condensation with the silica surface silanols. These oligomers could extend away from the surface or lie flat on it and could, furthermore, be linear or network polymers. These possibilities are shown in Scheme 3.

For comparison with Si-TES, another trifunctional silane $\text{H}_2\text{C}=\text{CHSi}(\text{OMe})_3$ (VTM) which can also oligomerize was examined. Under the same reaction conditions used to make Si-TES, Si-VTM was prepared. The particle size of Si-VTM in acetone was only 4 nm larger (Table 1) than the Si-OH from which it was prepared (Scheme 3).

Electrophoresis and Colloidal Stability. Stöber silica is electrostatically stabilized through dissociation of the surface silanols in the presence of ammonia. Investigations on the electrokinetic properties of silica hydrosols have shown that at pH's above the isoelectric point (~ 2.2 for silica), the negative charge of the silica surface increases due to an increase in the degree of dissociation of the silanol groups.⁴ We wished to synthesize modified silica particles which required the use of organic solvents. It was of interest, therefore, to know how Stöber silica would behave, in a colloidal sense, in such solvents. Unfortunately there are limited data in the literature on the electrokinetic properties and colloidal stability of silica in organic media; hence, electrophoretic mobility measurements in acetone for the unmodified and modified silica dispersions were carried out. Microelectrophoresis in acetone (see Table 1) showed that the unmodified and functionalized particles were negatively charged. For example, the mobility of Si-OH was $-4.79 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$.²⁴

Following the surface modification of Si-OH with TES, the particle mobility in acetone (of Si-TES) decreased to $-3.87 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. In contrast, the electrophoretic mobilities of Si-DMES and Si-VTM were observed to be similar to the unmodified silica. For

example, the mobilities for Si-DMES and Si-VTM were -5.35×10^{-8} and $-4.41 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. The mobilities observed for Si-DMES and Si-VTM were comparable to Si-OH and are consistent with the particle diameter results obtained by DLS (vide supra, Table 1). Similarly, the mobility of Si-TES was lower than that of Si-OH, consistent with the larger particle diameter found by DLS. The changes in electrokinetic behavior and colloidal stability behavior between Si-TES and Si-DMES are examined in more detail elsewhere.²⁴

FT-IR Surface Characterization. The presence of Si-H groups on the silica particles was evident from DRIFTS; the most apparent difference between the spectra obtained for Si-OH and Si-TES was the presence of the Si-H peak at 2251 cm^{-1} (Figure 1). The grafting process occurred only to a significant degree at elevated temperatures ($\sim 60 \text{ }^\circ\text{C}$); no spectroscopic evidence for the Si-H group was observed when the modification reaction was carried out at room temperature. In the case of Si-DMES, the Si-H peak was observed to shift to 2147 cm^{-1} from 2225 cm^{-1} in TES.

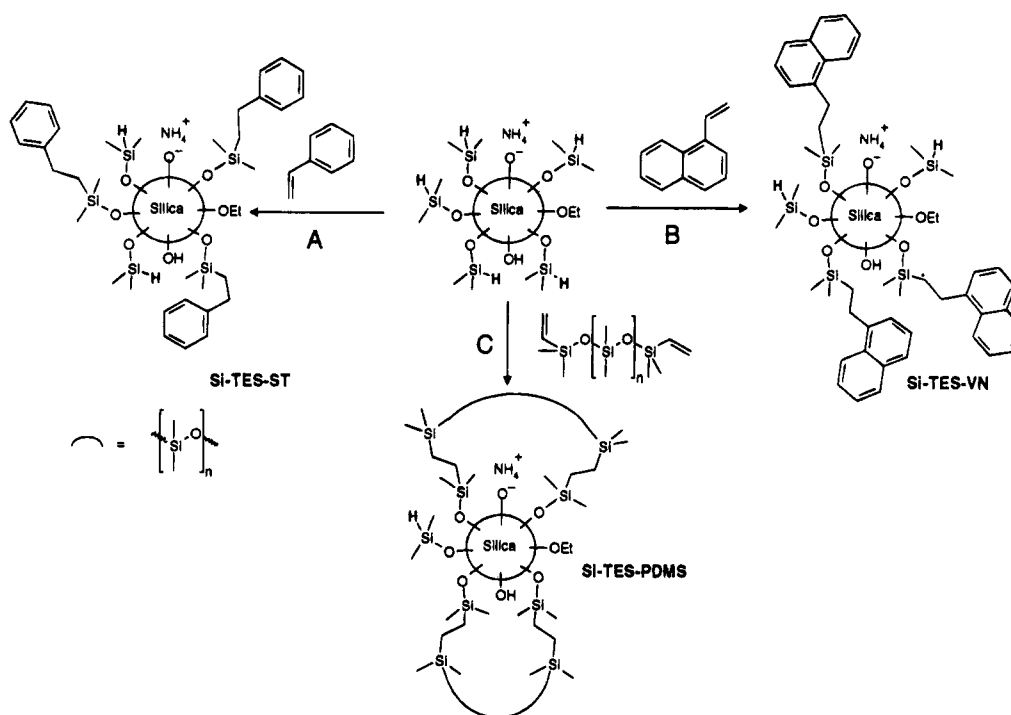
Surface Yield for Si-TES and Si-DMES Functionalization. An oxidative titration method was employed to determine the number of Si-H groups attached to the particle surface.²⁵ The coverage was found to be 6–8 Si-H groups/ nm^2 for Si-TES and 2–3 Si-H groups/ nm^2 for Si-DMES.²⁵

The degree of silane monomer coverage of the silica surface was also determined from the carbon content difference (see elemental analysis results in Table 1) between Si-OH, Si-TES, and Si-DMES. In the case of Si-OH, the carbon and hydrogen weight percent content were 2.04 and 1.25, respectively. Badley et al.¹⁰ have reported carbon contents of 2.25–2.53 wt % C for Stöber silica. It is noteworthy that Stöber silica has been shown to have high concentrations of unhydrolyzed ethoxy groups (within the particle core and on the surface) consistent with the high carbon contents observed in this work.^{10,11,26} The results in Table 1 show

(24) Ketelson, H. A. M.; Brook, M. A.; Pelton, R., manuscript in preparation.

(25) Harzdorf, C. Z. *Anal. Chem.* **1971**, *256*, 192. Smith, A. L., Ed.; *Analysis of Silicones*; Wiley: New York, 1991.

Scheme 4



that the carbon content for both Si-TES and Si-DMES are higher than Si-OH. For Si-TES and Si-DMES, the carbon contents were 4.12 and 2.14 wt %, respectively. The higher carbon content observed for Si-TES indicates the presence of unhydrolyzed Si-OEt and that TES multilayers are grafted to the particle surface.

Investigations of silylated surfaces have shown that multilayers having thicknesses up to 30 nm can be incorporated on the particle surface.⁹ Factors which can affect the degree of silane coverage include the water content, pH, reactivity and availability of surface groups and the nature of the organosilane agent. A further factor which affects the silane coverage is the porosity of the silica particle. It has been shown that Stöber silica has a microporosity of 10–15%³ and that residual concentrations of ammonia and water remain trapped inside the particle matrix.²⁷ Although elemental analysis of Si-OH (Table 1) detected no nitrogen, the possibility of ammonia leaching out over time should not be ruled out. One major problem associated with the presence of ammonia on the particle surface is its effect on the hydrosilation surface reactions. For example, the addition of amines to hydrosilation reaction mixtures has been observed to act as poisons toward platinum catalysts.²⁸ Thus, the efficacy of the surface hydrosilation will be modulated by the degree of catalyst poisoning.

Unmodified silica dispersions aged in acetone for a few months were observed in some cases to develop a yellow discoloration which was presumed to arise from chemical complexes of ammonia and acetone leaching out of the particle interior. However, characterization of the Si-TES and Si-DMES dispersions in acetone using DLS, electrophoresis, and DRIFTS following a 1

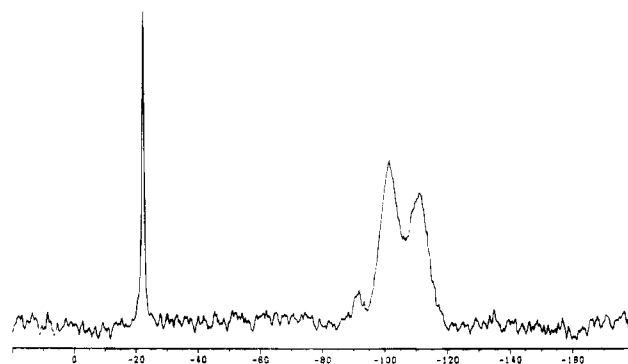


Figure 2. ²⁹Si MAS NMR of Stöber silica modified with silicone by the Pt-catalyzed hydrosilation reaction between Si-TES and VT-PDMS (MW = 62 700).

year aging period showed results similar to those obtained with the freshly prepared modified samples. No discoloration or change in colloidal stability was observed during this time period. It is believed that the surface modification reaction blocks the pores with the organosilanes which effectively traps any residual ammonia within the particle interior. Further experiments are currently in progress to study the silica particle porosity.

Surface Modification by Hydrosilation. The Si-H bond is an extremely useful functional group. Its reactivity can be exploited through hydrosilation under very mild conditions in the presence of a variety of catalysts, the most efficacious of which are platinum-based (Scheme 2A,E). Because of the importance of this reaction to the silicone industry, a great deal is known about the reaction mechanism and the types of reagents susceptible to the reaction.²⁹ The synthetic value of this method lies in the ability of the Si-H group to add to

(26) van Blaaderen, A.; Van Geest, J.; Vrij, A. *J. Colloid Interface Sci.* **1992**, *154*, 481.

(27) Jelinek, L.; Dong, P.; Rojas-Pazos, C.; Taibi, H.; Kovats, E. S. *Langmuir* **1992**, *8*, 2152.

(28) Lukevics, E. *Russ. Chem. Rev.* **1977**, *46*, 264.

(29) Musolf, M. C.; Speier, J. L. *J. Org. Chem.* **1964**, *29*, 2519. Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693. Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

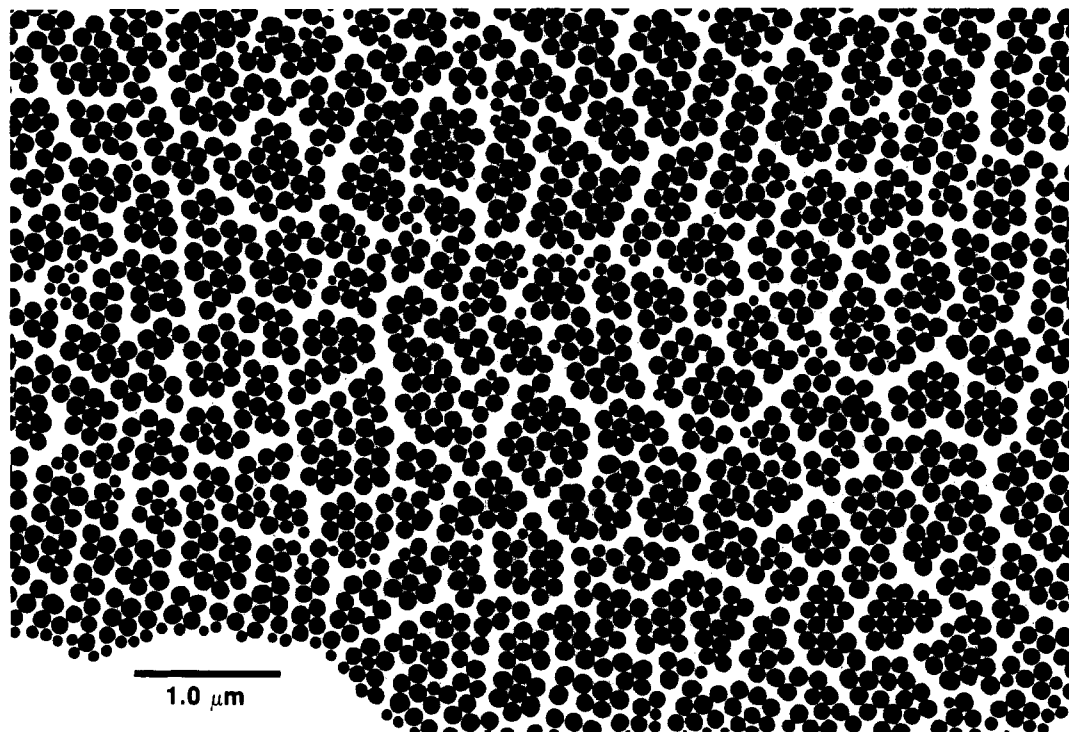


Figure 3. TEM of Stober silica modified with poly(dimethylsiloxane) (MW = 62 700). The particle diameter as measured by DLS is 242 nm. The hydrodynamic thickness of the PDMS layer corresponds to 50 nm.

most π -bonds forming stable covalent bonds (Si-X, X = C, O, N, etc.), particularly with terminal π -bonds such as $\text{H}_2\text{C}=\text{CR}_2$, $\text{HC}\equiv\text{CR}$ and $\text{O}=\text{CR}_2$. The hydrosilation reaction occurs with high yields, typically >90%, under mild conditions and is simple to perform. Thus, one can use the silica surface bound Si-H group for grafting a wide selection of organic moieties containing the functional groups listed above to the silica surface.

This synthetic approach was utilized to prepare the model silica systems illustrated by the examples shown in Scheme 4. Both small organic molecules and polymeric chains were grafted to the particle surface. Following the reaction of Si-TES with vinyl naphthalene and styrene, respectively, the presence of the naphthalene and styrene moieties on the silica surface were qualitatively detected by ultraviolet (UV) absorption. In the case of Si-TES-VN, the fluorescence spectrum showed a maximum at about 350 nm which corresponded to that obtained with vinyl naphthalene dissolved in CH_2Cl_2 . Figure 5 compares the UV-vis spectra obtained for Si-TES, Si-TES-VN, and Si-TES-ST in 2-propanol. For Si-TES-VN, an absorption band occurred at approximately 280 nm which corresponds to the excitation wavelength for the naphthalene group. In the case of the UV absorption spectra of Si-TES in 2-propanol, no comparable absorption was observed. Figure 5 shows the UV absorption spectrum obtained following the hydrosilation reaction using styrene. In comparison to Si-TES, intense absorption bands occurred between 220–250 nm for Si-TES-ST which corresponds to the typical absorption bands associated with aromatic rings. If any of the vinyl groups of styrene remained unreacted, the absorption band in the Si-styrene spectrum would be expected to shift toward 280 nm.

An estimation of the degree of grafting of the vinyl precursors was obtained by combustion analysis. For example, the carbon content increased from 4.12 for Si-

TES to 4.85 and 4.47 for Si-TES-VN and Si-TES-ST, respectively. The number of groups grafted to Si-TES can be estimated using the carbon content difference before and after the hydrosilation reaction. For example, for Si-TES-VN and Si-TES-ST the carbon weight percent differences were 0.73% and 0.35%, respectively. For silica having a diameter of 177 nm and a density of 2.0 g cm^{-3} , the specific surface area is about $20 \text{ m}^2 \text{ g}^{-1}$. On this basis, the number of naphthalene and styrene groups hydrosilated to the silica surface corresponds roughly to 1.5 and 2.0 groups nm^{-2} , respectively. Since 6–8 Si-H groups nm^{-2} were estimated from the titration results to be present on the surface of Si-TES, only a small fraction of the available Si-H groups appear to participate in the hydrosilation surface reaction. Residual Si-H groups were observed in the IR spectra for Si-TES-VN and Si-TES-ST. Further work is needed to confirm whether these low grafting yields are due to steric factors, particle porosity, the reaction conditions or a combination of these and other factors.

Vinylsilicones ($\text{H}_2\text{C}=\text{CHSiMe}_2[\text{OSiMe}_2]_n\text{SiMe}_2\text{CH}=\text{CH}_2$) (where $\text{MW} \approx 28\,000$ and $62\,700$, respectively) were also reacted with Si-TES using the hydrosilation reaction in a mixture of acetone and *n*-hexane (Scheme 4C). The ^{29}Si MAS solid state NMR spectrum of the silicone modified silica shown in Figure 2 shows a signal at -22 ppm which was consistent with the presence of D units (Me_2SiO)_n on the particle surface. The other peaks in the spectrum at -110 , -102 , and -93 ppm corresponded to the $\text{Si}(\text{OSi})_4$ (Q_4), $\text{Si}(\text{OSi})_3\text{OH}$ (Q_3), and $\text{Si}(\text{OSi})_2(\text{OH})_2$ (Q_2) environments, respectively, in colloidal silica.^{10,11} Figure 1b shows the spectra obtained using DRIFTS. The intensity of the Si-H peak at 2251 cm^{-1} was found to decrease significantly following the hydrosilation reaction. Moreover, the sharp absorption signal at 1259 cm^{-1} in the DRIFTS spectrum confirmed the presence of the silicone D units.

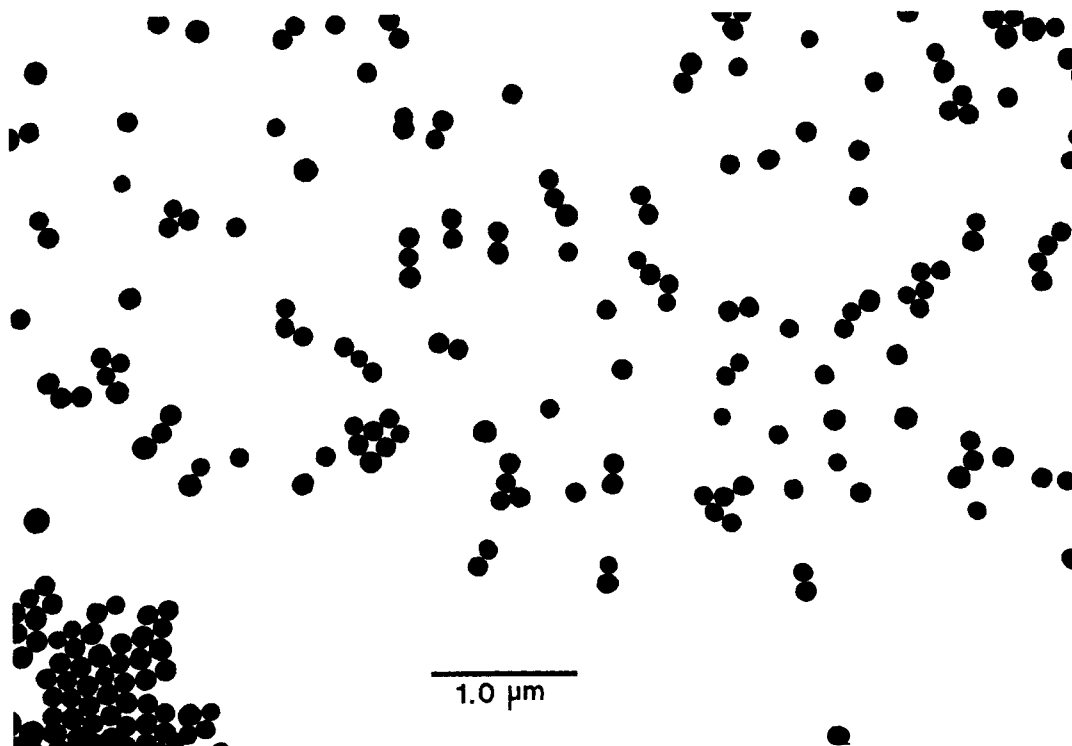


Figure 4. TEM of Stöber silica (Si-OH).

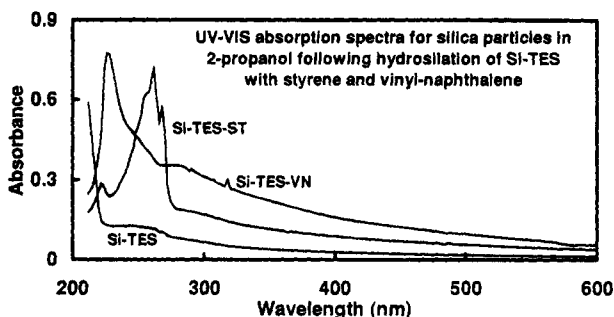


Figure 5. UV-vis absorption spectra for Si-TES-VN and Si-TES-ST following hydrosilation reaction using Si-TES particles.

Residual Si-H groups can also be seen in the IR spectra indicating several of the Si-H groups remained unreacted. From the DLS measurements of the latex, the particle diameter increased from 192 (Si-TES) to 242 nm (Si-TES-PDMS) following the hydrosilation reaction with silicone (MW \approx 62 700).

Figure 3 shows the TEM of the Si-TES-PDMS particles dried from *n*-hexane. Note the ordered packing arrangements of the particles and the migration of the small particles toward the boundaries.³⁰ The interstitial space between the particles is approximately 20–25 nm. This separation may result from the thickness of surface polymer layers on adjacent particles. For comparison, the TEM of the precursor Si-OH particle shown in Figure 4 in which the particles are clearly making contact.

To ensure that all of the silicone observed spectroscopically was grafted to the particle surface, several

qualitative tests were carried out. Si-TES-PDMS remained stable upon transfer to CHCl_3 or heptane but flocculated in polar solvents such as acetone, DMF, or water. If the hydrosilation reaction was attempted using Si-OH, the silica coagulated. Further research will be carried out in the future that is directed toward obtaining quantitative information on the surface concentration of silicone necessary to sterically stabilize silica using the hydrosilation reaction.

Conclusion

The Si-H-containing silylation reagent TES is a useful silyl coupling agent. Stöber silica may be surface functionalized with TES and the resulting Si-H-modified particles can be used to carry out Pt-catalyzed hydrosilation surface reactions with organic molecules such as vinyl-naphthalene, styrene or polymers such as vinyl-terminated silicones. This general procedure should be equally applicable to many other interesting moieties which can lead to the preparation of novel model systems.

A significant difference in the degree of silane surface coverage was observed using TES and VTM. Although TES and VTM can both oligomerize to a network polymer (silsesquioxane) through three functional sites, TES formed a dense, 13 nm layer on the silica surface, whereas a surface layer of only 4 nm resulted with VTM. The origin of this difference, which could involve the relative size of H versus $\text{CH}=\text{CH}_2$ groups, needs to be clarified.

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(30) The silica sample used to prepare Si-TES-PDMS was taken from a batch which contained two populations of particles which was periodically obtained during the early stages of this study. The TEM micrograph of this sample is shown here for the purposes of illustrating the interesting migration behavior of the smaller particles toward the periphery of the larger particle clusters having an ordered arrangement.