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Temperature-Dependent Nanostructure of an End-Tethered Octadecane Brush in Tetradecane and Nanoparticle Phase Behavior

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The phase behavior of a molecular brush- C_{18} grafted to the surface of both a silicon wafer and SiO₂ nanoparticles was investigated as a function of temperature using neutron reflectometry (NR) and small-angle neutron scattering (SANS), respectively. The experiments demonstrate a phase change in the brush layer characterized by a straightening of the molecular configuration, increase in shell thickness, and increase in solvent concentration with decreasing temperature that corresponds to gelation in the nanoparticle dispersion.

Introduction

Particle surface modifications, through either chemical grafting or molecular adsorption, provide an avenue for steric stabilization. Examples which rely on such treatments are commonly encountered and include colloidal silica,¹ cements,^{2,3} inks,⁴ iron oxide nanoparticles for cancer detection,⁵ and polymer gene delivery carriers.⁶ In such instances, the surface molecular layer provides sufficient separation between particles to prevent particle aggregation by dispersion forces. More recently, there has been an increased interest in exploiting the surface interactions of functionalized colloids and substrates for innovative applications, such as probes for biomolecular interactions,^{7,8} protein adsorption and separation,⁹ controlled self-assembly,¹⁰ tunable cushions for model biomembranes,¹¹ and controlled surface energies.¹² In all the examples mentioned, the function of the surface layer is intimately linked to the molecular phase behavior.

Well over 60 refereed journal articles have been published using an organophilic silica nanoparticle dispersion to study aggregation, phase separation, and gelation. The nanoparticles consist of a SiO₂ spherical core coated with a relatively thin oligomeric surface layer. This method was patented by Iller in 1957, ¹³ and the

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solvent for the oligomeric surface layer, the dispersions are stable. However, in certain solvents, which usually have a marginal solvent quality for the molecular brush, the dispersion stability can be controlled via temperature. For example, at high temperatures, the dispersion is stable, but upon lowering the temperature there is a loss in steric stability that leads to reversible flocculation or, at sufficient particle concentrations, gelation. A specific example which is the focus of this work is octadecyl coated silica¹ suspended in tetradecane, where the particles are stable above ~30 °C but flocculate and/or gel at lower temperatures.¹⁴

synthesis was later improved by van Helden et al.¹ In a good

Although the phase behavior, structure, and rheology of this model system have been heavily studied, the molecular mechanisms driving the attractions which lead to particle aggregation remain unclear. Early works attribute the transition to a change in the solvent quality with temperature, such that the brush becomes "sticky" at low temperatures when the solvent quality for the brush becomes poor.¹⁵ However, adiabatic calorimetry by de Kruif and van Miltenburg,¹⁶ and pressure-induced phase transition experiments by de Kruif and Schouten¹⁷ have indirectly shown that particle aggregation correlates with an order to disorder phase transition of the molecular brush itself. Specifically, a disordered, solvated brush provides steric stability at higher temperature or lower pressure. Upon lowering the temperature or increasing the pressure, the brush undergoes a phase transition to an ordered crystalline state. This density change leads to a stronger van der Waals attraction, which in turn results in particle aggregation.^{16,17} Further support for this phase transition is found in recent sum-frequency generation (SFG) spectroscopy which probes the conformational order of the brush molecules via their vibrational modes and the characteristic tilt of the straight molecules with respect to the local surface plane.^{18,19}

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Letter

Results of these measurements support the hypothesis that particle aggregation is linked to a phase transition of the surface-grafted molecules. Specifically, at high temperatures, SFG experiments show that the brush is in a state of conformational disorder. As the temperature is lowered, the molecules become rigid and order to a specific tilt angle of $52 \pm 5^{\circ}$. Furthermore, SGF measurements suggest the presence of one or more additional ordered solvent layers that form on top of the crystallized surface layer, an interpretation which is debatable.¹⁹ Still, the thickness of the shell layer and penetration of the solvent remain unclear.

In this Letter, we provide direct measurements of the molecular changes in the oligomeric brush and surrounding solvent through the phase transition, when grafted to both planar surfaces and nanoparticles. In the first experiment, octadecane is grafted to a silicon wafer and the structure measured via neutron reflectometry (NR). In the second experiment, the same octadecane brush is grafted to silica nanoparticles and the structure measured via small-angle neutron scattering (SANS). At high temperatures, above the phase transition, NR reveals a surface layer consistent with that of a solvated alkane brush. As the system temperature is lowered, a phase transition of the molecular brush is observed, characterized by an increase in the average height of the brush layer as well as the amount of solvent within the layer. This is consistent with a straightening of the C-C backbone and crystallization of the surface layer by interdigitation of the solvent with the grafted molecules. SANS measurements of the nanoparticle brush demonstrate a similar phase transition that correlates directly with the aggregation of the nanoparticles. Note that, although the experiments reported here pertain solely to endtethered octadecane in tetradecane (solvent), the experimental techniques could be employed to study the surface molecular changes of other systems.

Materials and Experimental Methods

Preparation of Octadecane Coated Silicon Wafers. Silicon wafers (n-type Si:P[100], 100 mm \times 6 mm, El-Cat Inc.) were cleaned using a 7/3 (v/v), H₂SO₄/H₂O₂ (98.09% and 31.4%, respectively, from Fisher Scientific) piranha solution at 100 °C for 1 h resulting an 11–12 Å thick thermal oxide layer. The wafers were then heated to a temperature of 210 °C in a 1-octadecanol (97%, Alfa Aesar) bath for 4 h. Esterification between the alcohol moieties and silanol surface groups resulted in a diffusion limited monolayer of octadecane on the substrate surface. The modified surface was thoroughly washed with chloroform (99.9%, Fisher Scientific) and dried. The thickness of the dry surface layer was measured using a Bruker D8Advance X-ray reflectometer (XR) at the National Institute of Standards and Technology Center for Neutron Research (NCNR, Gaithersburg, MD), prior to neutron reflectivity experiments.

Preparation of Octadecane Coated Nanoparticles. Colloidal silica dioxide, 28 nm diameter, was obtained commercially under the trade name Ludox TM-50 (50% mass fraction in H₂O with sodium stabilizing counterion) from Sigma-Aldrich. Octadecane was grafted to the surface following the method of van Helden et al.,¹ by a similar alcohol/silanol esterification reaction protocol used to functionalize the surface of the silicon wafers. Following the reaction, the particles were thoroughly washed in a 60/40 mixture of chloroform/cyclohexane (chloroform and cyclohexane 99.9%, Fisher Scientific) using an ultracentrifuge (Beckman and Coulter Optima L-100 XP). Finally, the particles were suspended in cyclohexane and stored; no visual sedimentation was present after 2 months. The percent mass of octadecane grafted to the surface was determined by pyrolysis of the octadecyl molecules using a Mettler and Toledo thermogravimetric analyzer TGA/DSC1.

Preparation of Nanoparticle Dispersions. Uncoated silica samples were prepared for SANS contrast match experiments by diluting stock Ludox TM-50 with $D_2O/H_2O\,(D_2O;99.9\%$ isotope substitution, Cambridge isotopes) mixtures. Octadecyl coated silica samples were prepared by drying the particles suspended in cyclohexane under a nitrogen stream and under vacuum for 24 h before suspending in deuterated tetradecane (99.2% isotope substitution, Cambridge Isotope Laboratories, Inc.). The percent of isotope substitute was measured using an Agilent GC/MS instrument and determined to be at company specifications within measurement error. The dispersion particle size was measured before and after sample preparation to ensure particle stability with fiber optic quasi-elastic light scattering (FOQELS; Brookhaven Instruments 90Plus). FOQELS was also used to determine the temperature at which particle aggregation occurs in the nanoparticle dispersion.

Neutron Reflectometry (NR). All neutron scattering experiments were performed at the NCNR. NR measurements were performed on the NG7 horizontal reflectometer. Silicon wafers were encased in a temperature controlled liquid cell in which the octadecane coated surface was in contact with solvent, deuterated tetradecane. The temperature of the liquid cell was controlled using a NESLAB circulating bath. Reflectivity profiles were measured using a wavelength of 0.475 nm. The neutron beam has a 35 mm width, and the vertical size of the beam was varied by increasing the size of the collimating and detector slits to maximize the intensity and keep the relative resolution of the wavevector in the direction normal to the surface, q_z , approximately constant $(\delta q_z/q_z \approx 0.04)$. The beam footprint length on the sample was 40 mm. The reflectivity intensity normalized by the incident intensity $R(q_z)$ was measured at various temperatures for three samples to ensure reproducibility. Data were corrected for both the varying slit size and background scattering using RE-FLPAK,²⁰ an open source software created by NCNR staff for NR users. The scattering length densities (SLDs) of the individual components including silicon, silicon dioxide, octadecane, and deuterated tetradecane were calculated using a web-based scattering length density calculator provided by NCNR.²¹ The solvent density, ρ_s , was measured using an Anton Paar DMA-48 densitometer at each temperature to ensure accurate calculation of the solvent SLD.

The temperature range over which initial NR experiments were performed, 25–40 °C, correlates to temperatures beyond the boundaries at which aggregation was observed in octadecyl coated silica dispersions measured using FOQELS. The critical temperature, T_c , at which particles begin to aggregate, determined by an increase in the hydrodynamic diameter, D_H , was found to be concentration dependent and occurred over a range of 27–31 °C for dispersion volume fractions $\phi = 0.05-0.5$, respectively (data not shown). The phase transition of the octadecyl coated wafers was found to occur within the range of 28–32 °C. Repeated NR measurements on additional samples were performed only at 25 and 40 °C to ensure the samples were well within the fluid and solid phase regions.

Small-Angle Neutron Scattering (SANS). SANS experiments were performed on the NG3 30 m SANS instrument. Samples were loaded into 1 mm path length demountable titanium cells. The cell temperature was maintained to ± 0.1 °C using the 10CB 10-position sample holder with a NESLAB circulating bath. A large dynamic range in scattering wavevector, Q, was obtained by combining the sector averaged scattering intensity from three different instrument configurations at 1, 4, and 13 m detector distances (with focusing lenses at 13 m only). SANS data reduction and analysis of the scattering intensity, I, versus Q was performed using the SANS

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reduction and analysis program with IGOR Pro available from NIST. $^{\rm 22}$

Results and Discussion

The experimental neutron reflectivity profiles for the octadecyl coated silicon wafer in contact with deuterated tetradecane at both 25 and 40 °C are shown in Figure 1a, plotted as Rq_z^4 versus q_z . NR data sets were fit using the Parratt formalism,²³ which can also be seen in Figure 1a. The cumulative sums of the normalized residual error are less than 1.7. SLDs obtained from modeling the data are shown in Figure 1b; inset depicts an expanded SLD versus depth profile. At 40 °C, the solvated brush has an average thickness of 20.0 ± 0.1 Å and an SLD of 5.72×10^{-7} Å⁻². As the system is quenched to 25 °C, the SLD profiles show three distinct and reproducible differences: (1) the thickness of the layer increases, (2) the SLD of the solvent increases, and (3) the SLD of the brush layer increases. In addition, the NR experiments show no indication of any additional ordered solvent layers on top of the first as suggested by Roke et al.¹⁹ The difference in the film thickness is slight, but closer inspection of Figure 1b inset reveals a change of 1.3 ± 0.1 Å. The increased SLD of the solvent is explained by a temperature dependence of the density. A linear fit to densitometry measurements for deuterated tetradecane over the temperature range of 25–40 °C (data not shown) reveals $\rho_s =$ $-9.1 \times 10^{-4}T + 0.8989$, $R^2 = 0.998$. However, the change in the SLD of the brush layer cannot be explained through a simple density change with temperature, but it can be explained with the increased concentration of the solvent in the brush layer. Because the octadecane brush and deuterated solvent have significantly different SLDs, the volume fraction of solvent within the brush layer can be calculated. Using this approach, the volume fraction of solvent ϕ_s within the surface layer was found to be $\phi_s = 0.19$ and 0.14 for 25 and 40 °C, respectively. This result correlates well to the ϕ of solvent calculated by a mass balance of the system. The total volume of octadecane in the system is fixed, as the molecules are covalently bonded to the surface and can be calculated from XR measurements of the dry film thickness, 15.56 ± 0.02 Å, and the density of octadecane, 0.7768 g/cm³ (CRC Handbook²⁴), to give a octadecane grafting density of $\sigma = 2.9$ chains/nm² calculated by $\sigma = N_A h \rho / M_w$, where N_A , h, ρ , and M_w are Avogadro's number, the height of the film, density, and molecular weight, respectively. For nonporous amorphous silica, there are roughly 4-5 silanol reactive groups per square nanometer which relates to a grafting density of $\sim 60\%$ of the maximum.²⁵ Using an assumption that the increased height of the solvated film is that of the solvent, one can calculate $\phi_s = 0.27$ and 0.22 for 25 and 40 °C, respectively.

The mechanism by which the brush thickness changes is depicted in Figure 1c. At high temperatures, the molecules are in a "relaxed" fluid state of conformational disorder with the solvent molecules. As the system is quenched, the increase in shell thickness is explained by a disorder to ordered phase transition characterized by a straightening of the C–C backbone. Solvent molecules interdigitate with the grafted molecules to form a dense crystalline layer at the surface. It is commonly observed in self-assembled monolayers of alkanes, long chain alcohols, and so on that crystalline layers of alkane molecules, which pack at their van der Waals contact distance, tilt until the crystalline density is achieved.²⁶



Figure 1. Neutron reflectivity data and analysis of the octadecyl coated silicon wafer in contact with deuterated tetradecane measured at 25 and 40 °C: (a) $R(q_z)q_z^4$ versus q_z and fit using Parratt formalism, error bars represent ±1 "standard deviation". (b) SLD versus depth. Inset in (b) depicts an expanded view of the interface between the octadecane layer and solvent. (c) Schematics of the structure of the grafted layer extracted from NR analysis at 40 °C (left) and 25 °C (right).

The length of the octadecyl chain is 27.61 Å, calculated from known bond lengths C-C = 1.54 and C-O = 1.43 Å.²⁷ Hence, the average contact angle between the octadecyl chains and the surface can be calculated ($50.5 \pm 0.3^{\circ}$). This agrees well with Roke et al.¹⁸ who directly measured the contact angle by SFG of a similar system to be $52 \pm 5^{\circ}$.

Contrast matching SANS experiments on the uncoated SiO₂ nanoparticles were performed to accurately determine the SLD, average size, and polydispersity of the nanoparticles. The results of the solvent contrast variation (D₂O/H₂O), used to determine the SLD of the uncoated particles, can be seen in Figure 2a which depicts the scattering intensity at the low-*Q* limit, I_o , normalized by ϕ versus the SLD of the solvent for various samples. All samples were prepared such that $\phi \leq 0.008$ and the particle–particle interaction to the scattering intensity could be neglected. The background or incoherent scattering contribution to I_o , as determined through a linear fit to a Porod plot of $I(Q)*Q^4$ versus Q^4 , was subtracted. A linear fit to the data points in Figure 2a results

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Figure 2. SANS data of Ludox, $\phi \le 0.008$, in various D₂O/H₂O solvent mixtures and model fits to (a) contrast match series leading to a particle SLD = $3.553 \times 10^{-6} \text{ Å}^{-2}$ and (b) scattering intensity, *I*, versus scattering wavevector, *Q*, for two samples, S-1 and S-2, with solvent SLDs of 2.00×10^{-6} and $5.00 \times 10^{-6} \text{ Å}^{-2}$, respectively. Fit of S-1 and S-2 resulted in a mean particle radius, $r_{\rm m}$, and polydispersity, PD, of $r_m = 140.0$ and 140.4 Å, and PD = 0.095 and 0.1, respectively.

in a particle SLD = $3.553 \times 10^{-6} \text{ Å}^{-2}$. Figure 2b shows I(Q) versus Q for the uncoated Ludox nanoparticles in two different D₂O/H₂O mixtures ($\phi = 0.008$) with a combined solvent SLD of 2.00×10^{-6} and $5.00 \times 10^{-6} \text{ Å}^{-2}$ for samples S-1 and S-2, respectively. A polydisperse (Schulz distribution) hard sphere model was used to fit the data and determine the mean particle radius, $r_{\rm m}$, and polydispersity, PD,^{22,28} for S-1 and S-2 which resulted in $r_{\rm m} = 140.0 \pm 0.5$ and 140.4 ± 0.5 Å, and PD = 0.095 ± 0.05 and 0.1 ± 0.05 , respectively. The particle radius and polydispersity of the core particles were confirmed using transmission electron microscopy (TEM, data not shown).

The SANS scattering intensity profile for the octadecyl coated SiO₂ can be seen in Figure 3 for one sample $\phi = 0.05$ at two temperatures of 20 and 40 °C. Figure 3a inset depicts the dispersion which is a fluid at 40 °C and a gel at 20 °C. As the temperature is quenched from the fluid state, particle aggregation begins at 28.2 ± 0.1 °C, as determined by FOQELS, but a gel does not form until 27.5 \pm 0.1 °C, as determined through time-temperature superposition (see, for example, Winter and Chambon²⁹). The SANS scattering profiles show a distinct structure at both temperatures. At 40 °C, where the dispersion is in the fluid state, the scattering profile is that of a homogeneous dispersion of spherical particles. However, at 20 °C, the low-q scattering intensity shows a power-law dependence with a slope of -2.2. This profile is indicative of a fractal-like structure where the slope is the fractal dimension, and confirms the particles are aggregated. In the high-q region of Figure 3a, it would appear that there is no change in the scattering intensity, but an expanded view,



Figure 3. SANS intensity profiles for the octadecyl coated SiO₂ nanoparticles, $\phi = 0.05$, in deuterated tetradecane at two temperatures 20 and 40 °C. (a) Complete intensity profile; inset shows the dispersion in the gel and fluid states at 20 and 40 °C, respectively. (b) Expanded view of the SANS profile.

Figure 3b, reveals a distinct change with temperature that is completely reversible. The scattering profiles were fit using a polydisperse (Schulz distribution) core-shell model.^{22,30} All model parameters were known from independent experiments except for the shell thickness, $H_{\rm shell}$, and SLD, which were determined to be $H_{\rm shell} = 18.5 \pm 0.5$ and 21 ± 0.5 Å, and SLD_{shell} = 2.0×10^{-6} and 2.6×10^{-6} Å⁻² at 40 and 20 °C, respectively. This relates to the volume fraction of solvent $\phi_{\rm s} = 0.46$ and 0.33 for 20 and 40 °C, respectively. The tilt angle of the octadecane molecules with respect to the tangent plane to the particle surface was calculated to be 49.5 ± 1.6° from the height of the shell layer at 20 °C.

A mass balance similar to that performed on the octadecyl coated wafer experiment is made for the nanoparticle dispersion. The mass fraction of octadecane, X_{C18} , in the system was measured using thermogravimetric analysis (TGA) and found to be $X_{C18} = 0.087$. This relates to a shell thickness of 12.0 Å and a grafting density of 2.4 chains/nm². Using an assumption that the increased height of the solvated film is that of the solvent, one can calculate $\phi_s = 0.46$ and 0.38 for 20 and 40 °C, respectively.

The NR and SANS experiments previously discussed represent two independent measurements of the film height and solvent concentration for end-tethered octadecane spanning the temperature range in which a phase transition occurs. The major findings of these experiments and the analysis of results can be found in Table 1. While the results show similar trends in behavior, there are distinct differences which we attribute to two sources: the octadecyl graft density and the system geometry. Both surfaces were functionalized using a similar reaction protocol, leading to a similar graft density with a slight increase for the silicon wafer. More significantly, the curvature of the nanoparticle surface leads to a lesser brush thickness (shell height) in the fluid state as compared to the brush on the silicon wafer. However, the solid

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Table 1. Volume Fraction, ϕ , of End-Tethered Octadecane and Solvent in the Surface Layer^{*a*}

	wafer	nanoparticles
graft density, chains/nm ²	2.9	2.4
shell height, Å (fluid-phase)	20	18.5
shell height, Å (solid-phase)	21.3	21
tilt angle, deg	50.5	49.5
ϕ -solvent SLD, Å^{-2} (fluid-phase)	0.14	0.33
ϕ -solvent SLD, Å ⁻² (solid-phase)	0.19	0.46
ϕ -solvent MB, Å ⁻² (fluid-phase)	0.22	0.38
ϕ -solvent MB, Å ⁻² (solid-phase)	0.27	0.46

^{*a*} Values were calculated from a mass balance (MB) and from the SLD measured by NR and SANS.

phases are nearly identical on both substrates. The lower graft density and curvature of the nanoparticle leads to an increase in the solvent volume fraction in the brush both in the fluid and crystalline states, as compared to the silicon wafer.

Depending on the reaction mechanism by which the octadecane chains are deposited, various grafting densities and thicknesses can be achieved. Tidswell et al.³¹ obtained complete monolayers ($\sim 27-28$ Å) of octadecyltrichlorosilane by selfassembly. Later on, Kojio et al.³² demonstrated that octadecane chains deposited by the Langmuir process were more densely packed than those deposited by chemisorption even though the thicknesses (22–24 Å) they obtained were lower than those for complete monolayer. It is well-known that condensation reactions yield low grafting densities and incomplete monolayers as with the octadecane layers reported here.

The results of this work, specifically the interdigitation of the solvent with the brush, were counterintuitive. Previous studies which consider the effect of solvent quality, near the theta temperature, on the brush density profile have shown that as the temperature is quenched further into the poor solvent region, solvent leaves the surface layer, resulting in a collapse of the brush.^{33,34} In this system, the brush does not collapse with a

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decrease in solvent quality but induces a phase transition leading to a solid crystalline state. The interdigitation of the solvent with the brush is a direct consequence of the low grafting density in which the solvent facilitates crystallization of the surface layer leading to particle aggregation. For the experiments described in this work, deuteration of the solvent was necessary to optimize contrast between the molecular brush and solvent. With respect to the solvent itself, it has been suggested that solvents that do no facilitate crystallization, such as benzene, would result in a collapse of the brush when the system is quenched.¹⁹ Future experiments will test this hypothesis and will be the topic of additional publications.

Conclusion

In conclusion, we used two independent neutron scattering experiments, NR and SANS, to study the phase behavior of an end-tethered brush as a function of temperature. The measurements allowed us to directly probe the surface molecular mechanisms directly related to aggregation and gelation of the nanoparticle dispersion. At high temperatures, in the fluid state, the brush is in a relaxed state of conformational disorder with the solvent molecules. As the temperature is quenched, a phase transition occurs characterized by a straightening of the molecular configuration, increase in shell thickness, and increase in solvent concentration in the brush. The fluidized brush thickness decreases and the solvent concentration increases in going from the silicon wafer to the silica nanoparticles. We confirm that the nanoparticle aggregation is directly linked to the phase transition of the octadecane brush in which the solvent molecules interdigitate to form a dense crystalline layer. Furthermore, the NR experiments clearly show that the molecular ordering is limited to the monolayer and multilayer formation is not observed.

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