

Template-Induced Enhanced Ordering under Confinement

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We report a surprisingly strong ordering of Si-(CH₃)₂ groups upon confinement between two surfaces, an oxidized poly(dimethyl siloxane) (PDMS^{ox}) elastomer and a methyl-terminated self-assembled monolayer (octadecyltrichlorosilane (OTS)) on sapphire substrates. This enhanced ordering is induced by the template of ordered methyl groups of OTS and is not observed for other surfaces (fluorinated monolayers and sapphire substrates). This strong ordering is reminiscent of layering observed for confined symmetric molecules between two mica surfaces but was expected to vanish between rough macroscopic surfaces. These results provide new insights on confined structure at the interface between two solids and are important in the understanding of surface-controlled processes of practical importance.

Understanding the structure of molecules confined between two solids is important in the areas of rheology, adhesion, adhesion hysteresis, tribology, grain boundary phases of composite materials, and colloidal particles. Liquids confined between smooth mica surfaces at separations comparable to their molecular dimensions show remarkable properties such as oscillatory force profiles, extreme enhancement in viscosity and relaxation time constants, and stick-slip behavior that is reminiscent of a solid-to-liquid transition.^{1–3} It has been suggested that upon confinement the symmetric molecules align in discrete layers.^{1,4} In the case of rough surfaces, the oscillatory force profiles vanish, which has been explained by the absence of layering.^{5,6} These results can also be interpreted as local layering that is not correlated over large areas. However, no direct measurement of the structure of confined molecules has been reported. Here, we describe direct observations of a confined structure between two rough surfaces, an oxidized poly(dimethyl siloxane) (PDMS^{ox}) elastomer and a methyl-terminated self-assembled monolayer (octadecyltrichlorosilane (OTS)) on sapphire surfaces, using surface-sensitive sum frequency generation spectroscopy (SFG). Surprisingly, the methyl groups of short PDMS chains at this interface exhibit a strong orientation that is comparable to that of a well-packed OTS, and this enhanced ordering is not observed for other systems (PDMS liquid next to OTS, PDMS elastomer in contact with OTS, and PDMS^{ox} in contact with sapphire or sapphire modified with low-energy fluorinated monolayers). These results indicate that the enhanced ordering is induced by both the template of methyl groups and confinement at the interface.

One common difficulty in directly probing the structure of confined fluids is the requirement of a large uniform contact area. We have taken advantage of the deformable

elastomer, poly(dimethyl siloxane) (PDMS), to create a uniform contact with a rough sapphire substrate modified with a low-energy self-assembled alkylsiloxane monolayer (OTS).⁷ We have exposed PDMS sheets to a short oxygen plasma before contact. This results in the formation of a brittle silica-like layer of ~5 nm thickness (depending on the time of exposure) and short PDMS chains.⁸ Using a variety of techniques, it has been shown that both linear and cyclic short PDMS chains are generated in this process.⁹ The exact length or architecture of PDMS chains does not affect the conclusions reported in this letter because we are directly probing the local orientation of Si-(CH₃)₂ groups of the PDMS repeat unit at the interface. On exposure to air, the short PDMS chains diffuse out over a period of hours to days through the cracks in the silica-like layer.^{8–10} This surface reconstruction is known as “hydrophobic recovery”. Here, the PDMS sheets were pressed against OTS surfaces immediately after plasma exposure. The migration of short PDMS chains is faster under finite pressure because of increased cracking of the silica-like layer. In this geometry, the short PDMS chains are locally confined between the silica-like layer and OTS. This is similar to a contact interface between macroscopic rough surfaces where a liquid is confined between flattened asperities.

Interface-sensitive infrared-visible sum frequency generation spectroscopy (SFG)¹¹ in total internal reflection geometry has been used to probe hidden polymer interfaces.^{12,13} In brief, SFG involves mixing a visible high-intensity laser beam of frequency ω_1 with a tunable infrared wavelength source of frequency ω_2 . According to the dipole approximation, the generation of SFG photons (at frequency $\omega_1 + \omega_2$) is forbidden in the centrosymmetric

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(7) Root-mean-square roughness (r) values of ~12 nm for OTS and ~0.6 nm for PDMS (or PDMS^{ox}) were measured by AFM over an area of $5 \times 5 \mu\text{m}^2$. A stable static water contact angle (~110°) and the stable SFG spectra for OTS in contact with water indicate a well-packed OTS film.

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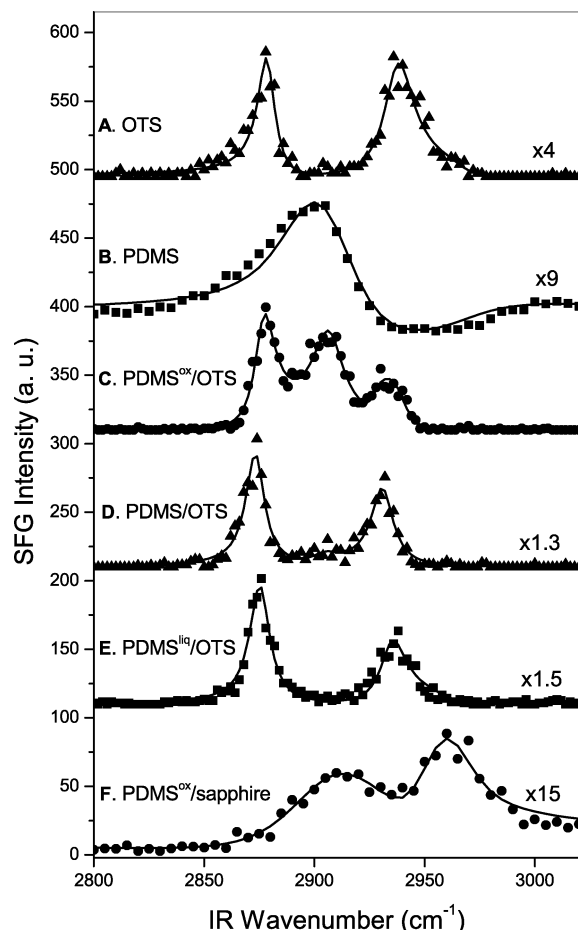


Figure 1. SFG spectra of (A) OTS, (B) PDMS, (C) PDMS^{ox}/OTS, (D) PDMS/OTS, (E) PDMS^{liq}/OTS, and (F) PDMS^{ox}/sapphire. The solid lines are fits to the square of the sum of the Lorentzian functions (eq 1). B and F are taken with a broader wavenumber resolution (full width at half-maximum (fwhm) ≈ 20 cm⁻¹) to improve the signal-to-noise ratio. The SFG spectra were offset along the y axis by an arbitrary amount and were scaled for clarity. In C and D for OTS, the methyl Fermi band is slightly red shifted, and the ratio of the symmetric methyl and methyl Fermi intensity has changed upon contact. This effect is reversible because the spectra before and after contact are indistinguishable. The slight shifts are not related to changes in orientation because well-packed SAM chains are known to resist high pressures up to 300 MPa.¹⁸

bulk but allowed at the interface where the inversion symmetry is broken. The SFG intensity is a function of both the number density of molecules present at the interface and the orientation of the molecules. By the proper choice of incident angles, we have selectively probed the hidden interface while reducing the contribution from the other interfaces.

Figure 1 summarizes the SFG results in the SSP polarization.¹⁴ Parts A and B of Figure 1 are SFG spectra for OTS and PDMS, respectively, before contact. The y axis is the SFG intensity, which is related to the number and orientation of the molecules at the interface. Figure 1A is a typical spectrum for a well-packed OTS monolayer with ordered methyl groups (symmetric vibration at 2879

cm⁻¹ and Fermi resonance at 2938 cm⁻¹).¹⁵ The methylene peaks (symmetric vibration at 2850 cm⁻¹ and asymmetric vibration at 2920 cm⁻¹)¹⁵ are absent for an all-trans conformation.¹⁶ In Figure 1B, the two main peaks are assigned to the methyl groups bonded to silicon (symmetric vibration at 2906 cm⁻¹ and asymmetric vibration at 2962 cm⁻¹).¹⁷ The 2906 cm⁻¹ peak will be referred as the Si-(CH₃)₂ peak hereafter. In the case of PDMS^{ox}, the oxygen plasma treatment oxidizes the surface, and the SFG spectrum from 2800 to 3200 cm⁻¹ does not have any resolvable features (spectrum not shown).

Figure 1C shows the spectrum for the PDMS^{ox}/OTS interface. The Si-(CH₃)₂ peak is extremely strong at this interface. Because the PDMS^{ox} surface before contact has no methyl peaks, this indicates a significant interfacial reconstruction. The presence of PDMS chains after interfacial reconstruction is also evident in the adhesion experiments (Figure 2A).¹⁹ For the PDMS^{ox}/OTS contact, once the highest load is reached the reconstruction is completed and the unloading proceeds with an equilibrium interface. The strain energy release rate on unloading is equal to 43 mJ/m². This value is similar to that expected for the thermodynamic work of adhesion of PDMS in contact with OTS (shown in Figure 2B). For example, the work of adhesion between PDMS and OTS is $\sim 2\sqrt{\gamma_{\text{PDMS}}\gamma_{\text{OTS}}} = 40\text{--}45$ mJ/m² ($\gamma_{\text{PDMS}} = 20\text{--}25$ mJ/m² and $\gamma_{\text{OTS}} = 20$ mJ/m²) assuming only dispersion forces. These adhesion measurements of PDMS/OTS and PDMS^{ox}/OTS are consistent with the SFG results.

Interestingly, the strong Si-(CH₃)₂ peak observed at the PDMS^{ox}/OTS interface is much weaker at the PDMS/OTS interface as shown in Figure 1D. The spectrum is dominated by methyl peaks associated with the OTS layer. We can also quantitatively calculate the contribution from OTS and PDMS methyl groups by fitting the spectra using the following Lorentzian equation, shown as solid lines in Figure 2.¹³

$$I(\text{SFG}) \propto \left| \chi_{\text{eff,NR}} + \sum_q \frac{A_q}{\omega_{\text{IR}} - \omega_q - i\Gamma_q} \right|^2 \quad (1)$$

where A_q , Γ_q , and ω_q are the strength, damping constant, and angular frequency of a single resonant vibration, respectively. $\chi_{\text{eff,NR}}$ is the nonresonant part of the signal. The ratio $|A_{q,\text{PDMS}}/A_{q,\text{OTS}}| \approx 0.29$ and 0.74 for PDMS/OTS and PDMS^{ox}/OTS interfaces, respectively. This indicates that at the PDMS^{ox}/OTS interface the methyl groups of PDMS have strong orientational order comparable to that of a well-ordered OTS, whereas the order is weaker at the PDMS/OTS interface. The only difference between the two interfaces is the presence of short chains as a result of oxygen plasma treatment and interfacial reconstruction.

The important question is whether the presence of short PDMS chains next to the OTS surface is sufficient to observe ordered Si-(CH₃)₂ groups. For this purpose, we have studied the SFG spectrum for low-molecular-weight PDMS^{liq} ($M_w = 1250$ g/mol) in contact with OTS (Figure

(14) The details of the SFG setup have been published elsewhere.¹³ The spectra taken with the same setup have broad wavenumber (fwhm ≈ 20 cm⁻¹) resolution. For narrow wavenumber (fwhm < 5 cm⁻¹) resolution, we have used a SpectraPro-500i monochromator in front of the detector. An incidence angle of 43° was used to probe (PDMS or PDMS^{ox})/air and OTS/air interfaces before and after contact, and 8° was used during contact. All of the experiments were done in SSP (S-polarized SFG, S-polarized visible, P-polarized IR) polarization.

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(19) All experiments were performed with an elastomeric PDMS kit (Sylgard-184) using the procedure outlined in ref 21. The radius of curvature of the lenses was ~ 1 mm. The PDMS samples that are presented here are not extracted, and the extracted samples show similar behavior.

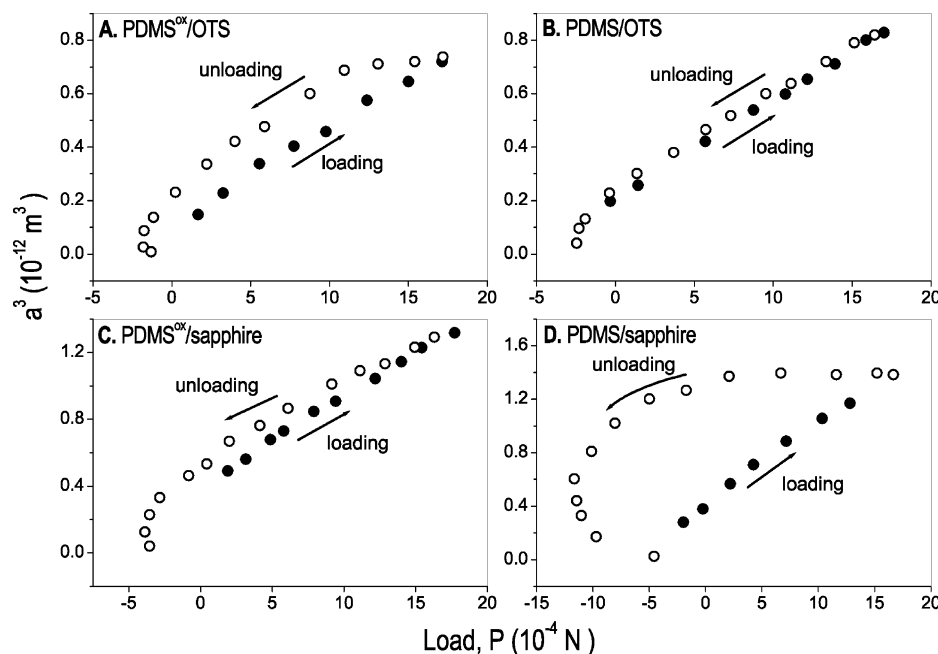


Figure 2. JKR plot of (A) PDMS^{ox}/OTS, (B) PDMS/OTS, (C) PDMS^{ox}/sapphire, and (D) PDMS/sapphire. The contact radius cubed, a^3 , is plotted as a function of the applied load. The strain energy release rate on unloading for both PDMS^{ox}/OTS and PDMS^{ox}/sapphire depends neither on the contact time within each load increment nor the time at maximum load.

1E). Here, the complete cell is filled with the PDMS^{liq} without any confinement. The SFG spectrum shows methyl signals of the OTS layer with a weak contribution from PDMS chains. This indicates that confinement is necessary to observe the enhanced ordering of Si-(CH₃)₂ at the PDMS^{ox}/OTS interface.

We also studied the contact of PDMS^{ox} with a high-energy sapphire and a disordered low-energy fluoroalkyl-siloxane monolayer (FC) to understand the role of surface energy in the ordering of PDMS chains at the interface. The spectrum of the PDMS^{ox}/sapphire interface is shown in Figure 1F. It is dominated by symmetric and asymmetric peaks associated with PDMS methyl groups signifying a reconstruction. However, the intensity of the Si-(CH₃)₂ peak is much weaker in comparison to that of the PDMS^{ox}/OTS interface. This can be attributed not only to weak orientation but also to partial reconstruction. However, the adhesion measurements of the PDMS^{ox}/sapphire contact (Figure 2C) give a clear indication of the presence of short PDMS chains at the interface. Strong adhesion and adhesion hysteresis are observed for PDMS/sapphire contact (Figure 2D) because of the formation of hydrogen bonds between the hydroxyl and silane groups. The hysteresis decreases significantly at the PDMS^{ox}/sapphire interface because of the enrichment of the interface in low-molecular-weight PDMS chains, thus forming a weak boundary layer (less energy dissipation due to reduced chain pull out).²⁰ Consequently, on the basis of the adhesion results, the PDMS^{ox}/sapphire interface has been reconstructed with the diffusion of short PDMS chains. However, these short chains are poorly ordered next to the sapphire surface, unlike the PDMS^{ox}/OTS interface. For the PDMS^{ox}/FC interface, we did not observe any detectable Si-(CH₃)₂ signal between 2800 and 3200 cm⁻¹. Compared to OTS, FC does not pack into a condensed film, and fluorocarbon groups are larger than the hydrocarbon groups.²¹ This indicates that short PDMS chains require not only confinement but also an ordered template provided by the methyl groups of OTS.

We believe that the strong ordering of Si-(CH₃)₂ groups at the PDMS^{ox}/OTS interface is a signature of layering that was observed for PDMS confined between two mica surfaces (surface forces apparatus),⁴ PDMS thin films on silicon substrates (X-ray scattering),²² and PDMS oligomers next to hydroxylated α -quartz [molecular dynamics simulation (MD)].²³ The common ingredient in the past studies is the presence of smooth substrates. To confirm that the PDMS chains are layered next to OTS and develop a physical picture at the PDMS^{ox}/OTS contact, we have compared the SFG with the MD results. In the MD simulation, the PDMS melt was first equilibrated for about 4 ns and then brought in contact with the α -quartz surface. Once the melt was completely adsorbed, further equilibration for approximately 2 ns was performed, and then the atom positions were recorded every picosecond for later analysis.

The ratio of the asymmetric to symmetric mode strengths is related to the tilt angle θ , the angle between the symmetry axis of the CH₃ molecule, and the surface normal²⁴

$$\left| \frac{A_{q,\text{asym}}}{A_{q,\text{sym}}} \right| = \left| \frac{\beta_{\text{caa}} \times (x - x^3)}{\beta_{\text{ccc}} \times \left(\frac{(1-r)}{2} \times (x - x^3) + r \times x \right)} \right| \quad (2)$$

where $x = \langle \cos(\theta) \rangle$, $r = \beta_{\text{aac}}/\beta_{\text{ccc}}$ and the β 's are molecular hyperpolarizabilities. We have used $r \approx 2.35$ and $\beta_{\text{aac}}/\beta_{\text{ccc}} \approx 1$ to determine the tilt angles.¹³ Because the asymmetric peak assignment for the methyl groups of OTS and Si-(CH₃)₂ overlap at 2960 cm⁻¹ and the line strength can take positive or negative values, we can estimate only the upper bound on the orientation of Si-(CH₃)₂. This comparison gives us values of $|A_{q,\text{asym}}/A_{q,\text{sym}}| \approx 0.3$ and $x \approx 0.85$ for PDMS^{ox} in contact with the OTS monolayer

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