

# Comparative FM-AFM Observations of PDMS on HOPG in Liquid and Air

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Frequency-modulation atomic force microscopy (FM-AFM), which enables high-resolution observation of solid surfaces under various environmental conditions, is a powerful tool in surface nanoscience. Observing the same sample with the same instrument under different environmental conditions is crucial for understanding and controlling molecular processes such as molecular film formation; however, this remains a significant technical challenge.<sup>[1]</sup> To address this, we have built a qPlus-type FM-AFM capable of stable measurements at both liquid/solid and air/solid interfaces.<sup>[2]</sup>

In this study, we present comparative FM-AFM measurements of polydimethylsiloxane (PDMS) in miscible and immiscible liquids, as well as in air. As shown in Figure 1, PDMS is an organosilicone polymer with siloxane bonds (Si–O–Si), attracting attention as a coating material due to its chemical resistance, high thermal stability (up to ~200°C), and optical transparency. While previous studies have predominantly focused on micrometer-thick PDMS film,<sup>[3,4]</sup> investigations of nanometer-thick PDMS films and liquid/solid interfacial structures of PDMS have been insufficiently investigated despite its importance.

For sample preparation, a freshly cleaved HOPG surface was used as the substrate. Liquid PDMS was diluted in either toluene (miscible solvent) or N,N-dimethylformamide (DMF) (immiscible solvent), and then dropped onto the HOPG substrate. During FM-AFM measurements in liquid, only the AFM tip was immersed to a depth of about 200–300  $\mu\text{m}$  into the liquid. For measurements in air, the sample was annealed at 100°C for 30 min to evaporate the solvent, leaving PDMS on the HOPG surface.

At the liquid/solid interface on HOPG in the miscible toluene-PDMS solution, PDMS molecules were not directly visualized until the toluene evaporated. After evaporation, we observed randomly adsorbed PDMS molecules forming a monomolecular film with a thickness of about 1 nm in air. In contrast, for the immiscible DMF-PDMS solution, a layered structure was observed, as shown in Figure 2. Further analysis revealed that this layered structure is a densely packed PDMS monolayer. Our comparative FM-AFM measurements in different conditions, spanning from air to liquid environments, highlight the environmental dependence of molecular film formation.

## Reference

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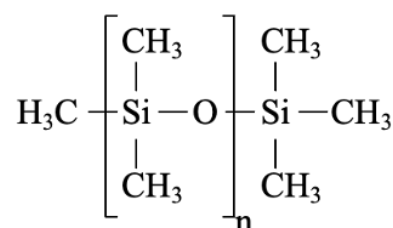


Figure 1. Chemical structure of PDMS.

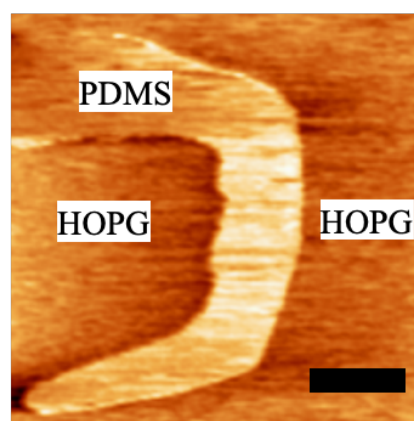


Figure 2. FM-AFM image of PDMS film on HOPG in DMF solution. Scale bar represent 200 nm.