

Supporting Information for:

**On the Origins of Sudden Adhesion Loss at a Critical Relative Humidity:
Examination of Bulk and Interfacial Contributions**

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The phase separation of moisture at the interface cannot be determined from the neutron reflectivity data presented in the manuscript. However, *in-situ* atomic force microscopy (AFM) images of polymer films supported on silicon wafers exposed to water strongly suggest this phase separation. As the interfacial moisture excess occurs only within several nm of the substrate surface, thin films of a polymer were prepared (approximately 15 nm thick). Figure S1 shows a representative image of the dry film. This is relatively featureless as expected.

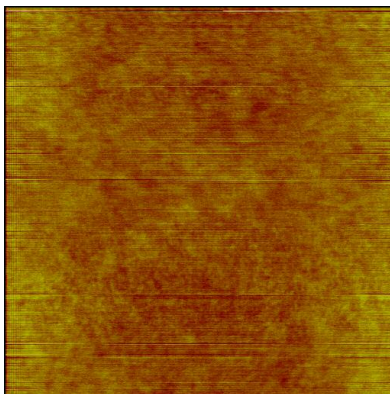


Figure S1. Image of a dry polymer film surface.

Two different surfaces are examined: native oxide (glass) and a methylated surface. The former surface is extremely hydrophilic and known to exhibit poor adhesion in wet environments. The later surface is somewhat hydrophobic and exhibits minimal adhesion loss when exposed to moisture.

The *in-situ* AFM images of these two polymer films with nearly identical thickness, but extremely different surfaces are shown in Figure S2. The polymer film on the hydrophobic surface remains relatively featureless, but the film on the hydrophilic surface exhibits a blistered surface. We attribute these blisters to water phase separation at the interface. For even thinner films, holes emerge when the film on a hydrophilic substrates exposed to water.¹

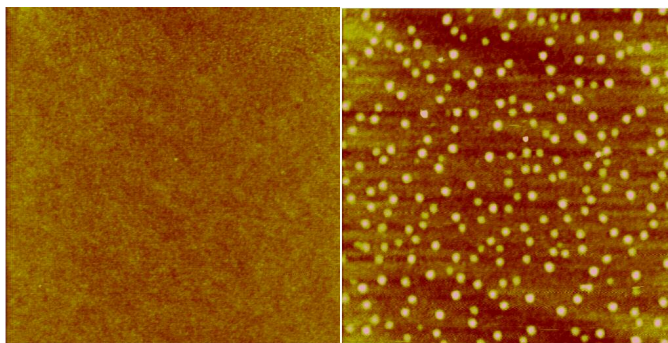


Figure S2. AFM images of polymer surfaces while exposed to water for (a) hydrophobic and (b) hydrophilic surfaces.

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Reference

1. Vogt, B. D.; Soles, C. L.; Wang, C.-Y.; Prabhu, V. M.; McGuiggan, P. M.; Douglas, J. F.; Lin, E. K.; Wu, W.; Satija, S. K.; Goldfarb, D. L.; Angelopoulos, M. Water immersion of model photoresists: Interfacial influences on water concentration and surface morphology. *Journal of Microlithography, Microfabrication, and Microsystems* **2005**, 4 (1), 013003.