

# Nanoscale Forces in Complex Systems of Multi-Layered Polymer Brushes and Compliant Individual Molecules

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## INTRODUCTION

The recent advancements in the design and construction of compliant polymer surfaces with the built in ability to be tailored to a specified state has implications new applications ranging from materials science to drug-delivery and biological processes. However, to fully exploit the capabilities of smart, self-adaptive interfaces, intermolecular forces and nanoscale mechanical properties of these materials must be fully understood. Direct measurement of these interactions is possible only with atomic force microscopy (AFM) probing capabilities at such high spatial resolutions.<sup>1</sup> However, the majority of these AFM based experiments are mainly limited to qualitative visualization of the surface stiffness distribution, while most probing of single molecular forces and binding interactions are carried out in the tensile, or pull-off regime.<sup>2,3</sup>

Here, we provide examples whereby nanomechanical properties of polymer brushes with various glassy-rubbery-glassy combinations and individual macromolecules are quantitatively determined through the compression regime. Elastic models proposed to date fail to describe systems with such interfacial ordering. A new model is proposed that takes into account transition (interface) zone thicknesses using multi-step graded functions.

## EXPERIMENTAL

**Materials.** Polymer brush layers are composed of macromolecules chemically grafted to a solid silicon substrate through a mediating functionalized self-assembled monolayer. In the case considered here, a binary polymer brush layer was prepared from rubbery poly(methyl acrylate) (PMA) and glassy poly(styrene-co-2,3,4,4,5,6-pentafluorostyrene) (PSF) sequentially grafted to a silicon wafer by the grafting from approach as described elsewhere.<sup>4</sup> Various patterns of vertical segregation (for example, glass to rubber) were induced by exposing the binary brush to selective solvents in which one component will have favorable interaction with the solvent, while the other avoids interaction by collapsing at the core of the layer.<sup>5</sup>

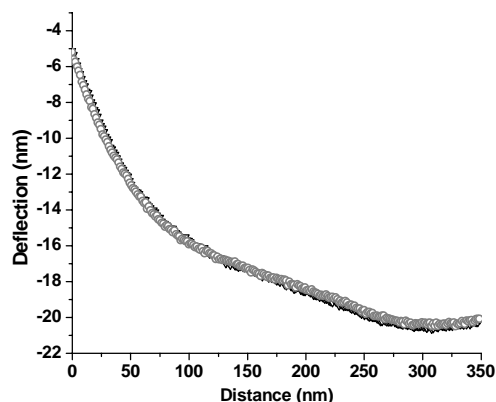
For single molecule studies, we choose dendritic molecules, specifically, hyperbranched polyesters, which are known for forming complaint nanoparticles with a diameter of several nanometers, as an example of molecules whose nanomechanical properties cannot be tested with tensile regime AFM.

**Methods.** Experiments were carried out in dry environments and under fluid (organic solvents) using a Dimension 3000 and Multimode AFMs. Spring constants and tip radius were well characterized according to procedure.<sup>6</sup> Modified and unmodified tips were used. Resulting force-distance curves were collected in force volume mode with 5 – 30nm resolution, and processed by *MMA*Analysis software developed in our lab.

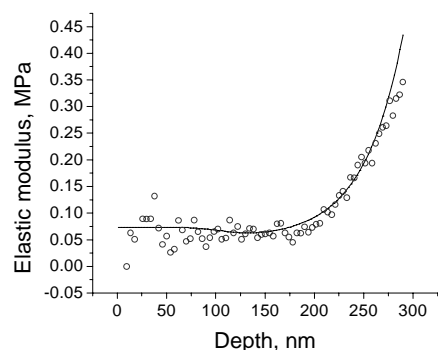
## RESULTS AND DISCUSSION

A typical force curve for a tri-layered polymer brush is shown in Figure 1. In this case, force measurements were done under a selective solvent resulting in a layered surface where PMA swells over collapsed PSF, with a small amount of PSF chains locked near the top

the brush ( $T_g$  for PSF = 109°C). Modeling of the data quantitatively determined the mechanical properties of the binary brush in various solvent conditions, while also describing the transition zones (Figure 2).<sup>7</sup>



**Figure 1.** Force-distance curve of the binary brush in selective solvent for PMA. Black curve is retracing, grey is approaching curve.



**Figure 2.** Depth profile of the elastic modulus for binary brush in selective solvent obtained by modeling of the force-distance curve shown in Fig. 1.

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