

# Experimental evidence of ultrathin polymer film stratification by AFM force spectroscopy

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Confinement effects are widely accepted to seriously affect the molecular dynamics and in turn the glass transition temperature. Interest in understanding the physics governing the onset of the glass transition temperature in ultra thin films is driven by the need to exploit polymers for advanced material applications in nanotechnology where excessive embrittlement, material flow, and surface roughness need to be avoided. In spite of a wealth of experimental and theoretical studies on this topic, there is still an intense controversy over the role played by interfaces on the occurrence of Tg.<sup>[1]</sup> This controversy is nourished by reports in the literature of contradictory results on similar samples because in the case of supported thin polymer films, a clear influence of the nature of the polymer/substrate interaction, and of the conformation of polymer chains at this interface has been clearly evidenced.<sup>[2]</sup>

In the simplest model (i.e. the layered model), the total film thickness is divided into a three-layered stack: a first layer in contact with the substrate with chain dynamics dependant of the substrate polymer interaction, a middle layer assimilated to bulk material, and a more mobile top layer due at the air/polymer interface.<sup>[3]</sup> Although the layered model appears to be the most successful model in the community, no clear experimental reason has been given to choose this approach over another. Indeed, methods such as ellipsometry, dielectric spectrometry and nano-DSC usually probe the material properties averaged across the whole thickness of the film and thus measurement leads to a unique averaged Tg.<sup>[4]</sup>

Although we were among the first to detect multiple transitions in thin PS films using multi-wavelength ellipsometry,<sup>[5]</sup> the measurement of Tg for such thin films remains difficult. Alternatively, glass transition temperature of thin films has been studied by Atomic Force Microscopy (AFM) using a different approach: AFM nanoindentation experiments have mainly confirmed the existence of an enhanced mobility of polymer chains at the free interface by probing the evolution with temperature of the mechanical properties of the film.<sup>[6]</sup> To our knowledge, none of these teams has observed multiple transitions. Lateral or shear force measurements led to some contradictory results: some have found a Tg dependency with thickness,<sup>[7]</sup> others no dependency,<sup>[8]</sup> and some by using low load force measured multiple transition temperatures.<sup>[9]</sup> These discrepancies probably result from the strong dependency of the measured forces on load force and tip scanning speed.<sup>[10]</sup>

In this work,<sup>[11]</sup> by performing Atomic Force Microscopy measurements of pull-off force as a function of the temperature, we were able to probe the dynamic of supported thin polystyrene (PS) thin films. Thermal transitions induce modification in the surface energy, roughness and surface modulus that are clearly detected by AFM and related to PS chain relaxation mechanisms. We demonstrated the existence of three transition temperatures that

can be associated to the relaxation of polymer chains located at different depth regions within the polymer film (Figure 1-left).

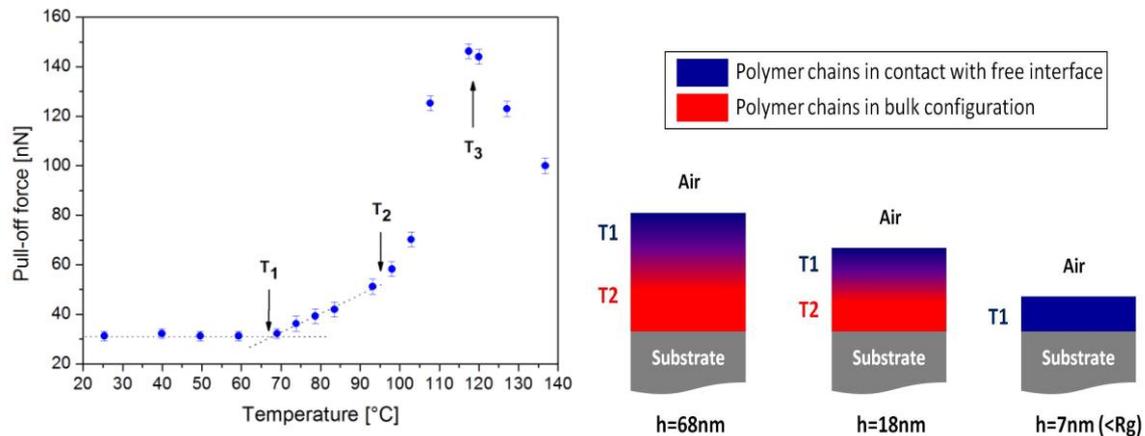


Figure 1. Left: Evolution with temperature of the pull-off force measured on PS film (thickness=68nm). Dash lines are used for the determination of T<sub>1</sub> and T<sub>2</sub>. Right: Sketch representing polymer chains and their associated transition temperatures for different PS film thicknesses.

Independently of the film thickness, we have confirmed the presence of a region of high mobility for the polymer chains at the free interface. The thickness of this region is estimated to be above 7nm. The detection of a transition only present for film thicker than R<sub>g</sub> is linked to the dynamics of polymer chains in a bulk conformation (i.e. not in contact with the free interface) (Figure 1-right). We claim here that our results demonstrate, in agreement with other techniques, the stratification of thin polymer film depth profile in terms of relaxation behavior. The originality of our approach allows us to give more insight on the analysis of the glass temperature behavior of thin PS films.

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