

# Adhesion and Friction Between Supported pH Sensitive Polymeric Nanoparticles Monolayers

L. Giraud<sup>1</sup>, S.Giasson<sup>1,2</sup>

<sup>1</sup>Faculty of Pharmacy, Université de Montréal, lucie.giraud@umontreal.ca

<sup>2</sup>Department of Chemistry, Université de Montréal, suzanne.giasson@umontreal.ca  
C.P. 6128, succursale Centre-Ville, Montréal, QC, Canada, H3C 3J7

## ABSTRACT

We investigated core/shell polystyrene (PS)/ polyacrylic acid (PAA) nanoparticles (NPs) which are weakly charged and therefore sensitive to pH and ionic strength. These NPs made of PAA can undergo changes in volume, in surface potential and structure in response to changes in pH and/or ionic strength. Such NPs are promising materials for designing smart carriers whose surface properties (adhesion, permeability) and interactions with the surrounding environment can be modulated in response to an external stimulus or signal. The NPs monolayers were irreversibly attached on amino-functionalized mica and silica substrates to prevent cleavage and/or slipping of the NPs at the polymer/substrate interface during force measurements. We have demonstrated that immobilized NPs maintained their responsiveness properties.

**Keywords:** pH sensitive nanoparticles, adhesion, friction, surface properties, polymer conformation, amino-functionalized monolayers

## 1 INTRODUCTION

The unique property of polymers responding to external stimuli has made this class of smart materials very promising for applications such as intelligent medical tools, microelectromechanical systems, and sensors, to name but a few. Surfaces can be rendered stimuli-responsive by attaching polymers that respond to external stimuli of the surrounding environment<sup>1</sup>. A particular approach that has been widely used over the past decades is the chemical anchoring of end-functionalized linear polymers to substrates<sup>2,3</sup>. The resulting polymer brushes present properties that are contingent on grafting density<sup>4</sup>, layer thickness<sup>4</sup>, external conditions (solvent, pH...)<sup>5</sup>. The use of polyelectrolyte (PE) brushes has often been proposed for their remarkable lubricating properties<sup>6,7</sup>. Numerous studies of various PE-bearing surfaces in aqueous media have been reported, however, the precise way in which the polymer conformation and ionization control the resulting surface properties is still debated.

## 2 METHOD

To attempt better understanding of the underlying mechanism, we investigated the behavior of supported core/shell polystyrene (PS)/polyacrylic acid (PAA) nanoparticles (NPs). These NPs made of a cross-linked PAA shell are weakly charged and can undergo changes in surface potential and volume in response to external pH. In this study, direct surface forces measurements between supported NPs monolayers were carried out using the Surface Forces Apparatus (SFA)<sup>8</sup>. To establish reliable structure/properties relationship, NPs immobilization is required to prevent cleavage and/or slipping at the polymer/substrate interface. Therefore, the NPs were covalently attached onto an amino-functionalized monolayer also covalently attached on mica substrates (Figure 1) to create stable and immobilized NPs supported monolayers (Figure 2).

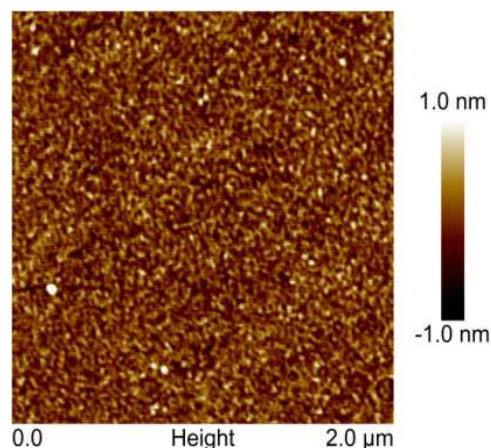


Figure 1. AFM images in air of amino functionalized monolayer on mica, RMS=0.27± 0.03nm.

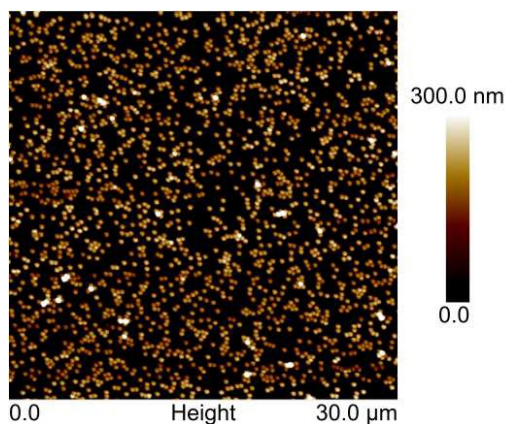


Figure 2. NPs monolayers deposited on amino-functionalized mica for suspension concentration of 0.3% w/w and  $2.51 \pm 0.14$  NPs/ $\mu\text{m}^2$ .

### 3 RESULTS

We have demonstrated that immobilized NPs maintained their swelling properties (Figure 3). Normal and lateral forces measured between these supported NPs as a function of pH will be compared with different classes of solvated polymer-bearing surfaces in order to elucidate the role of the conformation, elasticity and electrostatic interaction of the polymer chains in controlling friction and adhesion between surfaces in aqueous media.

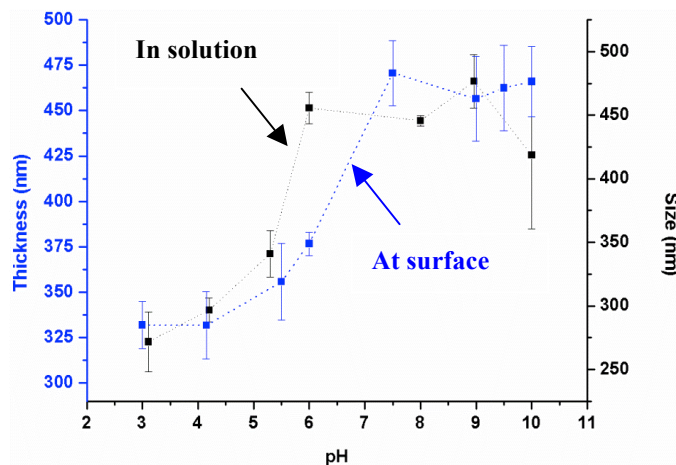


Figure 3. Variation in the relative thickness of supported NPs monolayers and variation in the NPs size in water as a function of pH. The thickness of the supported NPs monolayers is determined from the force profiles measured using the Surface Forces Apparatus.

### REFERENCES

- [1] Azzaroni, O, J. Polym. Sci. A Polym, 50, 3225, 2012.
- [2] Idota, N. et al, Langmuir, 22, 425, 2006.
- [3] Raviv, U. et al, Langmuir, 18, 7482, 2002.
- [4] Singh, N et al, Biomaterials, 28, 763, 2007.

- [5] Zhulina, E.B et al. Macromolecules, 33, 4945, 2000.
- [6] Raviv, U. et al, Nature, 425, 163, 2003.
- [7] Barbey, R et al, Chem. Rev., 109, 5437, 2009.
- [8] Israelachvili, J et al, Rep. Prog. Phys., 73, 1, 2010.