



# Adsorption of Poly(2-vinylpyridine) Wormlike Polyelectrolyte Brushes on Mica Studied *in situ* with MAC Mode<sup>®</sup> AFM

## Application Note

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### Introduction

Over the past several years, advances in polymer chemistry have opened new avenues in the preparation of macromolecules possessing well-defined three-dimensional shape and rich functionality of the molecular surface. Molecules like dendrimers (1), cylindrically shaped brushes (2), and monodendron-jacketed polymers (3) are of particular interest in nanotechnology. These molecules have exceptional film-forming properties and can be utilized as molecular containers for drug delivery, construction units for molecular motors, polyfunctional catalysts, and templates for nanolithography. All of these applications take advantage of the well-defined morphology and synthetic versatility of such molecules, which enables control of their size, shape, interior structure, and surface functionality.

The unique capabilities of scanning probe microscopy can be used to acquire information about the structure and ordering of these so-called molecular particles. This application note focuses on the monitoring of the adsorption process of charged, cylindrical, brushlike molecules onto a solid substrate with molecular resolution. Long-range electrostatic interactions between charged molecules, as well as between the molecules and the substrate, control the ordering of the particles in the vicinity of the flat, charged wall. The observations were done *in situ* under controlled environmental conditions (e.g., temperature, concentration, pH, and ionic strength of the solvent).

### Cylindrical Polymer Brushes

Cylindrical brushes of poly(2-vinylpyridine), or PVP, were prepared by polymerization of the corresponding macromonomers (2). Due to the strong overlapping of the side chains, these macromolecules adopt a stiff cylindrical shape and are characterized by a wormlike conformation in solution, as shown in Figure 1. Grafting density and length of the side chains were controlled synthetically. Furthermore, PVP can be converted to a polyelectrolyte by a quaternization reaction yielding, in our case, 20 charges per PVP side chain.

### Method

Adsorption of polyelectrolyte PVP brushes on mica from aqueous solutions at different ionic strength was studied using MAC Mode atomic force microscopy (AFM). This patented AFM technique from Agilent Technologies is an oscillating cantilever method of imaging that enables stable visualization of soft samples in a liquid environment (4-6). A cantilever with a paramagnetic coating is driven directly by an alternating magnetic field generated by a solenoid placed under the sample (2). A schematic representation of the experimental setup is shown in Figure 2.

Similar to other oscillating probe techniques, in MAC Mode the cantilever is driven at frequencies in the kHz range and the surface is monitored via changes

in the cantilever's amplitude. Because the cantilever is driven directly by the external magnetic field, the cantilever mounting assembly (the cantilever holder, the cantilever chip, the liquid cell, etc.) is not vibrated, leading to far better control over the cantilever's oscillation and allowing operation at much smaller amplitudes. Consequently, lower vertical forces are applied to the sample during imaging. This reduces surface deformations, a critical advantage when studying soft organic materials.

Aqueous solutions of polyelectrolyte PVP brushes were inserted directly into the liquid cell of an Agilent scanning probe microscope (SPM) without any pretreatment of the mica substrate. The large volume of the liquid cell (up to 600  $\mu$ l) provided an ample reservoir of molecules.

Other features of the Agilent SPM that were important for these studies included:

- An environmental chamber that enabled measurements in fast-evaporating organic solvents like toluol and methanol
- A flow-through liquid cell that enabled the direct exchange of liquid during imaging for observation of the influence of ionic strength on film formation *in situ*



### Observation of Individual Molecules

Figure 3 shows individual molecules of the polyelectrolyte brushes on mica in an aqueous environment. In this case, water caused partial ionization of both PVP and mica. Due to the strong interaction between the positively charged brushes and the negatively charged substrate, the same surface area was imaged over the course of hours without observing any changes.

The electrostatic interactions influenced the aggregation behavior and orientation of molecules on the mica substrate strongly. In contrast to the uncharged PVP brushes (2), which aggregate into a uniform monolayer and form "hairpin" folds, the ionized molecules repelled each other and appeared as single rods lying flat on the surface. The width and the height of the molecules were measured to be  $8 \pm 1$  nm and  $2.8 \pm 0.2$  nm, respectively. Furthermore, the adsorbed molecules either aligned in parallel, oriented at an angle of about  $90^\circ$ , or lay across each other.

As both ends of the molecules were resolved, their length distribution could be evaluated quantitatively. Figure 4 shows a histogram of the molecular length distribution obtained from the MAC Mode AFM micrographs by grain-size analysis software. A number average contour length  $L_n = 51$  nm and a weight average contour length  $L_w = 116$  nm were determined for a set of 664 molecules.

### Film Formation

The formation of a polyelectrolyte PVP film on mica was studied as a function of polyelectrolyte concentration (Figure 5). Remarkably, coverage appeared to be invariant over a very broad concentration range from  $10^{-3}$  –  $10^{-1}$  g/l (Figure 6). A maximum coverage of  $25 \pm 5\%$  was achieved.

The coverage of mica with the polyelectrolyte brushes was increased by adding NaCl to the polyelectrolyte solution. Direct exchange of liquid during

experiments allowed the study of the adsorption process as a function of the ionic strength *in situ*.

Figure 7 shows a series of images measured sequentially before, during, and after adding a portion of 0.5 M NaCl solution to 200 ml of a 0.05 g/l solution of the polyelectrolyte. The scan directions are marked by arrows next to the images. A sudden increase in coverage was observed 81 seconds after adding 50  $\mu$ l of NaCl solution (Figure 7b). From the Einstein-Smoluchovsky equation, this time interval corresponds to the diffusion time of  $\text{Na}^+$  ions to the scanning area. As a result, an almost twofold increase of coverage (i.e., 45%) was achieved (Figure 7c).

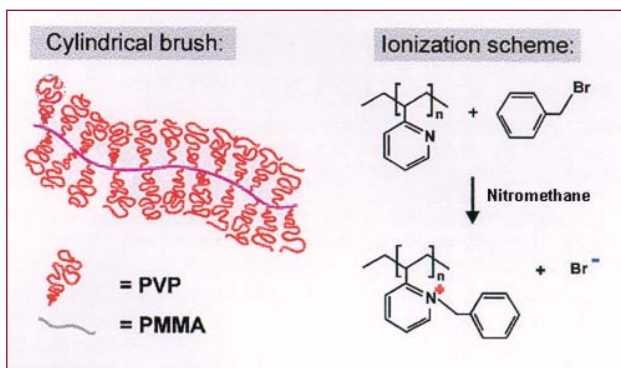


Figure 1. Schematic illustration of a poly(2-vinylpyridine) brush (left) and quaternization reaction (right).

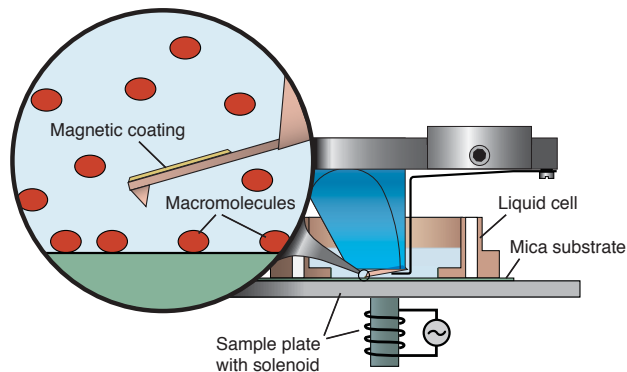


Figure 2. Schematic setup of MAC Mode AFM with a liquid cell.

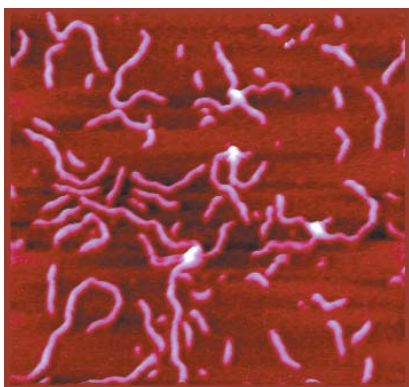


Figure 3. Single molecules of PVP cylindrical brushes adsorbed onto mica in water. Scan area: 390 nm.

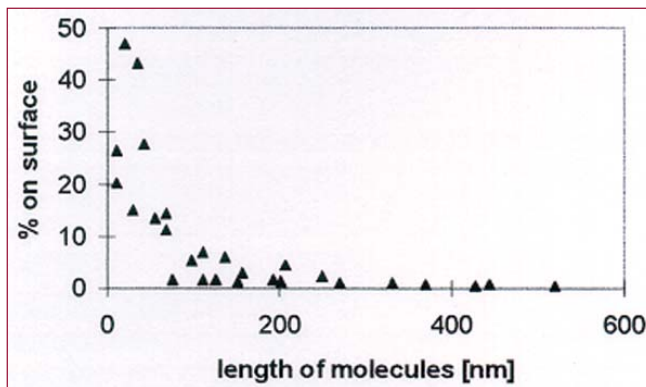


Figure 4. Histogram of chain length distribution measured by MAC Mode AFM.

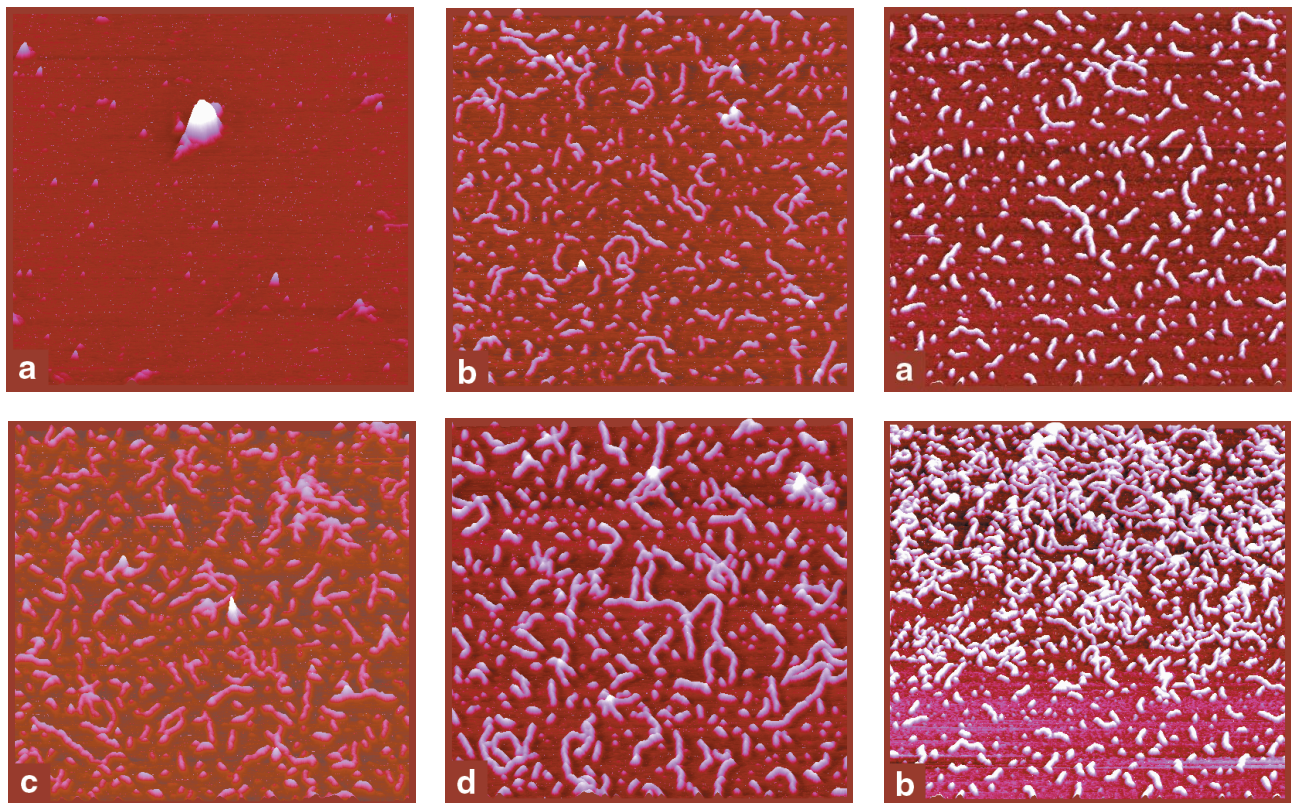


Figure 5. MAC Mode AFM micrographs of the PVP brushes observed upon adsorption from aqueous solutions of various concentration: g/l  $10^{-4}$  (a),  $10^{-3}$  (b),  $10^{-2}$  (c),  $10^{-1}$  (d). Scan area:  $1 \mu\text{m}$ .

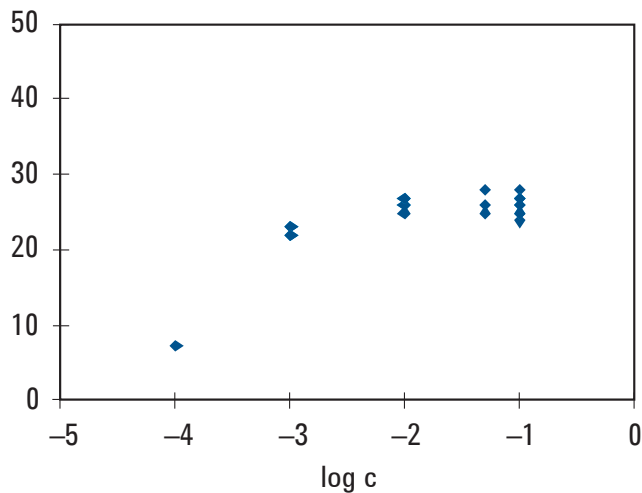


Figure 6. Coverage of mica with PVP brushes as a function of concentration.

### Summary

MAC Mode AFM can provide a powerful means to monitor adsorption of single polymer molecules onto a solid substrate. Cylindrically shaped macromolecules of polyelectrolyte brushes of poly(2-vinylpyridine) were visualized upon adsorption to mica

in a controlled environment. Temperature, concentration, pH, and ionic strength, which are crucial for formation of the PVP thin film, were varied during imaging. Imaging was stable over several hours in water and methanol.

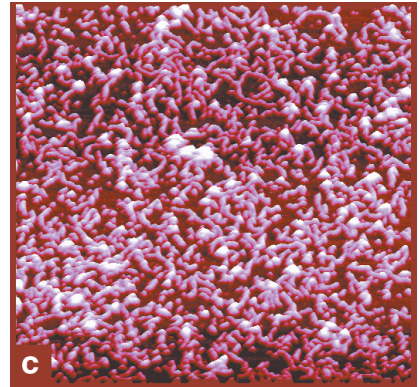


Figure 7. Adsorption of PVP brushlike molecules on mica before (a), during (b), and 30 minutes after (c) the addition of NaCl. Scan area:  $1 \mu\text{m}$ .

## References

1. S.S. Sheiko, A.M. Muzafarov, R.G. Winkler, Langmuir, 1997, 13, 4172.
2. P. Dziezok, S.S. Sheiko, K. Fischer, M. Schmidt, M. Möller, Angew. Chem. Int. Ed. Engl., 1997, 36, 2812.
3. V. Percec, C.-H. Ahn, G. Ungar, D.I.P. Yeardley, M. Möller, S.S. Sheiko, Nature, 1998, 391,161.
4. W.Han, S.M. Lindsay, T. Jing, Appl. Phys. Lett., 1996, 69, 4111.
5. S. Lindsay, J. Zhu, J. Hudson, American Laboratory, Nov. 1997, 15.
6. W. Han, S.M. Lindsay, M. Dlaki, R.E. Harrington, Nature, 1997, 386, 563.

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