2-Dimensional chain conformation of adsorbed bottle brushes

I. Raguzin[1], N. Puretskiy[1], L. Ionov[1], V. Körstgens[2], C. Birkenstock[2], P. Müller-Buschbaum[2], and M. Stamm[1]

[1]Leibniz Institute of Polymer Research Dresden, Hohe Straße 6, 01069 Dresden, Germany

[2]Technische Universität München, Physikdepartment E13, Lehrstuhl für Funktionelle Materialien, James-Franck-Str. 1, 85747 Garching, Germany

[3]HASYLAB, DESY, Notkestr 85, 22607 Hamburg, Germany

Bottle brushes are the complex polymer constructs consisting of main polymer chains with side-grafted polymer chains. Bottle brushes were demonstrated to be very promising templates for fabrication of inorganic nanostructures. The shape as well as properties of possible inorganic nanostructures is guided by the conformation of polymer chains. The conformation of bottle brushes, on the other hand, depends on many parameters such as length and grafting density of side polymer chains are well as character of their interactions with solvent. Recently, bottle brushes with grafted polymer chains of one sort were intensively investigated using atomic force microscopy.

We fabricated thermoresponsive bottle brushes with poly(N-isopropylacrylamide) (PNIPAM) side chains (Figure 1a). PNIPAM exhibits Low Critical Solution Temperature (LCST) behavior in aqueous solutions and, thus, demonstrates very pronounced responsive properties. The bottle brushes adsorbed on a substrate form periodic patterns and the pattern periodicity is expected to depend on the length of side groups as well as on their conformation, which in its turn depends on temperature.

To investigate the conformation of PNIPAM bottle brushes on the surface of silicon wafer the GISAXS measurements at beamline P03, HASYLAB were used. Different types of brushes with the same length of backbone (contour length is 200-250 nm, Mw of backbone is 150kDa) and different length of side polymer chains were investigated. The length of side polymer chains was varied by polymerisation time, which was in the range between 5 min and 90 min. The bottle brushes were deposited by spincoating from highly diluted solutions of molecular brushes on a preliminary washed silicon wafers. The samples were measured with 250 µm steps. On the each step we exposed the sample for one second and captured the picture from the detector. We repeated these scans for several times in order to obtain the average picture. The figure 1d shows the typical average. To study these pictures in details the q_y and q_z cuts were made (fig. 2). Different curves correspond to different time of polymerization of a side chain and thus different thickness of the bottle brush.

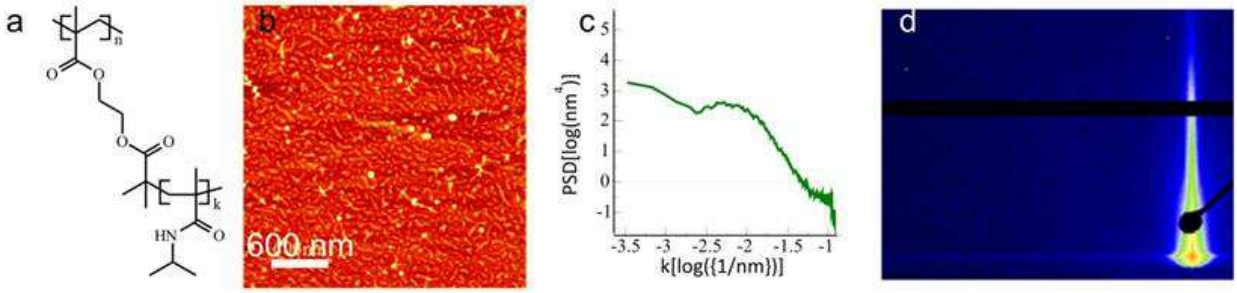

Figure 1. Chemical formula (a) AMF image (b) with FFT of AFM image (c) and GISAX (d) of poly(N isopropylacrylamide) bottle brushes.

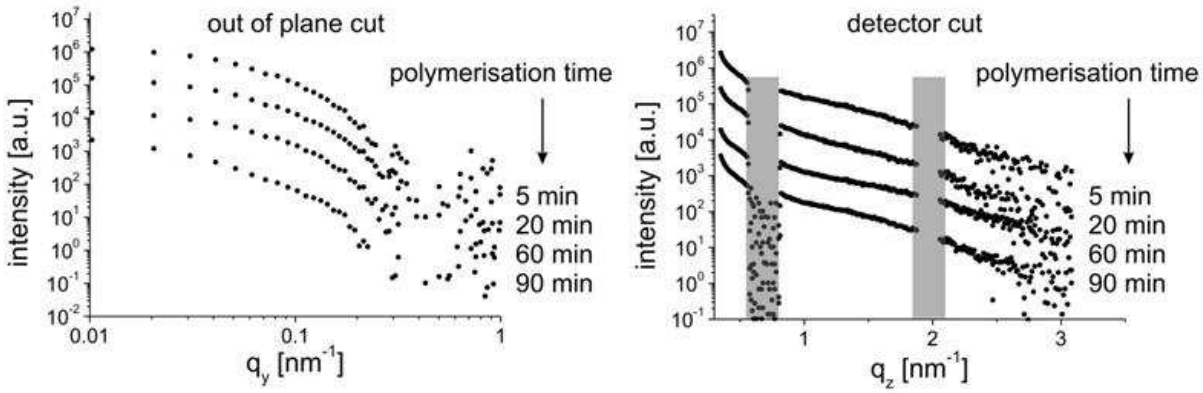

Figure 2: The qy and qz cuts of the scattering on bottle brushes obtained by polymerisation during different time (5-90 min).

Fast Fourier transform (FFT) of topographical AFM images clearly shows a peak corresponding to characteristic length to about 100 – 150 nm that is the distance between backbones of bottle brushes on the surface. On the other hand, no peak is observed on GISAXS images (Figure 1d) and corresponding cuts (Figure 2). The reason of this discrepancy could be the week scattering ability of thin layer formed by the polymer bottle brushes. In order to circumvent this problem in the next set of experiments, we plan to investigated conformation of bottle brushes decorated with nanoparticles formed by heavy atoms such as gold, platinum and palladium. For further analysis and modelling these results will be compared with cryo-TEM and AFM experiments. We acknowledge financial support from DFG and IPF.

References

[1] He, G. L.; Messina, R.; Lowen, H.; Kiriy, A.; Bocharova, V.; Stamm, M. *Soft Matter* **2009,** 5, (16), 3014-3017.

[2] Lages, S.; Lindner, P.; Sinha, P.; Kiriy, A.; Stamm, M.; Huber, K. *Macromolecules* **2009,** 42, (12), 4288-4299.

[3] Tsitsilianis, C.; Stavrouli, N.; Bocharova, V.; Angeiopouios, S.; Kiriy, A.; Katsampas, I.; Stamm, M. *Polymer* **2008,** 49, (13-14), 2996-3006.