VAPOUR-INDUCED CONFORMATIONAL TRANSITIONS OF INDIVIDUAL MACROMOLECULES VISUALISED IN REAL TIME BY SCANNING FORCE MICROSCOPY

Marat Gallyamov¹*, Alexei Khokhlov¹, Krzysztof Matyjaszewski², Martin Moeller³ Moscow State University, Physics Department, Moscow, Russia

² Department of Chemistry, Mellon Institute, Carnegie Mellon University, Pittsburgh, USA ³ Institut fuer Technische Chemie und Makromolekulare Chemie, RWTH Aachen, Germany * e-mail: glm@spm.phys.msu.ru

Scanning force microscopy (SFM) is now widely used as a convenient and powerful technique to study macromolecular conformational transitions at the single-molecule level in real time [1-3]. The SFM-observable conformational changes can be induced, for example, by an exposure of adsorbed macromolecules to a controlled liquid environment [1]. Recently, we have also reported a possibility to manipulate the macromolecular conformation of comb-like PMA-*g*-P*n*BuA [2] as well as linear P2VP [3] macromolecules by means of exposure to different vapours. By SFM we have been able to observe step-by-step reversible coil-to-globule conformational transitions of individual macromolecules in situ, in real time. The PMA-*g*-P*n*BuA brushes collapse in vapours of amphiphilic compounds with low surface tension values (alcohols, ethers, etc.) and extend in vapours of compounds having high surface tension (water, DMSO, DMF, etc.). Similar reversible collapse-decollapse dynamics is observed for the P2VP molecules exposed to ethanol or water vapour.



Figure 1. Sequence of SFM micrographs demonstrating the extension of individual PMA-g-PnBuA brush molecules on mica in DMSO vapour. a: Initial image of previously collapsed molecules (as deposited on the substrate and exposed to a alcohol-saturated vapour). b-f: The same molecules in DMSO-saturated atmosphere 2 h (b), 4 h (c), 7 h (d), 11 h (e), and 20 h (f) after injection of DMSO into the environmental chamber of a SPM device. Bar size: 250 nm, height scales: 3 nm(a,b,e), 4 nm (c,d), 2 nm (f).

Although in general the vapour-stimulated behaviour of both the brush-like and linear macromolecules seems to be the same, there is some subtle difference in the spreading process. Preliminary compacted brush-like molecules unfold and untwine when they are exposed to, e.g., DMSO vapour, see Fig. 1. Their individual strands move apart from one another on the substrate and gradually decrease their curvature. This motion ceases with time and after equilibration the molecules still have a distinct curvature. The linear macromolecules unfold more abruptly, see Fig. 2 (obtained in water vapour). There is no gradual decrease of molecular curvature observed. After extension the chain dimensions can be described well by a two-dimensional self avoiding walks statistics. The difference in spreading dynamics is apparently determined by the molecular structure and will be discussed.



Figure 2. Sequence of SFM images demonstrating the unfolding of partially compacted P2VP molecules deposited on mica. Selected molecules are marked by coloured outlines. The molecules are extending in water-saturated atmosphere for 0.5 h (a), 1 h (b), 1.5 h (c), 2 h (d), 2.5 h (e), and 3 h (f). Bar size: 100 nm, height scales: 1 nm(a), 0.7 nm (b), 0.5 nm (c-f).

M.O.G. acknowledges the Alexander von Humboldt Foundation for an award of a Return Fellowship and the NATO Public Diplomacy Division for Reintegration Grant CBP.NR.RIG.981306 (Security through Science Programme). The work was also supported by the Russian Foundation for Basic Research (project no. 04-03-32297a).

References:

[1] M. Y. Ono and E. M. Spain // J. Am. Chem. Soc. (1999), **121**, 7330; A. L. Martin, *et al.* // FEBS Lett. (2000), **480**, 106; F. Nagami, *et al.* // Anal. Biochem. (2002), **300**, 170.

[2] M. O. Gallyamov, *et al*. // Chem. Eur. J. (2004), **10**, 4599; M. O. Gallyamov, *et al*. // J. Microsc. (2004), **215**, 245.

[3] M. O. Gallyamov, et al. // Macromol. Rapid Commun. (2005), 26, 456.