**Dynamics of a polymer brush**

Theoretical predictions of the static structure of polymers tethered to a surface at a high density have been experimentally confirmed. However, theories on the dynamic nature of these so-called grafted polymer brushes have been harder to support by experiment. Christophe Demaille and colleagues at the Université de Paris (France) have now been able to directly analyze the dynamic behavior of a grafted polymer brush by a combination of atomic force and scanning electrochemical microscopies.

The investigators studied a polyethylene glycol (PEG) polymer brush. The individual PEG chains were functionalized on both ends. One end carried a ferrocene (Fc) head, and the other had an N-hydroxysuccinimide-activated ester. The ester covalently attached to an amine-modified gold surface, allowing the formation of a well-defined, monolayer, polymer brush of Fc-PEG.

A spherical microelectrode was mounted on an atomic force microscope tip and biased at a positive enough potential to oxidize the Fc on the ends of the PEG chains to Fc⁺. The Fc⁺ moved down to the substrate, which was biased at the opposite potential. The surface reduced Fc⁺ back to Fc, causing it to move away from the substrate.

The flexibility of the PEG chains and the grafting density of the polymer brush controlled the cycling of Fc between two oxidation states. The small size of the microelectrode allowed the investigators to address a limited number of chains at a time and permitted quantitative analysis of the dynamic behavior of the polymer brush and its constituent PEG chains. The investigators also took force measurements as the tip compressed the polymer brush.

The investigators found that the height of the polymer brush increased as the grafting density of the PEG chains increased, as predicted from theory. The diffusion coefficient of the Fc head remained constant as grafting density increased, again supporting theoretical predictions. When the distance between the substrate and tip was small, atomic force microscopy measurements were able to detect a significant compression of the PEG chains in the brush. (J. Am. Chem. Soc. 2004, 126, 10,095–10,108)

**N-nitrosamines in drinking water**

Occurrence data for N-nitrosamines in drinking water are scarce, despite the fact that these disinfection byproducts are probable human carcinogens. The primary reason for this lack of data is that analytical methods are not sufficiently sensitive or selective to detect N-nitrosamines at the low nanogram-per-liter concentrations typically found in drinking water.

In anticipation of possible future regulations, Jeffrey Charrois and colleagues at the University of Alberta (Canada) have developed a new method for detecting eight N-nitrosamines in drinking water. The method uses solid-phase extraction (SPE) in conjunction with GC/MS ammonia positive chemical ionization (PCI). It is more sensitive and selective than previously reported methods, and it is relatively inexpensive. Detection limits ranged from 0.4 to 1.6 ng/L for all eight N-nitrosamines.

Because N-nitrosamines are hydrophilic, polar compounds, they are difficult to extract from water. To obtain high analyte recoveries, the researchers used two different SPE materials. In addition, they reduced the flow rate through the SPE bed to achieve better sample contact.

The new GC/MS PCI method produces fewer nondistinctive fragmentation patterns than other methods for detecting N-nitrosamines, such as GC/MS electron ionization. PCI is a “softer” ionization process that leads to less molecular fragmentation.

The researchers used the new approach to detect N-nitrosamines in drinking-water samples. They discovered, in addition to N-nitrosodimethylamine, N-nitrosopyrrolidine, and N-nitrosomorpholine, two N-nitrosamines that have not been previously reported in drinking water. (Environ. Sci. Technol. 2004, 38, 4835–4841)