Spherical polyelectrolyte brushes

Polymeric brush-like micelles show some remarkable properties

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Polyelectrolyte brushes consist of charged polymer chains attached to a substrate. They have huge technological potential in controlling processes such as gelation, lubrication, and flow behaviour, so have found wide-spread application – from stabilising colloidal suspensions in cosmetics and food products to encapsulating and delivering bioactive agents to living cells.

These systems can be prepared by anchoring the polyelectrolyte chains at an interface, or more interestingly, through the self-assembly of di-block copolymers (p.12). These comprise two linearly attached polymer chains – in this case, a polyelectrolyte, which is hydrophilic, and a neutral, hydrophobic polymer. In aqueous solvents, the copolymers arrange themselves into micelles so that the hydrophobic components are hidden from the water. The micelles thus comprise a core of self-assembled neutral chains (typically about 100), surrounded by a polyelectrolyte 'coronal brush' (see figure below right).

These micelles offer an excellent model system for investigating how spherical polyelectrolyte brushes behave, provided that their neutral cores are dense and stable (for example, sodium polyacrylate-polystyrene). Because the coronal brush is ionic, the micelles readily form dispersions in water. The polyelectrolyte dissociates into small positive counterions, and the negative polymer chains stretch out into the aqueous environment – unlike neutral brushes which coil up. Since technological formulations and biological environments usually contain other small ions, a significant aspect is the effect of adding salt (sodium and chloride ions). The addition of extra ions might be expected to screen the electrostatic repulsion between charged segments in the polymer chain, making it behave more like a tightly coiled neutral brush.

The key approach in understanding the behaviour of polyelectrolyte brushes under various conditions is to look at the structure of the micelle, going from the core outwards, in terms of polymer and ion density. We measured these density profiles using SANS (p.5), applying solute and solvent contrast variation techniques (p.5) to highlight or blank out the various components in the complex mixture of copolymer, salt and water.

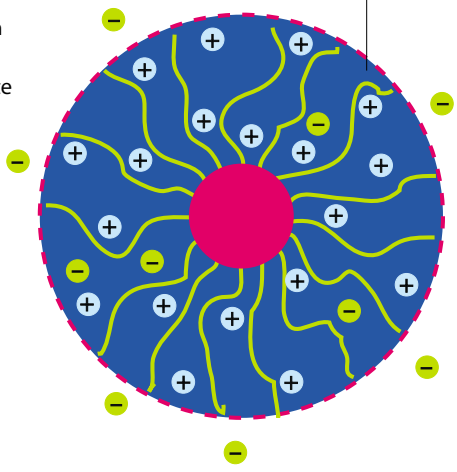
For a highly charged polymer and no salt added – so with minimal screening – we found that the corona chains are almost fully stretched and the density profile of the counterions follows that of polymer corona. But even when quite a lot of salt was added, the brush did not shrink much. This suggests that the stretching is primarily controlled by the counterions trapped in the corona, which draw in water osmotically, rather than by electrostatic effects.

High concentrations

We then extended our experiments to micelle concentrations high enough to cause the coronal brushes to shrink or interpenetrate. This is significant because many of their technological applications are derived from the fluid properties of dense micelle systems, and yet not much is known about how the brushes behave.

We were able to measure the sizes of the core and corona which gave the overall spread of the micelle; we also ascertained what the effective size of the micelles would be, packed as hard spheres in the solution. The difference between these two values gave the degree of interpenetration of the brushes.

The results showed that the polyelectrolyte brushes do shrink as the micelles are squeezed together. However, at high charge and minimal screening conditions – when the polyelectrolyte chains remain almost fully stretched – they start to interpenetrate above a certain concentration. Flow measurements showed that the viscosity increases by 1000 times, resulting in a gel. We conclude, therefore, that tuning the properties of the brush is of paramount importance in developing formulations with the right flow properties. ■



A spherical micelle with a neutral, solvent-free core and a polyelectrolyte coronal brush

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