Smart interfaces grafted with ionic polymers

Yvette Tran, Sarah Sanjuan, Nadège Pantoustier, and Patrick Perrin

Varying pH makes it possible to control conformational changes of polymer chains attached to stimuli-responsive interfaces.

Solid surfaces grafted with polyelectrolytes generate significant interest in a wide field of industrial and biological applications as well as in academic research. They have been extensively used to improve adhesion, lubrication, tribology, and wetting properties, as well as for colloidal stabilization. More recently, strategies have emerged for functionalizing surfaces with polymer brushes to design smart surfaces with switchable adaptive-responsive properties and to generate micropatterned polymer monolayers.1, 2

Responsive polymer brushes are attractive because their attached chains can undergo conformational changes based on external stimuli. For example, neutral polymer chains are sensitive to both good and bad solvents. (The force between polymer-coated surfaces depends on solvent quality. It tends to be repulsive in good solvents and attractive in bad solvents.) In the case of polyelectrolyte chains, the influence of the environment on their electric charge is decisive for stretching. It is important to distinguish between strong polyelectrolytes, in which charges are fixed, and weak ones, in which charges are pH-dependent.

Polyampholytes bear both positive and negative charges along the chain. With an excess of charge (positive or negative), polyampholyte chains exhibit polyelectrolyte-like stretching behavior. With an equal ratio of positive and negative charges, the chains collapse due to the attraction of oppositely charged monomers and the expulsion of counterions.3 The stimuli-responsive interfaces that we investigate are grafted with both polyelectrolytes and polyampholytes. We are particularly interested in the deformation amplitude of brushes as a function of pH.

Our synthesis work is performed with the ‘grafting from’ method using surface-initiated controlled polymerization to obtain dense polymer brushes with well-defined molecular mass and low polydispersity. In our procedure, the halogenated group-functionalized initiator is first anchored to a silica surface in self-assembled monolayers. Chains are then grown from the surface by atom transfer radical polymerization (ATRP). Finally, neutral polymer brushes are converted into polyelectrolyte or polyampholyte brushes by means of in situ chemical reactions.

We recently investigated the swelling of a poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) polybase brush as a function of pH and compared it with the stretching of a poly(2-trimethylaminoethyl methacrylate) (PTMAEMA) quenched brush. Further, a 1:1 PDMAEMA-st-PMMA random copolymer was also investigated as a possible polyampholyte brush. Neutron reflectometry determined the monomer volume fraction profile perpendicular to the surface. The swollen thickness was calculated and compared with values measured by ellipsometry.

Results showed that the swelling behavior of the homopolymer brushes was in good agreement with the scaling laws predicted by mean-field theories, including the models of the neutral polymer brush in good solvent and the polyelectrolyte brush in the osmotic regime. Figure 1 shows a plot of the swollen thickness of a PDMAEMA brush as a function of pH. The neutron reflectivity data was similar to ellipsometry values. There was no hysteresis effect with pH variation, indicative of brush swelling reversibility. The swelling behavior of the

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pH-responsive brush was intermediate between that of a neutral polymer in good solvent and that of a strong polyelectrolyte brush in the osmotic regime. The effective charge ratio of the polybase brush was then determined as a function of pH using Manning’s counterion condensation theory and the scaling law of the polyelectrolyte brush in the osmotic regime (see Figure 2). The calculation of the charge ratio is considered valid provided that the osmotic pressure of counterions is higher than that of monomers in a neutral polymer brush.

The conformational transition involved in the stretching-collapse of the polyanion attached chains could be reversibly controlled by pH. Figure 3 shows the swollen thickness of the PDMAEMA-st-PMMA brush as a function of pH for two grafting densities. Polyanion brushes behave like polyelectrolyte brushes at low and high pH owing to excess charge. They are significantly contracted in the pH range of zero net charge (i.e., in the isoelectric range), but they are not as collapsed onto the surface as a solvent-free brush. The density profile shows a nonmonotonic decrease with the distance from the surface. A higher density zone likely due to the attraction between oppositely charged units was also observed. This barrier-like zone could hinder ionization of monomeric units close to the surface. It could also prevent collective ionization and reduce the collapse of the polyampholyte brush. In addition, we observed that the deformation amplitude was higher in the pH range of zero net charge for the polyampholyte brush with the weak grafting density.

We are also interested in ion exchange and use scanning electrochemical microscopy to follow the release of specific ions from a polymer brush. In addition, using selective and sensitive microelectrodes, we attempt to detect polymer brush protons. Other activities include developing ionic polymer brushes in microfluidic devices. We build microchannels that have one of their walls covered by a polymer brush and investigate electroosmotic properties by determining the velocity of the flow under an electric field while varying the ionization of the polymer with pH.

Author Information

Yvette Tran, Sarah Sanjuan, Nadège Pantoustier, and Patrick Perrin
Physico-chimie des Polymères et des Milieux Dispersés
Ecole Supérieure de Physique et Chimie Industrielles
Paris, France

Yvette Tran is an assistant professor in the Laboratory of Physical Chemistry of Polymers and Dispersed Media at the Ecole Supérieure de Physique et Chimie Industrielles. Her research interests include developing and fabricating novel adaptive interfaces coated with responsive polymer brushes.

Patrick Perrin is a professor at Pierre and Marie Curie University (Paris). His research activities include the development of polymer-based emulsifiers to create new stimuli-responsive liquid-liquid dispersions.

References


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