

H4. PH-RESPONSIVE INTERFACES GRAFTED WITH POLYELECTROLYTE OR POLYAMPHOLYTE

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Interfaces grafted with polyelectrolytes are of great interest in a wide field of industrial and biological applications as well as in academic research. They are extensively used for the improvement of adhesion, lubrication, tribology, wetting properties or colloidal stabilization. More recently, some strategies are developed for the functionalization of surfaces with polymer brushes to realize smart surfaces with switchable-adaptative-responsive properties and to generate micro-patterned polymer monolayers.¹⁻² Responsive polymer brushes are attractive owing to the change of the conformation of attached chains according to external conditions. As example, neutral polymer chains are sensitive to a good or a bad solvent. For polyelectrolyte chains, the influence of environment on their charge is decisive for the stretching. An important distinction has to be made regarding “strong” polyelectrolyte for which charges are fixed and “weak” polyelectrolyte which are pH-dependent. Polyampholytes bear both positive and negative charges along the chain. With an excess of charge, polyampholyte chains are as stretched as polyelectrolyte chains. With an equal ratio of positive and negative charges, the chains are collapsed due to the attraction between oppositely charged monomers and the expulsion of counterions.³ Stimuli-responsive interfaces investigated here are grafted with polyelectrolyte and polyampholyte. In particular, we are interested in the deformation amplitude of brushes with the variation of pH.

The synthesis was performed by the “grafting from” method using surface-initiated controlled polymerization to obtain dense polymer brushes with well-defined molecular mass and low polydispersity. First, the halogenated group-functionalized initiator was anchored to the silica surface in self-assembled monolayers. Then, chains were grown from the surface by atom transfer radical polymerization (ATRP). Finally, neutral polymer brushes were converted into polyelectrolyte or polyampholyte brushes by *in situ* chemical reactions.

The swelling of poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) polybase brush was investigated as a function of pH and compared to the stretching of poly(2-trimethylaminoethyl methacrylate) (PTMAEMA) quenched brush. PMAA-*st*-PDMAEMA random copolymer of 1:1 molar ratio was investigated as polyampholyte brush. Neutron reflectometry allowed the determination of the monomer volume fraction profile perpendicular to the surface. The swollen thickness was deduced and compared to the values measured by ellipsometry.

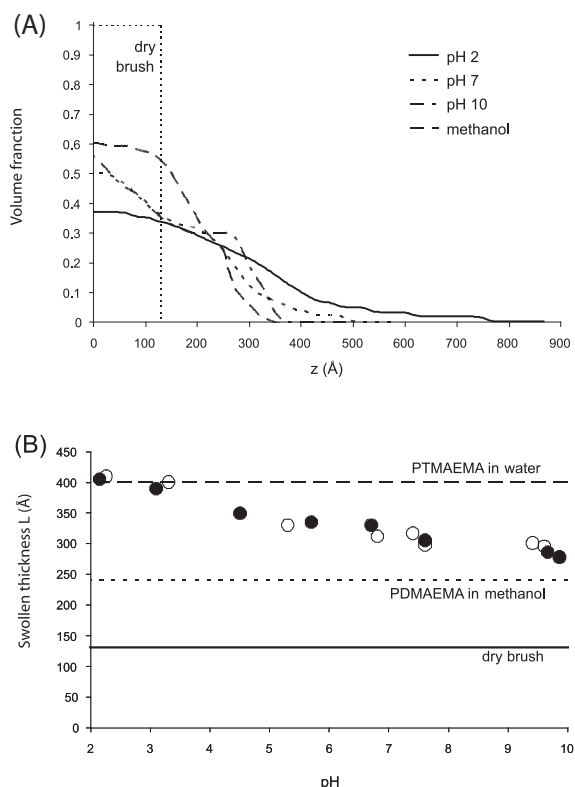


Figure 1. (A) Monomer volume fraction profile of PDMAEMA brush at various pH and in methanol. (B) Swollen thickness of PDMAEMA brush as a function of pH, measured by ellipsometry (○) and neutron reflectivity (●).

Figure 1A shows the monomer volume fraction profile of PDMAEMA brush at pH 2, pH 7 and pH 10 and in methanol. The profile of the dry brush was also given for comparison. The brush was less extended in methanol than in water and was more stretched as pH decreased. The shape of the profiles was analyzed in more detail by fitting the profiles with a parabolic function (predicted for a neutral brush in good solvent) or a Gaussian function (predicted for a polyelectrolyte brush in osmotic regime). The profile of PDMAEMA brush in methanol (respectively at pH 2) could be well adjusted by a parabolic function (respectively a Gaussian shape) as expected. In contrast, the profile at pH 10 was quite far from a Gaussian profile and is closer to a stepwise distribution as predicted for weakly charged polymer brushes.

The swollen thickness can be deduced by computing the normalized first moment of the density profile. These data obtained from neutron reflectivity technique were similar to the values measured by ellipsometry (Figure 1B). There was no hysteresis effect with the pH proving that the brush swelling was completely reversible. The swelling behavior of the pH-responsive brush was between the behavior of a neutral polymer in good solvent and a strong polyelectrolyte brush in osmotic regime, as expected.

We expected the polyampholyte brush to behave as a polyelectrolyte brush at very low and very high pH owing to an excess of charge. It should collapse in the pH range of zero net charge owing to the attraction between oppositely charged units of equal proportion.

The volume fraction profiles of PDMAEMA-*st*-PMAA brush at various pH are shown in Figure 7. The brush was rather stretched at pH 3. It was significantly contracted at pH 7 and the situation was intermediate at pH 10. The chains were not collapsed onto the surface as for a dry brush. The density profile shows a non-monotonic decrease with the distance from the surface. A higher density zone likely due to the attraction between oppositely charged units was observed. This barrier-like zone could hinder the ionization of monomer units close to the surface. It could prevent a collective ionization and reduce the collapse of the polyampholyte brush. In addition, it was found that the amplitude of deformation was higher in the pH range of zero net charge for less dense brushes.

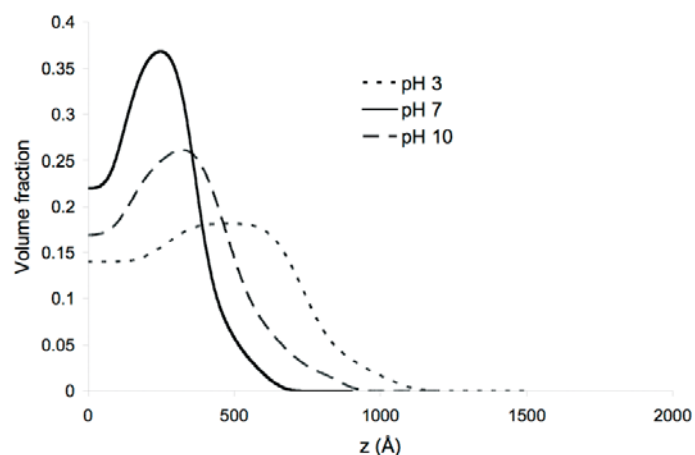


Figure 2. Volume fraction profile of PDMAEMA-*st*-PMAA polyampholyte brush at various pH.

An application of ionic polymer brushes in microfluidic devices is developed. We build microchannels with one-wall covered by the polymer brush. We investigate the electro-osmotic properties by determining the velocity of the flow under an electric field while varying the ionization of the polymer with pH.

We are also interested in the exchange of ions. Scanning Electro Chemical Microscopy (SECM) is used to follow the release of specific ions from the polymer brush. Using selective and sensible microelectrodes, we aim at the detection of protons of the polymer brush.

Neutron reflectivity experiments were performed on EROS with the help of Fabrice Cousin and Alain Menelle.

1 Advincula R. C., Brittain W. J., Caster K. C., R  he J. "Polymer brushes", Wiley-VCH, Weinheim, **2004**.

2 R  he J., Ballauff M., Biesalski M., Dziezok P., Gr  hn F., Johannsmann D., Houben N., Hugenberg N., Konradi R., Minko S., Motornov M., Netz R.R., Schmidt M., Seidel C., Stamm M., Stephan T., Usov D., Zhang H. *Adv. Polym. Sci.* **2004**, *165*, 79-150.

3 Dobrynin A. V., Colby A. H., Rubinstein M. *J. Polym. Sci. Part B, Polym. Phys.* **2004**, *42*, 3513-3538.