

Gradient Mixed Polyelectrolyte Brushes

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INTRODUCTION

Smart responsive materials are of great practical interest for engineering, medical applications, sensors, printing technologies, electronic devices, etc. Mixed polymer brushes constituted from two incompatible polymers grafted to the same substrate represent an example of responsive surfaces. In this case the microphase segregation of the polymers in the mixed brush results in the reversible change of the structure and the surface chemical composition, depending on external environment. Recently¹ we developed a method of the synthesis of mixed polyelectrolyte (PE) brushes constituted of two oppositely charged weak polyelectrolytes. Here we report on the approach which allows us to prepare mixed polyelectrolyte brushes with a 1D gradient of chemical composition. Such materials are promising for microfluidic technologies, for regulating adsorption of proteins, cells, and colloidal/nano particles.

EXPERIMENTAL

Synthesis of mixed polyacrylic acid (PAA) - poly(2-vinylpyridine) (P2VP) brush. The mixed brush was synthesized with a two-step procedure which is described elsewhere¹. Monocarboxyl-terminated poly(*tert*-butyl acrylate) (PBA Mn = 42 000, Mw = 47 000) was selected to be the first grafted polymer. Poly(2-vinylpyridine) (P2VP Mn=39 200, Mw=41 500) was grafted in the second step. The first grafted layer of PBA was prepared via a deposition of the thin polymer film on the Si-wafer preliminary covered with a primary thin layer (1.5 nm) of poly(glycidyl methacrylate)² and following annealing in a vacuum oven at 150 °C for 20 min. Afterward the ungrafted polymer was removed by a Soxhlet extraction in methanol for 3 h. The second polymer P2VP was then grafted using the same procedure, when a thin film of P2VP was spin-coated on top of the PBA brush. The grafting time was 15 h. The ungrafted polymers were removed by Soxhlet extraction in THF. PBA component of the mixed brush was then hydrolyzed by treatment in benzene saturated with p-toluenesulfonic acid monohydrate at 55 °C for 1 h.

Synthesis of gradient mixed PAA – P2VP brush. To fabricate the mixed brush with 1D gradient of the chemical composition the first step of the synthesis described above (grafting of PBA) was performed on a stage with the temperature gradient^{3,4}. The temperature gradient stage is constructed from a stainless steel plate with two opposite sides connected to the heating and cooling elements. The second polymer P2VP was grafted on the top of gradient PBA brush by annealing at 150°C. Afterwards PBA was hydrolyzed.

RESULTS AND DISCUSSIONS

The ellipsometric mapping of the PBA-P2VP gradient brush is shown in Figure 1. The brush composition changes gradually along the sample from the major fraction of P2VP in the layer (left hand side) to the 100% PBA brush (right hand side). The plot of water advanced contact angle vs. the distance from the left hand side edge of the sample presented in terms of the PAA-P2VP mixed brush composition (calculated from the data of Figure 1) is shown in Figure 2. On the left and right edges of the sample one of the polymers is strongly dominate. The brush in this area behaves as a mono component homopolymer brush from either P2VP, or PAA on the left and right hand sides, respectively. At low pH < 3 values the left side is much more hydrophilic than the right side due to protonation of P2VP. At pH > 3 the behavior switches into the inverse case when the left hand side is more hydrophobic than the right hand side. In the middle of the sample we

have the switching behavior demonstrating the switching range correlated with the brush composition. The higher fraction of PAA leads to the lower contact angle at a higher pH and the high fraction of P2VP leads to the lower contact angle at a lower pH.

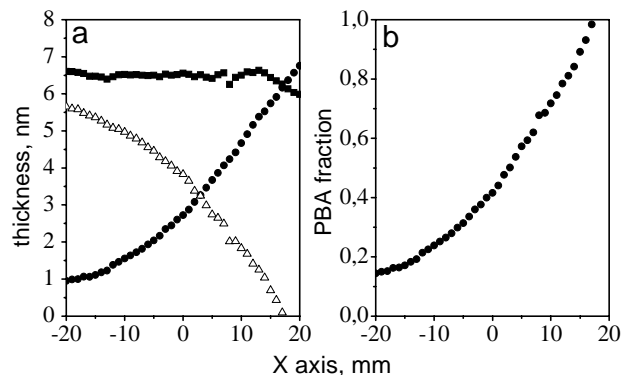


Figure 1. (a) Ellipsometric mapping of PBA-P2VP gradient brush, ■ - total thickness, ● - PBA layer, ▲ - P2VP layer. (b) fraction of PBA versus the point coordinate on the sample.

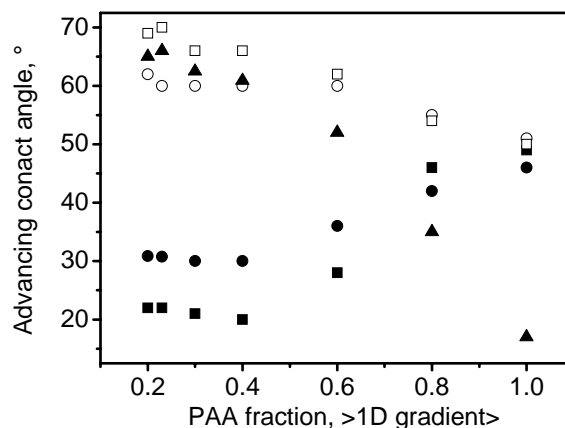


Figure 2. Contact angle at different pH (■ - pH = 2.2, ● - pH = 2.54, ○ - pH=3.24, □ - pH = 4.95, ▲ - pH=9.95) of PAA – P2VP brush vs. composition.

In summary, the 1D gradient mixed PE brush allows for the design of thin films with gradient of wetting behavior, electrostatic and hydrophobic interactions. The gradient can be reversibly switched between opposite sides of the sample. The properties are important for directed self-assembly of proteins and cells upon pH signal.

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REFERENCES

- Houbenov, N.; Minko, S.; Stamm, M. *Macromolecules* **2003**, *36* (16), 5897-5901.
- Iyer K. S.; Zdyrko B.; Malz H.; Pionteck J.; Luzinov I. *Macromolecules* **2003**, *36*(17), 6519-6526.
- Zdyrko, B.; Klep, V.; Luzinov, I.; Minko, S.; Sydorenko, A.; Ionov, L.; Stamm, M. *Polymer Preprints* **2003**, *44*(1), 522- 523.
- Ionov, L.; Zdyrko, B.; Sidorenko A.; Minko, S.; Klep, V.; Luzinov, I.; Stamm, M. *Macromol. Rapid Comm.* submitted.