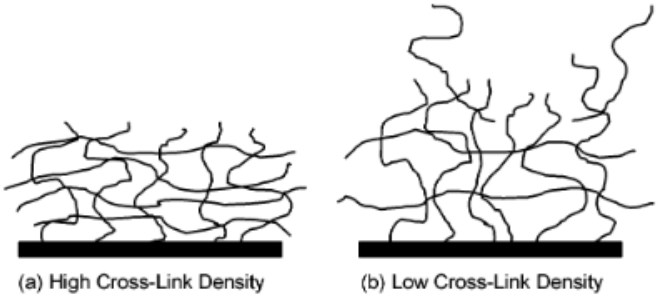
Master semester project

Proposal: Crosslinking of polymer brushes I

Description of the project:



[1]

Surface grafted polymer brushes possess outstanding non-fouling [2] and tribological [3] properties. Their properties derive from their special, via grafting density and solvent controllable conformation. This conformation can vary from mushroom (bad solvent, low grafting density) to stretched brushes (good solvent, high grafting density). Brush-mediated lubrication is a well-known phenomenon that is strongly dependent on the brush-conformation and can therefore be influenced by tuning of the cross-link architecture. Several ways to induce intermolecular cross-links in polymer brushes („brush-gels") have been reported in literature, mainly of covalent nature. Irreversible crosslinking of poly(2-hydroxyethyl methacrylate) (PHEMA) with ethylene glycol-containing bifunctional monomers and the influence of cross-links on the non-fouling properties of brush hydrogels have been reported [4]. Cross-links can also be induced by post-polymerization modifications, as reported for self-crosslinking poly (glycidyl methacrylate) (PGMA) brushes [5]. Covalent cross-links are irreversible while non-covalent cross-links renders gel-brushes reversible and potentially stimuli-responsive. Reversible, photoinduced cross-linking of PDMAEMA has been reported by Dong et al. [6] However, electrochemically driven cross-linking has not been reported yet and shows great potential in the formation of stimuli-responsive surfaces. Ion-ligand interactions can be one way to induce electrochemically switchable cross-links. In this project, a non-covalent, electrochemically driven way to cross-link polymer brushes will be performed. The brushes will be prepared via Surface-initiated atom transfer polymerization (Si-ATRP) of 2-(dimethylamino)ethyl methacrylate (DMAEMA). Characterization of the resulting brushes and brush-gels via ellipsometry, x-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and water contact angle (WCA) measurements will be performed as well as tribological experiments.

References:

1. Toomey R, Freidank D, Jürgen Ruhe. Swelling Behavior of Thin, Surface-Attached Polymer Networks. Macromolecules. 2004;37(3)882-887.

2. Chen H, Zhao C, Zhang M, Chen Q, Ma J, Zheng J. Molecular Understanding and Structural-Based Design of Polyacrylamides and Polyacrylates as Antifouling Materials. Langmuir. 2016;32(14):3315-30.

3. Mocny P, Klok H-A. Tribology of Surface-grafted Polymer Brushes. Molecular Systems Design & Engineering. 2016;1(2):141-54.

4. Dehghani E S, Spencer N D, Ramakrishna S N, and Benetti E M. Crosslinking Polymer Brushes with Ethylene Glycol-Containing Segments: Influence on Physicochemical and Antifouling Properties. Langmuir. 2016; 32(40):10317-10327.

5. Edmondson S, Huck W T S. Quasi-2D Polymer Objects from Patterned, Crosslinked Polymer Brushes. Adv. Mater. 2004;16(5):1327-1331.

6. Dong Z, Mao J, Wang D, Yang M, Ji X. Synthesis and Multi-Stimuli-Responsive Behavior of Poly(*N,N*-dimethylaminoethyl methacrylate) Spherical Brushes under Different Modes of Confinement in Solution. Langmuir. 2015;31 (32):8930–8939.

Contact: Friederike Metze – friederike.metze@epfl.ch