Degrafting of Zwitterionic Poly(2-Methacryloyloxyethyl Phosphorylcholine) Brushes from Silicon Substrates in Aqueous Media

J. N. Bleich[1], H. A. Klok[1]*

[1]Institut des Matériaux et Institut des Sciences et Ingénierie Chimiques, Laboratoire des Polymères, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Surface-initiated controlled radical polymerization (SI-CRP) is a powerful tool to densely graft chain-end tethered polymers usually referred to as polymer brushes from surfaces. This technique allows to control grafting density and chain conformation. Immersed in a good solvent, polymer brushes swell and individual chains are forced into an extended conformation. This extended chain conformation is an important contributor to the non-fouling and low friction properties, which were reported for a number of hydrophilic polymer brushes. While for a long time surface grafted polymer brushes were considered as very stable thin films, an increasing number of papers has been published within the last decade reporting degrafting of hydrophilic brushes in aqueous media. Hence, the stretched chain conformation is not only an important factor for the brush properties, but also influences the chemical reactivity at the substrate-brush interface. A fundamental understanding of this phenomenon, however, is still lacking. In the field of polymer mechanochemistry external force fields are usually applied to alter the polymer reactivity using techniques such as ultrasound sonication, and turbulent or elongational flow fields. Mechanochemical activation by swelling of a polymer brush may offer an alternative tool with the advantage that no external stimulus is needed.

With the objective to investigate the degrafting behavior of hydrophilic polymer brushes systematically, zwitterionic poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) brushes with various grafting densities and polymer molecular weights were prepared and degrafting in aqueous media was monitored. The brushes were grown via surface-initiated atom transfer radical polymerization (ATRP) from silicon substrates modified with a dimethylchlorosilane-based ATRP initiator. In order to vary the grafting density a mixture of the initiator and a corresponding dummy compound lacking the initiating moiety was used resulting in a lower initiator density and accordingly in a lower grafting density after polymerization. After incubation at 37 °C in water, phosphate buffered saline (PBS) and ethanol-water mixtures, the degrafting process was monitored by ellipsometry and apparent initial rate constants were determined from the degrafting profiles assuming pseudo- first-order kinetics. We will describe and discuss the analysis of these apparent rate constants and our attempts to correlate these with the swelling behavior of polymer brush films of different polymer molecular weights and grafting densities in different media.