

# Surface active poly(ethylene glycol) (PEG) catechol derivatives on metal oxide surfaces: influence of pH, pK<sub>a</sub> and isoelectric point on adsorption kinetics and adlayer stability

*B.Malisova*<sup>1</sup>, *K.Gademann*<sup>2</sup>, *S.Zürcher*<sup>1,3</sup>, *S.Tosatti*<sup>1,3</sup>, *M.Textor*<sup>1</sup>

<sup>1</sup> *Laboratory of Surface Science and Technology,*

*Department of Materials, ETH Zürich Switzerland*

<sup>2</sup> *Chemical Synthesis Laboratory, Institute of Chemistry and Chemical Engineering, EPF Lausanne, Switzerland*

<sup>3</sup> *SurfaceSolutionS GmbH, Zürich*

**INTRODUCTION:** A commonly used method to prevent surfaces from non-specific adsorption of proteins relies on chemical immobilization of poly(ethylene glycol) (PEG) e.g. bound via thiol or silane [1]. However most of the proposed techniques showed limitations in terms of substrate choice due to very specific molecule-surface interactions. Within this project a new binding chemistry for PEG based on catechol derivatives was used [2]. Catecholic hydroxy groups presented in these polymers have the special property of being much more acidic than other hydroxy groups e.g. present in alcohols or sugars and therefore are already dissociated at physiological pH [3]. The reactivity of such deprotonated molecules towards metal oxides and other materials is supposed to be higher than the reactivity of protonated molecules. The aim of this work is to achieve a deeper insight and a better understanding of the binding mechanism of different functionalized catechol derivatives on selected metal oxides. For this purpose the influence on the adsorption and stability of the polymers of parameters such as assembling solution pH or acidity (pK<sub>a</sub>) of the catechol protons in relationship with the isoelectric point (IEP) of the substrates, was investigated. These results will provide the basis for a novel surface modification platform, which can be used for the functionalization of biomaterials and biosensors.

**METHODS:** The molecules **1-5** (fig. 1) were investigated in terms of adsorption behavior and subsequent resistance against serum adsorption, using variable angle spectroscopic ellipsometry (VASE) and X-ray photoelectron spectroscopy (XPS). For polymer adsorption standard conditions were defined as follows: 0.1 mg/ml of polymer dissolved in cloud-point buffer, adsorption at 50°C for 4 hours. Adsorptions were done on TiO<sub>2</sub> resp. Nb<sub>2</sub>O<sub>5</sub> and SiO<sub>2</sub> coated silicon wafers.

**RESULTS:** Our results show that the charge of catechol PEG conjugates, together with the pK<sub>a</sub> of the catechol protons and the IEP of the substrates, have an influence on polymer adsorption and stability (fig. 2).

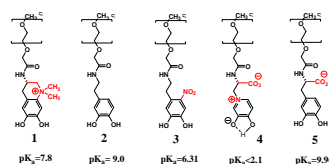


Fig. 1: PEG conjugate derivatives and the pK<sub>a</sub> values of their hydroxy groups.

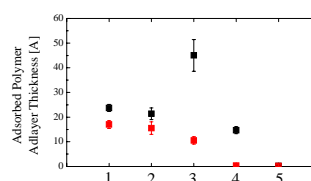


Fig. 2: Adlayer thickness of compounds **1-5** directly after adsorption close to cloud point conditions [4h, 50°C, 1.2 M ionic strength, pH=6.0] (black squares) and after immersion in physiological buffer solution [24 hours, RT, 0.15 M ionic strength, pH=7.4] (red squares).

**DISCUSSION & CONCLUSIONS:** The charge of a binding group combined with the acidity of hydroxy catechol groups effect the adsorption and stability, however it is hard to distinguish between these parameters. We will further try to characterize their contributions together with the influence of other parameters, such as pH.

**REFERENCES:** [1] a) J. Rundqvist, J. H. Hoh, D. B. Havilland, *Langmuir* 2005, 21, 2981. b) A. E. Moser, C. J. Eckhardt, *Thin Solid Films* 2001, 382, 202. [2] a) J. L. Dalsin, L. Lin, S. Tosatti, J. Vörös, M. Textor, P.B. Messersmith, *Langmuir* 2005, 21, 640. b) S. Zuercher, D. Waeckerlin, Y. Bethuel, B. Malisova, M. Textor, S. Tosatti, K. Gademann, *J. Am. Chem. Soc.* 2006, 128, 1064. [3] T. Ishimitsu, S. Hirose, H. Sakurai, *Chemical & Pharmaceutical Bulletin* 1978, 26, 74.