

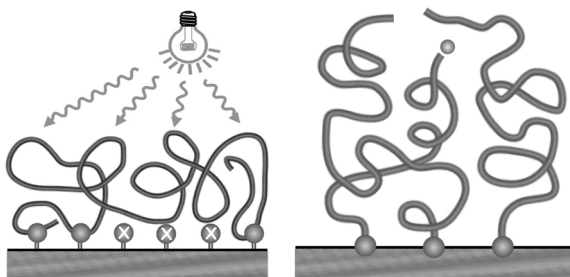
## FUNCTIONAL POLYMERIC COATINGS – FROM POLYMER SYNTHESIS TO HEART VALVE IMPLANTS TO ENDOTRACHEAL TUBES

R.Toomey, H.Murata, B.J.Chang, H.Zhang, R.Konradi, D.Freidank, S.Golze, O.Prucker, H.Klapproth, M.Dahm<sup>1</sup> & [J. Rühe](#)

*Chemistry and Physics of Interfaces, Institute for Microsystems Technology (IMTEK), University of Freiburg, Germany.*

<sup>1</sup>*Department of Cardiothoracic and Vascular Surgery, University Hospital Mainz, Germany*

**INTRODUCTION:** The coating of materials with thin layers of polymers, which have been attached to the surfaces of solid substrates through covalent chemical bonds, represents an attractive strategy to improve the surface properties of materials used in biological or medical applications. While layers, which have been deposited through physical processes only, can be removed more or less rapidly through desorption or through the influence of a competing adsorbent present in the environment, layers, which have been coupled to the surface through a chemical bond exhibit strongly improved long term stability. In the paper several new pathways for the synthesis of surface-attached ultrathin polymer layers will be described. Examples are the generation of polymer brushes through growth polymer molecules at the surface of the substrate *in situ*, the photolinking of molecules to surfaces and the generation of thin surface-attached networks (Fig. 1).



*Fig. 1: Methods for the covalent attachment of polymer layers to solid surfaces a) photolinking b) growth of polymer brushes*

**METHODS:** Details on the generation of surface-attached polymer brushes have been described elsewhere [1] as well as the photochemical attachment of polymers using self-assembled monolayers with benzophenone moieties [2]. The fabrication approach for the generation of surface-attached polymer networks is based on the photocrosslinking of thin copolymer films that contain a photoactive monomer as well as water-soluble comonomers. Irradiation of the film with UV light ( $\lambda = 350$  nm) activates the benzophenone groups, which extract a hydrogen from almost any kind of neighboring aliphatic C-H group, forming a stable C-C bond cross-link, yielding surface-attached networks of hydrogels. After each deposition, UV illumination simultaneously crosslinks the layer and covalently attaches it to the layer beneath it. Multi-

layer structures can then be built up by depositing different copolymer systems on top of one another.

**RESULTS:** The preparation of highly grafted polymer monolayers in which each chain is tethered to the surface by one end is best done by directly growing the chains on the surface from surface-attached initiator monolayers. In our work we use self-assembled monolayers of azo compounds that are initiators for free radical chain polymerizations. Using this approach one can synthesize polymer brushes in which macromolecules with molecular weights up to  $10^7$  g/mol are end-attached to the substrate's surface at a density that corresponds to an average anchor distance of less than 3 nm. Furthermore, the free radical process tolerates the use of a large variety of monomers and comonomer mixtures which makes it possible to incorporate chemical and biochemical functionalities and to tailor the properties of the resulting layers in terms of their chemical composition, hydrophilicity, surface free energy, wettability as well as other physical properties. Here we describe one system in which these so-called polymer brushes have been used as the basis for a DNA chip. We show that the attachment of the DNA probes to the polymer chains of a suitably engineered brush instead of direct surface attachment leads to chips that show a significantly improved sensitivity and selectivity.

In a second approach (Fig. 2) towards surface-attached polymer monolayers we use monolayers that carry photoreactive groups such as the benzophenone unit for the attachment of pre-fabricated polymers [2]. Even though the thickness of the resulting layers stays in general lower than that prepared via surface-initiated polymerization this photochemical approach is often advantageous because the particulars of the photochemistry of benzophenone allows for the attachment of almost any polymer. Hence, off-the-shelf polymers can be used to create these layers as well as polymers that contain specific groups to serve a certain purpose. To give one example, we have used this approach to create a wide variety of polymer monolayers that were subsequently tested for ability to promote the growth of endothelial cells on substrates. As a result of this study we identified a number of suitable candidates of polymers that we now use in a slightly different approach for the modification of porcine heartvalve implants. The layers mask the toxic groups generated at the surface of the bioimplants

during a glutar aldehyde treatment that is needed to improve the mechanical stability of these xenografts [3].

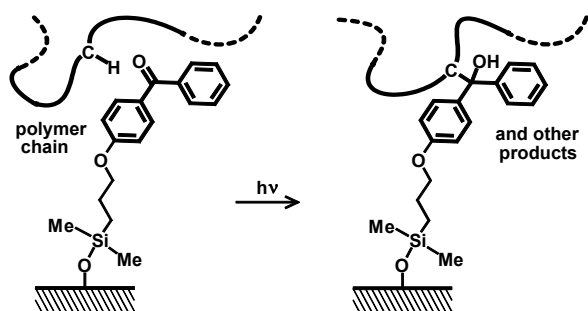


Fig. 2: Schematic illustration of the photochemical process used for the covalent attachment of polymers to solid surfaces.

For the generation of layers of thicknesses adjustable from the nanometer up to the millimeter scale we have chosen another photochemical approach that yields surface-attached polymer networks and that utilizes polymers that carry photoreactive units. If polymeric or biologic substrates are used both the crosslinking and the surface-attachment occur simultaneously. Through the choice of appropriate reaction conditions and (co)polymer composition surfaces with precisely tailored properties can be obtained. Especially systems in which the polymers carry functional groups, which can be used in sensor applications, can be prepared via this method easily.

We show that these surface-attached networks provide a convenient scaffold to host a number of other functionalities. Secondly, they can undergo substantial swelling and contraction in response to a varying environment, making them excellent candidates for “smart” surfaces that respond to specific stimuli. In order to understand and control such stimuli based on swelling, we have studied the swelling behavior of such layers in contact with aqueous solutions with multiple-angle null ellipsometry, the latter being an analytical technique

that yields information about the thickness and refractive index profile of the swollen layers.

In order to demonstrate the versatility of the system we will show how such layers can be used as barrier layers on the balloons of endotracheal tubes that keep body liquids from entering into the lungs of ventilated patients. This problem is often encountered in intensive care units at hospitals and in many cases these patients die from pneumonia caused by these liquids. In our system a water-swappable surface-attached polymer network sufficiently seals off all leaks between the tube and the trachea.

**DISCUSSION & CONCLUSIONS:** The novel methods developed for the coating of organic, inorganic and biological substrates show great perspectives, especially for biological and biomedical applications. The firm covalent bond between the polymer chains and the substrates provide the stability of the coatings that is needed for such systems. Using general and well-established procedures for polymer synthesis it is possible to engineer layers that serve several purposes at the same time such as the swellability of the layers and the chemical nature and number of functional groups. In other words, these chemistries allow a precise tailoring of surface-properties both in a homogeneous as well as in a spatially defined way (surface microstructuring).

**REFERENCES:** <sup>1</sup> J. Ruhe and W. Knoll, *Functional Polymer Brushes*, in *Supramolecular Polymers*, A. Cifferri (ed.), Marcel Dekker, New York, 565-613 (2000), <sup>2</sup> O. Prucker, C. Naumann, J. Ruhe, C. Frank and W. Knoll; *J.Am.Chem.Soc.* **121**; 8766-8770 (1999), <sup>3</sup> B.-J. Chang, O. Prucker; E. Groh; A. Wallrath; M. Dahm, J. Ruhe; *Coll. Surf. A*, **198**, 519-526 (2002).

**ACKNOWLEDGEMENTS:** The authors are indebted to the German Research Council (DFG, SFB 428), Tracoe GmbH and Genescan AG for financial support of this work.