Abstract Number: li0041

Surface Control Using Polymer Brushes Produced by Controlled Radical Polymerization

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Beamline(s): U7A

Introduction: The control of surface properties by polymer brushes is central to many applications ranging from coatings to biotechnology and advanced microelectronics. Traditionally, polymer brushes consist of block copolymers where one block is strongly adsorbed on a surface with the other block forming the brush layer. However, desorption of the brush can subsequently occur. Nitroxide-mediated controlled radical polymerization represents a promising synthetic approach to the preparation of a wide variety of polymeric materials, including polymer brushes. An increasing amount of interest has been devoted to the covalent attachment of polymer chains to surfaces. This can be achieved by grafting polymer brushes from a surface by surface initiated polymerization.

Methods and Materials: A surface attached living radical initiator, such as 1–phenyl–1–(2, 2, 6, 6–tetramethyl–1–piperidinyloxy) ethane, was used to grow fluorinated polystyrene-based polymers (Figure 1) from a silicon oxide surface. X-ray photoelectron spectroscopy (XPS) analysis proved the polymerization process to be living at the surface.

Results: Studies by near-edge x-ray adsorption fine structure (NEXAFS) showed that the surface orientation of the fluorinated side chains depended upon the thickness of the brush, with thicker brushes having more oriented side chains. The brush-modified fluorinated surfaces were highly hydrophobic and thermally stable.

Conclusions: Surface-grafted fluorinated polymer brushes 50 nm thick were successfully synthesized and proven to be oriented at the surface with a surface helix order parameter $S_{C\text{-}F\ helix}$ of about 0.17. The encountered surface orientation correlated with high hydrophobicity, as well as with stability of the surface towards reconstruction upon exposure to water.

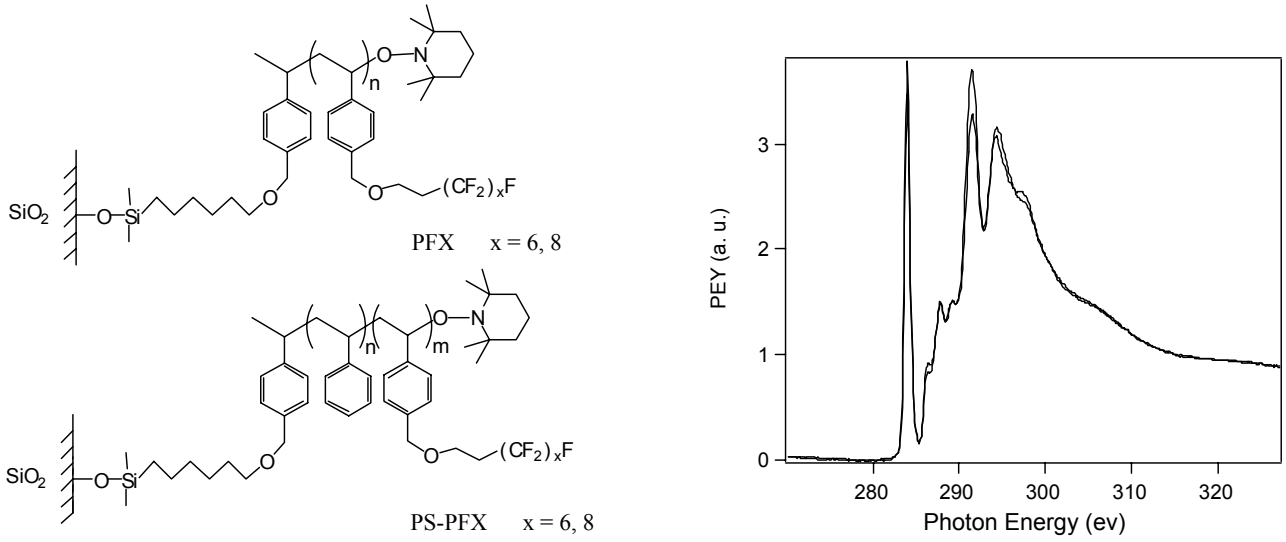

Figure 1. Chemical structures of fluorinated polymer brushes and NEXAFS spectra at the C-edge for θ between beam polarization vector and surface normal equal to 20° and 90° for a brush PS-PF8 with a thickness of 50 nm.