

Switchable Surfaces: Electrochemically Control of Polymers at Nanometer Level

Yiwen Pei,^{†,‡} Jadranka Travas-Sejdic,^{†,‡} David E. Williams^{†,‡}

[†]Polymer Electronic Research Centre, School of Chemical Sciences, University of Auckland, Private Bag 92019, Auckland 1142, New Zealand

[‡]MacDiarmid Institute for Advanced Materials and Nanotechnology, Wellington, New Zealand

We demonstrate the reversible electrochemical switching of conformation of surface-grafted polymer brushes, by grafting environmentally sensitive polymer brushes from an electrochemically active conducting polymer (ECP).^{1,2} We grafted zwitterionic betaine homopolymer of (3-methacryloylamido)propyl-N,N'-dimethyl(3-sulfopropyl)-ammonium hydroxide (MPDSAH), block copolymer of MPDSAH and methyl methacrylate (MMA), and a near-neutral random copolymer of MMA, methacryloxyethyltrimethylammonium chloride (METAC), and 3-sulfopropyl methacrylate potassium salt (SPMA) from an initiator, surface-coupled to a poly(pyrrole-*co*-pyrrolyl butyric acid) film by atom transfer radical polymerization (ATRP). The changes in ionic solution composition in the surface layer, resulting from oxidation and reduction of the ECP, trigger a switch in conformation of the surface-bound polymer brushes, demonstrated here by electrochemical impedance spectroscopy (EIS) and in a change of wettability. For homopolymer and block copolymer brush-grafted ECP films, the switch is dependent upon temperature in a way that is analogous to the temperature-dependent solubility and aggregation of similar betaine polymers in aqueous solution but has a quite different dependence on salt concentration in solution. The switch is fully reversible and reproducible. We interpret the switching behavior in terms of a transition to a "supercollapsed" state on the surface that is controlled by ions that balance the charge state of the ECP and are adsorbed to the opposite charges of the zwitterionic graft, close to the graft-ECP interface. The behavior is significantly modified by hydrophobic interactions of the block copolymer graft. The statistical polyampholyte differs from the polyzwitterion in that it is not strictly neutral and the charges do not have a defined spatial relationship to one another. We speculate that the synergistic combination of properties embodied in these "smart" materials may find applications in electrochemical control of surface wetting and in the interaction with biomolecules and living cells.³

Reference:

- 1) Pei, Y.; Travas-Sejdic, J.; Williams, D. E., *Langmuir* 2012, 28, 13241-13248.
- 2) Pei, Y.; Travas-Sejdic, J.; Williams, D. E., *Langmuir* 2012, 28, 8072-8083.
- 3) Strover, L.; Roux, C.; Malmström, J.; Pei, Y.; Williams, D. E.; Travas-Sejdic, J., *Synthetic Metals* 2012, 162, 381-390.