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Instability of Surface-initiated ATRP Polyelectrolyte Brushes in Aqueous Environments CASEY GALVIN, ERICH BAIN, Department of Chemical Engineering, North Carolina State University, Raleigh, NC, EVREN OZCAM, Department of Chemical Engineering, University of California - Berkeley, Berkeley, CA, ADAM HENKE, Department of Chemistry, Columbia University, New York, NY, JIRI SROGL, Institute of Chemistry and Biochemistry, Prague, Czech Republic, JAN GENZER, Department of Chemical Engineering, North Carolina State University, Raleigh, NC — Surface-bound macromolecules have been produced using a number of polymerization schemes, including free-radical polymerization (FRP), reversible addition-fragmentation chain transfer polymerization (RAFT), and atom transfer radical polymerization (ATRP). In order to prove useful in any technology, the tethered polymer chains must remain stable in a variety of environments over relatively long timescales. We have investigated the dependence of the pH and ionic strength of aqueous solutions on the stability of surface-bound polyelectrolyte chains (strong and weak) with varying molecular weights and grafting densities. Our findings suggest that the ester bond in the most common form of ATRP surface initiator (BMPUS) will hydrolyze over a broad pH range, leading to chain degrafting. We further compare the stability of a BMPUS derivative which has had the ester bond replaced with an amide bond, as well as a free-radical initiator containing only aliphatic carbons. Results related to the effect of chain tension on brush stability will also be presented. Finally, we discuss the likely mechanism of degrafting, and ways in which to improve stability.

> Casey Galvin Department of Chemical Engineering, North Carolina State University, Raleigh, NC

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