471g pH-Responsive Polymer Films and Membrane Skins

Dongshun Bai, Brian M. Habersberger, Steven Elliott, and Kane G. Jennings

Abstract: We have engineered a new class of pH-responsive polymer films on gold surfaces by first developing a controlled, surface-catalyzed polymerization to prepare a copolymer film consistent with poly(methylene-co-ethyl acetate) and subsequently hydrolyzing the ester side chains to carboxylic acids (denoted at PM-CO2H). When the acid groups become deprotonated or charged, the water solubility of the acid functional groups increases by ~ 4 orders of magnitude to greatly alter the film properties. The carboxylic acid content within the copolymer film can be adjusted by changing the monomer concentration ratio used in the polymerization process and varying the hydrolysis time. We have designed PM-CO2H films to consist predominately (>95%) of polymethylene (PM) so that the film is hydrophobic in the uncharged state, and thereby exhibits an extremely large pH-induced response in film capacitance that is kinetically rapid and reversible. The effects of polymer composition and thickness on pH response were investigated by electrochemical impedance spectroscopy (EIS), reflectance-absorption infrared spectroscopy, and spectroscopic ellipsometry. At a 1% molar acid content, the copolymer film exhibits a five order of magnitude change in its resistance to aqueous transport over a very narrow pH range. The pKa of the film is strongly dependent on the acid composition, with a 1% acid film exhibiting an elevated pKa of ~8 and a 3% acid film showing a pKa of ~5. Thus, based on acid content and film thickness, the range and rate of the pH-induced response can be tailored. We have recently developed a method to grow these super-responsive films as ultrathin skins on nanoporous membranes to control the passage of ions in a pH-specific manner.