388b Photofunctionalization of Polymer Microfluidic Devices for Mass Spectrometry

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Introduction: Typical substrates for microchip devices coupled to mass spectrometry include glass, quartz and silicon. However, plastics have recently been used due to their ease of fabrication and low cost. In this work, we have been investigating surface modifications in these devices and determining their compatibility with mass spectrometry. In particular, we have utilized nitrine chemistry to chemically modify the surface of various polymeric devices. We have also used this form of modification to allow for enzyme immobilization and improved electoosmotic flow (EOF). Our results demonstrate that photofunctionalization provides a simple, spatially controlled approach to microchip functionalization, and these chips facilitate the investigation of on-chip processing and subsequent mass spectral characterization of proteins. Methods: Photofunctionalization for improved EOF polymer substrates were modified to increase surface charge using (4-Azido-3,5,6-trifluoror-1,2-phenylene)bis (N,N,N-trimethylmethanminium compound. Photofunctionalization for Enzyme ImmobilizationPolymer substrates were modified for immobilization of trypsin using 4-Azidotetrafluorobenzaldehyde. In all cases a thin film or drop of 0.1 % azide in methanol was applied to the substrates. After drying with nitrogen, the substrates were irradiated in a homemade UV box with a medium pressure, quartz, mercury-vapor lamp housed in Pyrex immersion well. Preliminary Data: Herein we report a method, which uses perfluorinated aromatic azides to topochemically modify the surface of a polymer inside a microfluidic network. We demonstrate the chemical functional group of the polymer can be tailored to the desired application. Fluorinated azides were synthesized according to literature. Comparison of the surface topography of the pristine polymer to the polymer surface modified using azide1 provides a quantitative tool for assessing the effects of surface modification. Atomic force microscopy images after photofunctionalization showed a 1.5 fold increase in surface roughness (rms roughness = 0.68 and R = 1.021) as compared to pristine polymethymethacrylate (PMMA). Sessile contact angle measurements were obtained for the pristine PMMA and PMMA modified with azide. The average water contact angle for pristine PMMA was found to be 69 ± 2°, which correlates well with the literature value of 67° for a highly ordered methyl ester-terminated monolayer. PMMA surfaces modified using azide1 resulted in a contact angle of 42 ± 2°, a value consistent for self-assembled monolayers terminated with hydrophilic functional groups. Reflective absorbance infrared spectroscopy was also employed and allowed for band assignments to be made for pristine, azide1 coated and azide reacted PMMA surfaces. To demonstrate that these chemical modifications could be patterned on a microfluidic device, azide2 was synthesized and grafted to various polymer surfaces. Trypsin enzyme was covalently bound to the aldehyde moiety of azide. A photolithographic mask was used to spatially control the modification of the polymer surface. Once the enzyme was immobilized, 5-(aminoacetamido)fluorescein dye was attached to the free carboxyl groups of the enzyme and analyzed using confocal microscopy. On chip digestions of myoglobin were analyzed using MALDI-TOF. In this presentation, we will discuss the novelty of using photofunctionalization as a means to spatially control chemical modifications and the applicability with mass spectrometry.