Surface Modification of Plastics: Polymer Surface Chemistry for Microanalytical Devices

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The use of polymeric materials as substrates for the construction of microanalytical devices¹ has become important due to the fact that such materials can be readily formed into functional microdevices using molding, embossing, and machining techniques.^{2,3} A key issue in the development and use of polymer-based microanalytical devices is the ability to control and manipulate the surface chemistry of the plastic at hand so as to render the surface amenable to immobilization of molecules, which will in turn impart new, desired characteristics to the device.⁴

We discuss here the surface modification of a variety of polymers currently being investigated for use in the construction of microanalytical devices, such as capillary electrophoresis "chips", DNA arrays, enzyme digestion chambers, and analyte preconcentration assemblies. Poly(methyl methacrylate), PMMA, surfaces can be derivatized to yield amine termini.⁴⁻⁶ Further derivatization of the amine-terminated PMMA leads to surfaces that can be hydrophobic (for use in capillary electrochromatography), are patterned with chemical functionalities (for use in array construction), or are covered with stimuli-responsive materials (analyte preconcentration). Similar protocols can be used to modify the surface of poly(carbonate), PC. In particular, sulfonation and amination of PC is readily achieved through the use of solution and gas-phase methods.

Upon amination of PMMA surfaces, a variety of



Figure 1. Reflection-absorption IR spectra (Upper) and contact angle measurements (Lower) of AT- and C18-PMMA.

functionaities can be attached to the aamine-terminated PMMA (AT-PMMA).⁴ For example, hydrophobic materials appropriate for use as stationary phases in electrochromatography applications can be made. As seen in Figure 1, the surface of AT-PMMA can be modified such that a well-ordered octadecyl (C18) layer is present. The dramatic difference in water contact angle observed is due to the hydrophobic C18 layer. In addition, the order of the C18 layer (crystallinity of alkane chains) is reflected by the presence of progression bands

(Tx and Wx modes). We will discuss the use of such C18-PMMA surfaces in microdevice separation of biological species. The AT-PMMA surfaces can also be elaborated with stimuli-responsive materials so as to tune the relative hydrophobicity of the surface and thus the retention of analytes.

Poly(carbonate) surfaces can also be nondestructively modified using both solution- and gas-phase reactions. For example, sulfonation of PC microchannels using SO₃ gas leads to changes in the electroosmotic flow (EOF) as a function of pH that are quite different than that



Figure 2. Upper – Sulfonation of PC. Lower – EOF measured by current monitoring method at 150 V cm⁻¹ in a hot embossed 4 cm long, 30 mm wide and 60 mm deep polycarbonate channel before and after sulfonation.

for native PC, Figure 2. The larger EOF values at low pH (vs. the native PC) are the result of the anionic sulfonate groups on the PC surface.

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