

8. SUPPORTING INFORMATION

Plasma polymerization of furfuryl methacrylate (Aldrich, 97% purity, further purified using several freeze-pump-thaw cycles) was carried out in a cylindrical glass reactor connected via a liquid nitrogen cold trap to a mechanical rotary pump (base pressure = 1×10^{-3} mbar, leak rate = 1.2×10^{-9} mol s^{-1}). A copper coil wrapped around the reactor was coupled to a 13.56 MHz radio frequency power supply through an LC matching network. Prior to each experiment the chamber was cleaned using a 50 W air plasma at 0.2 mbar pressure. Monomer was then introduced via a fine control needle valve at a pressure of 0.2 mbar and 1.5×10^{-7} mol s^{-1} flow rate, followed by film deposition for 30 min. In the case of pulsed plasma polymerization a signal generator was used to trigger the RF power supply, and the pulse shape was monitored with an oscilloscope. Typical film thicknesses employed in this study were 20-100 nm.

Subsequent Diels-Alder surface reaction with maleic anhydride (Aldrich, 99%) was carried out by immersing the coated glass slides in a 1% w/v solution of maleic anhydride in toluene (Fisher, 99.8%) for 18 hours. The substrate was then rinsed several times in toluene prior to analysis.

X-ray photoelectron spectroscopy (XPS) analysis was performed using a Kratos ES300 spectrometer equipped with a Mg $K\alpha$ X-ray source and an hemispherical analyser operating in fixed retard ratio mode (22:1). Photoelectrons were collected at a take-off angle of 30° from the substrate normal. Surface elemental composition was calculated using sensitivity factors derived from chemical standards, C(1s) : O(1s) equals 1.00 : 0.57. All binding energies were referenced to the C(1s) hydrocarbon peak at 285.0 eV.

Transmission infrared spectra of plasma polymer films deposited onto KBr plates were acquired on a Perkin Elmer Spectrum One FTIR instrument equipped with a DTGS detector operating at a resolution of 4 cm^{-1} and averaged over 16 scans. A reference spectrum of the monomer was acquired by placing a drop of liquid between two KBr plates, whilst a diamond ATR accessory (Specac) was employed for maleic anhydride. The Diels-Alder reaction was monitored with a grazing angle reflection accessory (Specac) fitted to the infrared spectrometer. In this case, a silicon wafer was employed as the substrate in combination with a liquid nitrogen cooled MCT detector.