

**MATRIX ASSISTED LASER DESORPTION IONIZATION MASS SPECTROMETRY OF
POLYPYRROLE.**

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Conducting polymers have a range of potential applications such as biosensors, chemical sensors, electrochemical catalysts, solar cells, electronics components, corrosion protection, separation membranes, batteries, electrochromics, actuators and anti-static coatings. Many of these applications rely on the polymer retaining its electroactivity and/or conductivity under an applied potential in environments containing oxygen and water. Under such conditions the polymer is often degraded irreversibly or "overoxidised". Overoxidised polypyrrole exhibits losses of conductivity, charge storage ability, electrochromism, electroactivity, conjugation, mechanical properties and adhesion to the substrate. In this work, polypyrrole samples including newly synthesised, overoxidised and samples from which the counter-ion has been removed have been examined by matrix assisted laser desorption mass spectrometry (MALDI-MS). This is a relatively novel application of MALDI which has not been used to any great extent for the structural analysis of conducting polymers.

Polypyrrole was "grown" from the pyrrole monomer by electrochemical oxidation from aqueous solution, the film having a thickness of approximately 4.5 μm . The counterion (dopant) employed was para-toluene sulphonic acid (pTS). The resulting film was subjected to three different overoxidising conditions or base de-doping with 0.1 M sodium hydroxide.

MALDI-MS was found to be useful in determining the numbers and location of imine-nitrogens and their role in overoxidation. The results indicate that overoxidation of the polypyrrole proceeds via the formation of adjacent imine-nitrogen groups over six monomer units in the polymer, this encouraging substitution one oxygen per hexamer. Further overoxidation results in the breaking of chains to form both oxygen containing and oxygen free pyrrole dimers, trimers and tetramers. Analysis of film subjected to base de-doping resulted in a relatively clean spectrum with no peaks due to pTS adducts and yielded only the polypyrrole hexamer with or without oxygen substitution.

When subjected to MALDI-MS analysis an as-grown film showed no peaks that could be attributed to molecular ions of polypyrrole. This indicated that the polymer was either sufficiently stable such that laser excitation was unable to ionise complete molecules or that molecules were desorbed but not ionised and hence not detected.

It appears that the polymer itself acts as an energy absorbing and dispersing matrix in place of the more common organic acid groups.