Secrets of plasma deposited polyoxazoline functionality lies in the plasma phase

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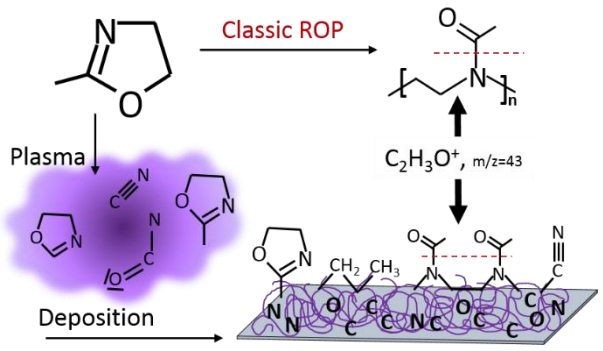
Plasma deposited Polyoxazoline thin films share many valuable properties with polyoxazoline prepared via conventional organic chemistry: they are biocompatible, non cytotoxic and low fouling.[1] What is more, they bind biomolecules covalently, support cell adhesion, and are generated in a solvent free, single step process.[2] Here we show that the secret for plasma deposited polyoxazolines' unique set of properties lies in both the chemical fragmentation processes occurring in the plasma phase itself *and* the recombination events subsequently occurring at the plasma-activated surface.[3]

Both the plasma phase and the polymeric films were analysed via spectroscopic techniques to established the mechanisms responsible for the formation of the reactive functional group setting plasma deposited polyoxazoline apart from their ring opening polymerized counterparts.

In situ plasma mass spectroscopy was used to elucidate the complex composition of the oxazoline plasma phase at different nominal power, ranging from 2 to 50W. It confirmed the stability of the un-opened monomer, but also revealed the formation of nitrile, isocyanate, and imine species. Gauged against those of the post-plasma XPS and ToF SIMS surface characterization data, these findings showed that reactive functional groups were plasma generated, while structures resembling those of conventional polyoxazoline arise from surface rearrangements.



Scheme 1. Plasma deposition of methyl oxazoline lead to the formation of films which in part share the polyamide structure of polyoxazoline synthesized via ring opening polymerisation (ROP) but also include plasma induced functionality such as nitrile and intact oxazoline rings, and hydrocarbons formed by rearrangement processes at the plasma activated surface

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[2] M. N. Macgregor-Ramiasa, A. A. Cavallaro, K. Vasilev, *Journal of Materials Chemistry B* **2015**, *3*, 6327-6337.

[3] M. N. Macgregor, A. Michelmore, H. Safizadeh Shirazi, J. Whittle, K. Vasilev, *Chem. Mater.* **2017**, *29*, 8047-8051.