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### Biodegradable drug delivery vehicles produced by controlled ring-opening polymerizations

Mthulisi Khuphe and Paul D Thornton University of Leeds, UK

Polymers are often employed as drug carriers to provide protection to encapsulated therapeutic molecules against premature metabolism and clearance *in vivo*. Proteolytic enzymes may be exploited to trigger the swelling and/or degradation of (poly) peptide-containing carrier vehicles, while reduced environmental pH may be exploited to trigger the hydrolysis of ester linkages in (poly) ester-containing carrier vehicles, resulting in controlled payload release, on-demand. We report the creation of several biodegradable polymeric nanomaterials from N-carboxyanhydride ring-opening polymerization (NCA ROP) and O-carboxyanhydride ring-opening polymerization (OCA ROP). A range of delivery vehicles, including nanoparticles, chemical hydrogels and vegetable oil-based organogels have been created that selectively release encapsulated payload molecules upon interaction with acidic environmental pH and/or enzymes that are over-expressed at particular disease sites.

cp11mk@leeds.ac.uk

#### Tuning the physicochemical properties of polysaccharides with microporous and mesoporous structure

Lee D Wilson<sup>1</sup>, Mohamed H Mohamed<sup>1</sup> and John V Headley<sup>2</sup>

<sup>1</sup>University of Saskatchewan, Canada

<sup>2</sup>Water Science and Technology Directorate- Environment Canada, Canada

Polyurethanes (PUs) were prepared by cross-linking β-cyclodextrin (β-CD) with two different types of diisocyanates, respectively. Materials with diverse structural and textural properties were obtained by varying the rate of diisocyanate addition: rapid (R) or drop-wise (D; 0.1 mL/min). Characterization of the structural and textural properties was investigated by spectroscopic (1H NMR in solution, solid state  $^{13}$ C CP-MAS solids NMR, dynamic light scattering, UV-vis, and IR), thermogravimetric analysis, powder x-ray diffraction, and scanning electron microscopy. The accessibility of the β-CD inclusion sites of the polymers was independently evaluated using an equilibrium dye adsorption method at equilibrium and in parallel with a kinetic dye-based uptake method. The characterization methods strongly support that drop-wise additions affords materials with greater cross-linking relative to the rapid addition method. Herein, we report the first example of a cross-linked polyurethane containing β-CD with tunable microporous and mesoporous structure and physicochemical properties according to the mode of cross-linker addition (R versus D) to control the reaction conditions shown in Scheme 1.

lee.wilson@usask.ca