Polymers are produced on a multi-million tonne scale per annum and are a high priority to move from non-sustainable petroleum based to sustainably based starting materials. Itaconic acid 1 and hydroxymethylfuran 2 are both available by fermentation or pyrolysis of sugars. We have recently shown that treatment of the cyclic anhydride of 1 with 2 led to oxanorbornene derivative 3 via a tandem ring-opening Diels-Alder sequence. Subsequent esterification of 3 with methanol (sustainably available by hydrogenation of carbon dioxide) gave monomer 4 which we have shown will undergo ring-opening metathesis polymerisation (ROMP) when treated with Grubbs second generation catalyst (Green Chemistry 2016, 18, 3945–3948).

Unfortunately, the ROMP homopolymer of 4 was found to be rather insoluble which has prevented its full characterisation, though copolymers with other norbornene derivatives could be prepared and characterised. Therefore, the first aim of this project is to replace the methyl ester in monomer 4 with esters derived from other sustainably sourced alcohols to obtain more soluble polymers. Examples of suitable alcohols are shown in structures 5-9. The resulting polymers will be characterised by GPC, Maldi-MS, TGA/DSC and IR and NMR studies will be used to demonstrate the living nature of the polymerisation and to investigate the regiochemistry and tacticity associated with the polymerisation. The synthesis of amides rather than esters will also be investigated.

Monomer 4 (and related esters / amides; and the hydrogenated versions of 4) could also undergo polymerisation by ring-opening polymerisation (ROP) of the lactone ring. The lactone ring in compound 4 is rather strained by being fused to the norbornene unit and so will be more prone than normal to undergo ROP. This type of polymerisation can be initiated by a wide range of catalysts including: transition metal alkoxides, lanthanide salts and nucleophilic organocatalysts. Each of these will be investigated. Monomer 4 should also be readily epoxidised to give monomer 10, which will be a substrate for epoxide ROP to give a polyether or epoxide ROP copolymerisation with CO₂ (to give a polycarbonate) or an anhydride (to give a polyester), thus allowing a wide variety of polymers to be prepared from a common biomass derived intermediate.

Application closing date: March 2017
Interview date: April 2017
Funding source: student to secure own funding
Eligibility: UK / EU / Overseas

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