Dynamic Kinetic Resolution of *rac*-manOCA

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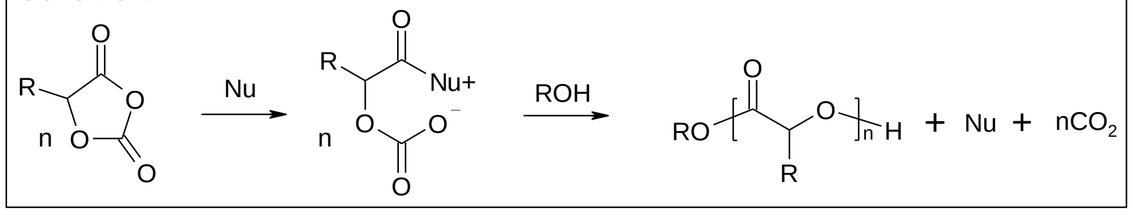
1. Background Information

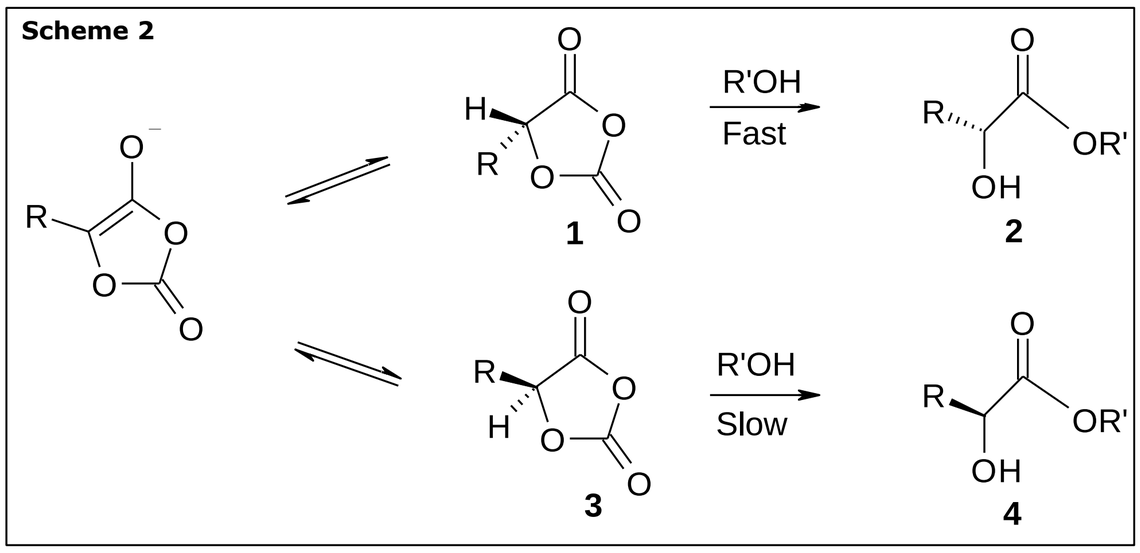
Polyesters are currently at the forefront of resorbable biomaterial technology.

Scheme 1



Scheme 1 shows the ring-opening polymerisation (ROP) of a generic *O*-carboxyanhydride (OCA) to form a polyester. A catalyst has been represented by Nu, since it is acting as a nucleophile, attacking a positively charged area of the molecule.

Scheme 2



Scheme 2 shows the reaction scheme for a dynamic kinetic resolution (DKR) of a generic OCA. **1** and **3** are known as enantiomers, molecules which are mirror images of one another. It is found that if the catalyst $(DHQD)_2AQN$ is added to a solution containing only **1**, then the catalyst acts as a base, removing the O**C**A's acidic hydrogen atom and converting 50% of **1** to **3** – this results in a mixture of equal parts **1** a**n**d **3,** a racemic mixture. The catalyst also acts t**o** ring-open **1** and **3**, converting them to **2** and **4** respectively. It has a preference for the co**n**versi**o**n of **1** to **2**, which is why this step is much faster than **3** to **4.** As the amount of **1** begins to decrease relative to the amount of **3**, some of **3** is converted to **1** so that the 50:50 composition of the racemic mixture is maintained. This means that the final reaction mixture should contain mostly **2** with negligible amounts of **4**. This is a dynamic kinetic resolution. In a kinetic resolution, the conversion **1** to **3** does not happen as the hydrogen atom is not acidic enough. This would mean an initial reaction mixture composed of 50% **2** and 50% **3**. It should be noted that when DMAP is used as a catalyst, the relative rates of steps **1** to **2** and **3** to **4** are not yet known.

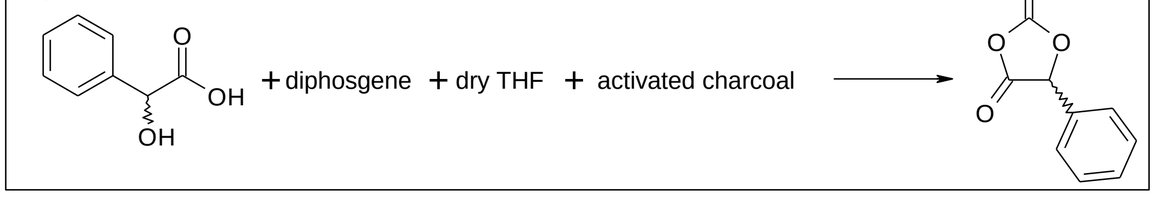
2. Concept

Combining the ideas of ROP and DKR, this project aims to enable some level of stereocontrol in the polymerisation of *rac*-ManOCA, an OCA where R is a benzyl group.

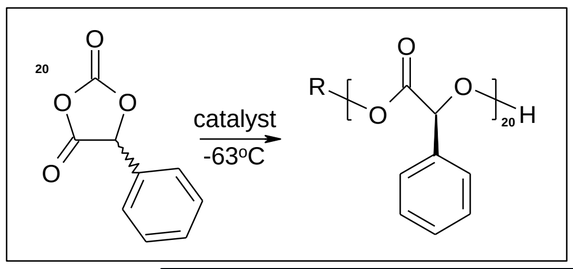
3. Results

Monomer Synthesis

Synthesis of *rac*-manOCA



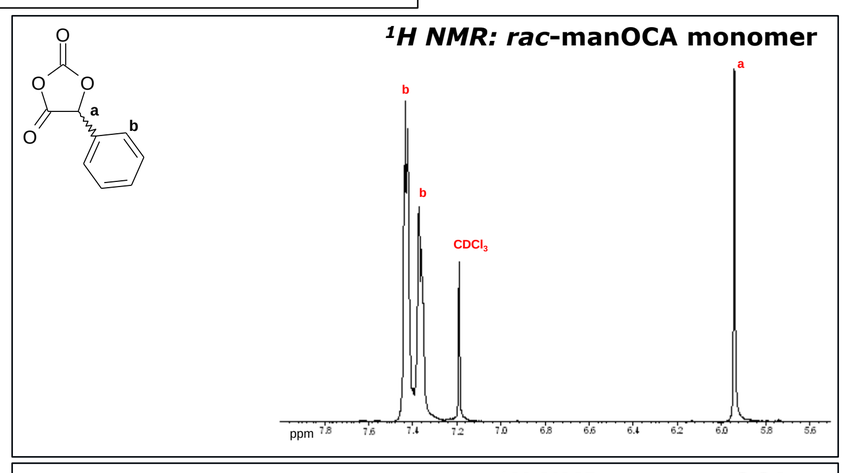
Ring-Opening Polymerisation

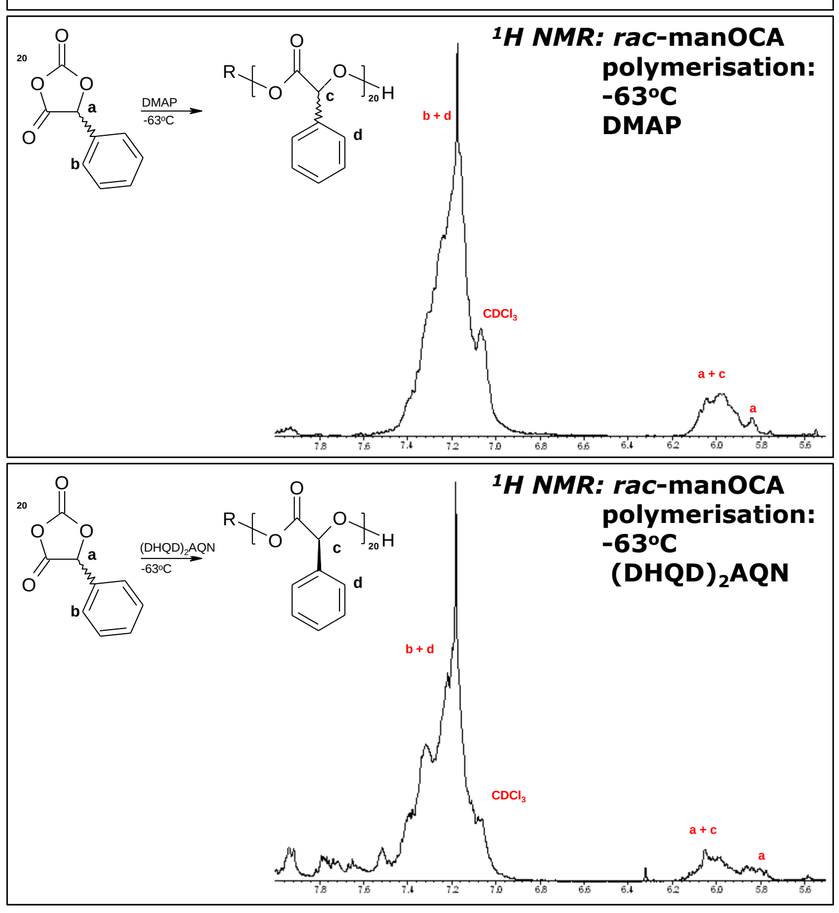


GPC results provided proof of the polymerisation

$M_n = 989$

PDI = 1.05





4.Conclusion

This is the first report of the ring-opening polymerisation of *rac*-manOCA. Stereocontrol results were ambiguous. Further work will proceed to confirm the dynamic kinetic resolution.

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