

Synthesis and ring-opening polymerization of cyclic diesters derived from malic acid.

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The ring-opening polymerization (ROP) of cyclic esters provides a simple and versatile route to the controlled synthesis of poly(ester)s. The process can be mediated by a variety of promoters including enzymes, metal complexes and organic catalysts providing excellent control over polymer chain length, polydispersity and end group functionality.¹

Research in this area has, in part, been driven by the desire to synthesize polymers from renewable resources. Indeed, poly(lactic acid), PLA derived from the ROP of lactide, the cyclic diester of lactic acid, is one of the most well known examples of this type of polymer and is now produced commercially.² To date, however, the use of polymers from renewable resources in advanced applications and nanoscale assemblies has been limited by the range of available functional monomers.

There have been several reports of functional δ -valerolactone and ϵ -caprolactone monomers,³ however, to date there are relatively few reports of cyclic diesters. These cyclic diester monomers offer the potential advantages of producing more highly functional and stereoregular polymers compared with other lactone monomers. Some recent studies have shown efficient methods of functional cyclic diester synthesis from amino acids.^{4,5} While efficient, the protected amino acids required are quite costly and their syntheses often require several steps. An attractive alternative is the application of malic acid, a naturally occurring α -hydroxy acid containing a pendant β -carboxylic acid. Malic acid, **1**, is commercially available as both the both enantiopure isomeric forms or as a racemic mixture. Malic acid has found application previously for cyclic ester monomer synthesis including β -lactone and cyclic diester synthesis.^{6,7} In this report, we will describe an improved synthesis of the difunctionalised cyclic diester, **2**, and the synthesis of the monofunctionalised cyclic diester, **3**, with subsequent ROP of both monomers using organocatalytic methods (Figure 1).

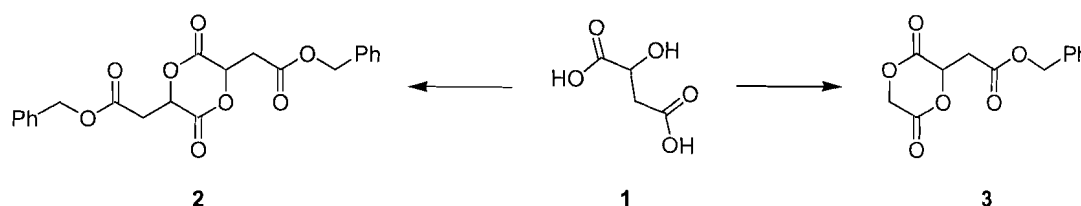


Figure 1. Structures of difunctionalised cyclic diester, **2**, and monofunctionalised cyclic diester, **3**, from malic acid, **1**.

References

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