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Daugaard, Anders Egede; Hoffmann, Christian; Andersen, Christian

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Functional bio-based polyesters by enzymatic polymerization

Anders Egede Dugaard¹, Christian Hoffmann and Christian Andersen

¹Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Technical University of Denmark

During recent years enzymatic polymerization has become increasingly popular as an alternative to classical polyesterification processes. The high regioselectivity observed for lipases permits preparation of novel polyesters with a high number of functional groups.¹ This is particularly interesting when considering monomers from bio-based feedstock that generally contain a high number of functional groups such as a both secondary and primary alcohols. Enzymatic polymerization can be conducted at relatively low temperature and thereby is well suited for sensitive monomers.

Recently enzymatic polymerization was applied to prepare functional water soluble polyesters based on dimethyl itaconate and poly(ethyleneglycol).² The monomer permits postfunctionalization using thiol-ene chemistry or aza-michael additions, which was used to illustrate the possibilities of preparing functional hydrogels. Hydrogels based on the polyesters were shown to be degradable and could be prepared either from the pure polyester or from prefunctionalized polyesters, though the thiol-ene reactions were found to be less effective. Since then a new monomer, trans-2,5-dihydroxy-3-pentenoic acid methyl ester (DPM) has been prepared directly from pentoses using tin containing zeolites.³ The monomer was prepared in yields of up to 32% and contains both a vinyl as well as a secondary alcohol in addition to the primary alcohol and ester functionality, and as such is an interesting building block for polymers. DPM was copolymerized together with ethyl-6-hydroxyhexanoate yielding copolymers with molecular weights of up to 12,000 g/mol. The polymers were postfunctionalized using trifluoroacetic anhydride, which resulted in 100% conversion of the secondary alcohols, illustrating the possibility to use the secondary alcohol for grafting. In addition to this, thiol-ene reactions using hexanethiol, mercaptoethanol, mercaptoacetic acid, 2-ethylhexanethiol and thiophenol were conducted on the internal double bond resulting in conversions of 32-100%. Given the lower reactivity of the internal double bond the extent of functionalization was found acceptable for use as a general method for dual functionality polyesters.

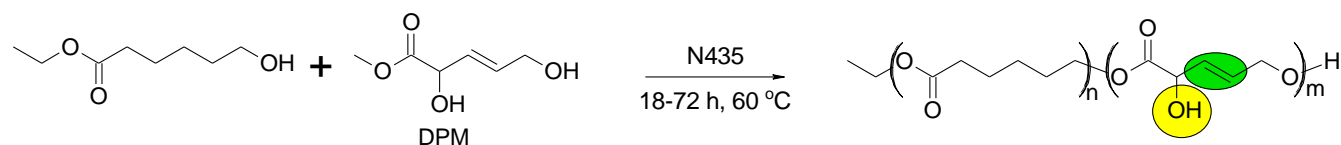


Figure 1. Enzymatic polymerization of functional monomers such as DPM (prepared from xyloses) gives possibility for post-polymerization derivatization.

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