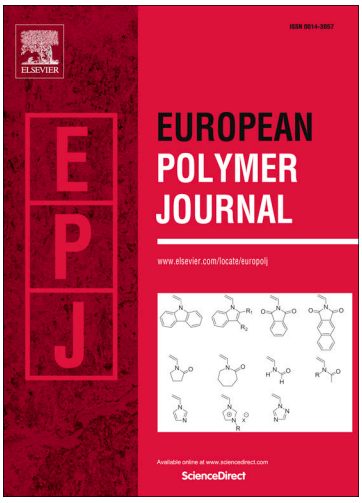

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Sara Brännström, Maja Finnveden, Mats Johansson, Mats Martinelle, Eva Malmström

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Itaconate Based Polyesters: Selectivity and Performance of Esterification Catalysts

Sara Brännström,[a] ‡ Maja Finnveden,[b] ‡ Mats Johansson,[a] Mats Martinelle,*[b] and Eva Malmström*[a]

[a]S. Brännström, Prof. M. Johansson, Prof. E. Malmström, Dept of Fibre and Polymer Technology, KTH Royal Institute of Technology, Teknikringen 56-58, SE-100 44 Stockholm, Sweden

[b]M. Finnveden, Assoc. Prof. M. Martinelle, Division of Industrial Biotechnology, KTH Royal Institute of Technology, AlbaNova University Centre, SE-106 91 Stockholm, Sweden

Supporting Information Placeholder

ABSTRACT: The performance of different esterification catalysts was studied for the use in synthesis of renewable polyesters from dimethyl itaconate (DMI), dimethyl succinate (DMS) and 1,4-butanediol (BD). Itaconic acid and derivatives such as DMI are interesting monomers because of their multiple functionalities and previous work has shown great potential. However, the multiple functionalities also pose challenges to avoid side reactions such as thermally initiated, premature, radical crosslinking and/or isomerization of the 1,1-disubstituted unsaturation. Additionally, the two carboxylic acids have inherently different reactivity. One key factor to control reactions with IA is to understand the performance of different catalysts. In this study, six esterification catalysts were investigated; immobilized *Candida antarctica* lipase B (CalB), titanium(IV)butoxide ($Ti(OBu)_4$), *p*-toluenesulfonic acid (*p*TSA), sulfuric acid (H_2SO_4), 1,8-diazabicycloundec-7-ene (DBU), and 1,5,7-triazabicyclodec-5-ene (TBD). CalB and $Ti(OBu)_4$ were selected for further characterization with appreciable differences in catalytic activity and selectivity towards DMI. CalB was the most effective catalysts and was applied at 60 °C while $Ti(OBu)_4$ required 160 °C for a reasonable reaction rate. CalB was selective towards DMS and the non-conjugated side of DMI, resulting in polyesters with itaconate-residues mainly located at the chain ends, while $Ti(OBu)_4$ showed low selectivity, resulting in polyesters with more randomly incorporated itaconate units. Thermal analysis of the polyesters showed that the CalB-catalyzed polyesters were semi-crystalline, whereas the $Ti(OBu)_4$-catalyzed polyesters were amorphous, affirming the difference in monomer sequence. The polyester resins were crosslinked by UV-initiated free radical polymerization and the material properties were evaluated and showed that the crosslinked materials had similar material properties. The films from the polyester resins catalyzed by CalB were furthermore completely free from discoloration whereas the film made from the polyester resins catalyzed with $Ti(OBu)_4$ had a yellow color, caused by the catalyst. Thus, it has been shown that CalB can be used to attain sustainable unsaturated polyesters resins for coating applications, exhibiting equally good properties as resins obtained from traditional metal-catalysis.

HIGHLIGHTS

- Quantification of selectivity and efficiency of different catalysts.
- A lipase was effective at 60 °C and selective towards the non-conjugated side of itaconate.
- A titanate was nonselective and required 160 °C for polyester synthesis.
- The catalysts yielded different monomer sequences in itaconate -based polyester resins.
- Resins from both catalysts were UV-curred to crosslinked films exhibiting equally good properties.

Key words: Enzyme catalysis; Organometallic catalysis; Biobased; UV-curing; Coatings