

# Lignin-derived aromatic/aliphatic polyesters using organocatalysis

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## Introduction

Lignin is the major component in wood and the second most abundant naturally occurring organic polymer. Despite lignin's highly functional character (i.e. rich in phenolic and aliphatic hydroxyl groups), it is rarely exploited as a raw material for chemical production. The design of biobased PET mimics, which exhibit similar thermal and gas permeability properties, will probably require such aromatic components. We plan to extend the range of lignin-derived aromatic polyesters and present herein an easily assessable synthetic route for the homo-polymer of dihydrocoumaric acid (**2c**).

## State of the art

The phenolic acids which can be derived from lignin are classified as *p*-hydroxycinnamic acids. Besides ferulic acid (**1a**), sinapic acid (**1b**) and coumaric acid (**1c**) are the most abundant ones (Figure 1).

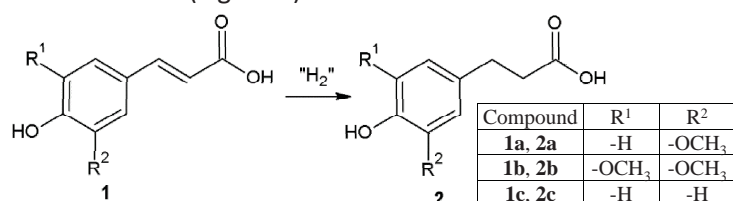


Figure 1: Reduction of the *p*-hydroxycinnamic acids

One strategy which is used for the synthesis of monomers for biobased PET mimics, is to reduce the double bond in the side chain of the *p*-hydroxycinnamic acids (Figure 1).<sup>1,2</sup> The monomers thus obtained are prepared into aromatic-aliphatic polyesters.

## Back to the drawing board

Previously, the polymerization of dihydroferulic acid (**2a**) was performed via the acetylation of the phenol group, followed by transesterification in the melt under vacuum using zinc diacetate dehydrate as a catalyst.<sup>1</sup> Acetylation of dihydrocoumaric acid (**2c**) proved to be impossible however.<sup>3,4</sup> Dihydrocoumaric acid was therefore esterified on the carboxylic acid group using a Fisher esterification with Amberlyst as heterogeneous catalyst (Figure 2).

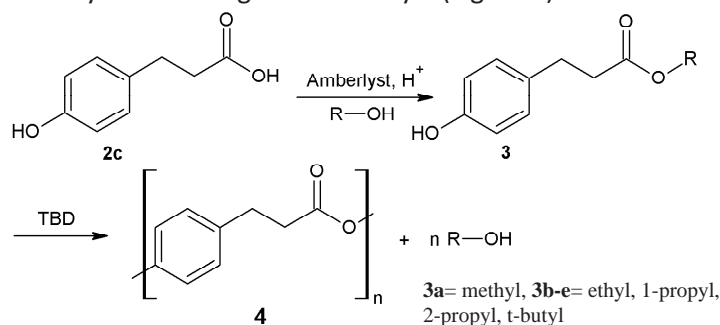
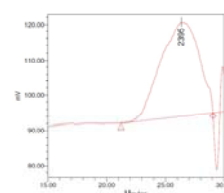


Figure 2: Esterification of dihydrocoumaric acid (**2c**) followed by a polymerization.

## Organocatalysis

The subsequent polymerization of monomer **3a** was performed under several conditions. Polymerization in the melt under nitrogen at atmospheric pressure with 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) as organocatalyst afforded only oligomers. Repeating the melt polymerization under vacuum resulted in polymers, albeit with very high polydispersities (Figure 3).



Retention time: 26,4 min  
 $M_n$ :  $1,9 \cdot 10^3$  g/mol.  
 $M_w$ :  $4,1 \cdot 10^3$  g/mol.  
PDI: 2,2.

Figure 3: GPC analysis of polymer **4**, obtained from monomer **3a** under vacuum using TBD.  $M_n$  &  $M_w$  were calculated using a PMMA calibration curve.

## Future work

We are currently investigating the effect of the ester group of monomer **3** on the molecular weight and polydispersity of the resulting polymers and plan to investigate the material properties of the products obtained.

## References

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