



New method for the synthesis of formaldehyde-free phenolic resins from lignin-based aldehyde precursors



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ABSTRACT

Phenolic resins are mainly obtained from phenol and the highly toxic and volatile formaldehyde. In order to synthesize new formaldehyde substituents for the synthesis of resol-type phenolic resins, we designed a method to functionalize phenolic compounds with aliphatic aldehydes by a two-steps reaction: the functionalization of an acetal group on aromatic hydroxyl functions and the subsequent deprotection of these acetal groups into aliphatic aldehyde groups. This method was used on the lignin-based aromatic aldehyde precursors i.e. 4-hydroxybenzaldehyde and vanillin to turn them into reactive and difunctional biobased aromatic aldehyde precursors. Those precursors proved to lead to formaldehyde-free and biobased phenolic resins with competitive thermal properties compared to the usual formaldehyde resins.

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1. Introduction

Phenolic resins have been industrially produced as the first synthetic polymer since 1911 [1]. After more than a hundred years of industrialization, their average global production reaches 6 millions of tons each year [2] and phenolic resins are now ubiquitous materials. They are used in a broad range of applications such as electric laminates, carbon foams, adhesives, molding compounds, acid-resistant coatings and fiber-reinforced composites among others [3]. With characteristically high cross-linking and aromatic density structures, phenolic resins are well-known for their long term thermal, chemical and mechanical stability, strength, high thermal insulating properties and excellent char yield properties. Two types of phenolic resins have been developed: resols and novolacs. As a main difference between those two, synthesis of resols takes place in alkaline conditions and then curing of resols can be performed stage-wise with heating only, without any additional input of cross-linking agents. Thus, resols are user-friendly polymers for applications such as heat resistant adhesives [4] or high char yield composites [5].

In industry, resols are mainly produced with formaldehyde and phenol. Those two precursors present ideal structures and reactivities for the synthesis of polymers with high cross-linking and aromatic densities. However, they are both petrobased and toxic. Especially, formaldehyde is highly volatile and classified as CMR (Carcinogenic Mutagenic Reprotoxic) by the ECHA (European Chemicals Agency) [6]. With fossil feedstock depletion and increasingly restricting health and safety regulations, substitution of formaldehyde becomes a major concern for the phenolic resin industry.

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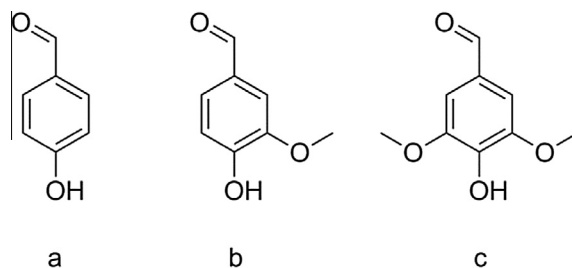
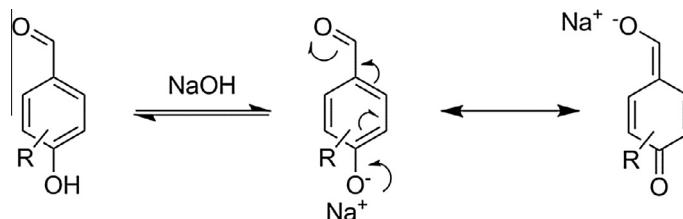
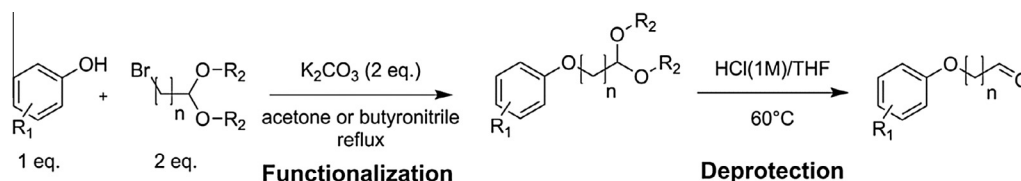


Fig. 1. Chemical structures of 4-hydroxybenzaldehyde (a), vanillin (b) and syringaldehyde (c).



Scheme 1. Deprotonation of 4-hydroxybenzoic aldehyde precursors with sodium hydroxide and mesomeric electron-donor effect of the resulting hydroxylate moiety (R: substituent H or OMe).



Scheme 2. Grafting reaction of aliphatic aldehyde groups onto phenolic compounds in two steps ($n = 1$ or 2 , R_1 and R_2 : CHO, OMe or aliphatic chain substituents).

The aromatic aldehyde precursors 4-hydroxybenzaldehyde, vanillin and syringaldehyde can interestingly be obtained from the cheap and abundant lignins [7–9] (Fig. 1).

Moreover, those biobased compounds are not toxic and their aromaticity is beneficial for the synthesis of polymers with high aromatic densities such as phenolic resins. However, those precursors all present phenolic hydroxyl functions located in para-position prior to their aldehyde function with pKa in water at 25 °C of respectively 7.6 [10], 7.4 [11] and 7.3 [11]. Those hydroxyl functions are more acid than the phenol's one with a pKa of 10 [10]. Thus, during resol synthesis, the alkaline catalyst deprotonates preferentially the hydroxy function of the aldehyde precursors instead of the phenol's. The resulting hydroxylate functions show strong +M electron-donor effect, which reduces by electronic delocalization the reactivity of the aldehyde functions in para position (Scheme 1). As a result, those lignin-based aldehyde precursors are not reactive and consequently not suitable for the synthesis of formaldehyde-free resols.

Then, one way to turn them into reactive precursors would be to functionalize those hydroxyl functions. Besides, phenolic resins show high performance properties above mentioned thanks to their characteristic high cross-linking densities. In order to synthesize phenolic resins without formaldehyde with such chemical structures and properties, our strategy is to substitute formaldehyde with reactive and difunctional biobased aldehyde precursors. Interestingly, aliphatic aldehyde functions usually exhibit higher reactivities than aromatic aldehyde ones toward phenolic compounds [12,13]. Therefore, when used on the lignin-based aromatic aldehyde compounds, this functionalization method would give access to reactive and difunctional biobased aromatic aldehyde precursors which might be interesting as formaldehyde substituents for the synthesis of phenolic resins.

Several methods have already been described in the literature to functionalize aliphatic aldehyde groups onto phenolic compounds [14]. Especially, a convenient method consists in the functionalization of the hydroxyl function with an acetal group via a Williamson reaction on a bromoalkylacetal compound followed by the deprotection of the acetal function into an aldehyde function by acid-catalyzed hydrolysis [15,16] (Scheme 2). To the best of our knowledge, this method has never been used to functionalize the lignin-based aromatic aldehyde compounds namely 4-hydroxybenzaldehyde, vanillin and syringaldehyde (Fig. 1). Also, it has only been used for organic chemistry applications and, so far, has never been used for the synthesis of phenolic resins precursors.

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