



Aromatic dialdehyde precursors from lignin derivatives for the synthesis of formaldehyde-free and high char yield phenolic resins

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ARTICLE INFO

Article history:

Received 6 January 2016

Received in revised form 19 February 2016

Accepted 23 February 2016

Available online 26 February 2016

Keywords:

Phenolic resins
Formaldehyde-free
Biobased
Vanillin
Resol
Lignin-based

ABSTRACT

Commercial resol-type phenolic resins are mainly synthesized from the highly toxic and highly volatile formaldehyde. Aromatic aldehydes such as 4-hydroxybenzaldehyde, vanillin and syringaldehyde are not toxic and are obtained by depolymerization of the cheap and abundant lignins. They can be green and environmentally benign surrogate of formaldehyde in resol-type phenolic resins. For this purpose, reactivity of aromatic aldehydes has been studied in function of the nature and positions of aromatic substituents prior to the aldehyde function. Results prove that those bio-based compounds are not reactive in resol synthesis reactions but their reactivity can be triggered by masking their free-hydroxy groups. A functionalization method from 4-fluorobenzaldehyde has been designed and new difunctional and bio-based aromatic aldehyde precursors were synthesized in excellent yields. Those starting materials proved to be excellent alternatives to formaldehyde leading to bio-based resol-type phenolic resins free of formaldehyde with higher thermal stability and char yield properties.

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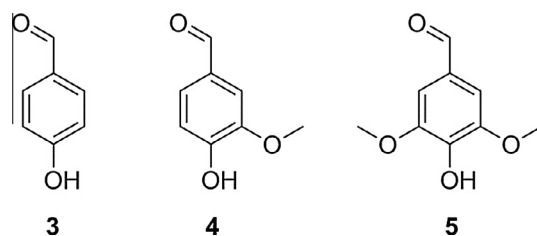
1. Introduction

Phenolic resins have been industrially produced as the first synthetic polymer since 1911 [1]. After more than a hundred year of industrialization, their average global production reaches the 6 millions of tons per 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 [3–6]. 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, synthesis of resols takes place in alkaline conditions and curing of resols can be performed stage-wise with heating only, without any additional input of cross-linking. Thus, resols are considered as user-friendly polymers for applications such as chemically resistant adhesives [5] or high char yield composites [7].

In industry, resols are mainly produced from the reaction of formaldehyde with phenol. These two precursors present ideal structures and reactivities for the synthesis of materials with high cross-linking and aromatic density. However, they

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Scheme 1. Chemical structures of 4-hydroxybenzaldehyde (**3**), vanillin (**4**) and syringaldehyde (**5**).

are both petroleum-based and rather toxic. Especially, formaldehyde is highly volatile and classified as CMR (Carcinogenic Mutagenic Reprotoxic) by the ECHA (European Chemicals Agency) [8]. With fossil feedstock depletion and increasingly restricting health and safety regulations, substitution of formaldehyde becomes a major concern for the phenolic resin industry.

Yet, substitution of formaldehyde for the synthesis of resols has raised several issues: (a) higher molecular weight aldehydes are less reactive than formaldehyde and may poorly cross-link phenolic networks [4], (b) enolisable aldehydes are prone to undergo aldol side-reactions in alkaline media [9], (c) higher molecular weight aldehyde compounds with additional aliphatic carbons compared to formaldehyde lead to phenolic resins with lower aromatic density and consequently with poorer thermal properties [5].

For those reasons, the synthesis of resols with high thermal properties requires bio-based formaldehyde substituents with sufficient reactivity and target chemical structures i.e. no α -hydrogen and low aliphatic carbon composition. As such, some previous studies described formaldehyde substitution with bio-based and reactive aldehyde compounds such as glyoxal [10–12] and furfural [13–16]. Although those aldehyde precursors are less volatile and less toxic than formaldehyde, they are nonetheless classified as CMR by the ECHA [8].

As wastes of the paper industry, lignins are a cheap and abundant bio-based resource of (poly)phenolic compounds [17–19]. Interestingly, they can be depolymerized into aromatic aldehyde precursors such as 4-hydroxybenzaldehyde (**3**), vanillin (**4**) and syringaldehyde (**5**) [20–22] (Scheme 1). Those compounds are not toxic and their high aromatic composition is potentially beneficial for the synthesis of polymers with high aromatic densities. Therefore, they have recently attracted much attention and been studied for the synthesis of thermoplastic [23–29] and thermosetting [26–28,30–36] polymers.

These non-enolisable aldehydes associated to their aromatic character make them particularly attractive for the synthesis of bio-based formaldehyde-free phenolic resins. Although previous works describe the synthesis of novolacs with those non-toxic and bio-based compounds [34–36], to the best of our knowledge, resol syntheses have never been described in literature.

We have first investigated the reactivity of those bio-based aldehyde precursors in resol syntheses. We gathered valuable information of the influence of substituents on aromatic aldehyde on the reactivity and on the thermal properties of the resulting phenolic resins after curing. Facing those results, we have redesigned new precursors with dedicated chemical structures from those lignin-based aldehydes. Finally, we have successfully synthesized formaldehyde-free and bio-based resols with those precursors. Characterizations of the resins clearly demonstrate that this new method gives an easy access to competitive formaldehyde-free and resol-type phenolic resins with high thermal stability and char yield properties.

2. Experimental

2.1. Materials

Commercial formaldehyde resol (**1**) was Ablaphene[®] RS 101 provided by Solvay and industrially used for the manufacture of high char yield composites [37]. All the solvents and reagents were of 98–99% purity. Benzaldehyde (**2**), 4-hydroxybenzaldehyde (**3**), vanillin (**4**), syringaldehyde (**5**), 4-methoxybenzaldehyde (**6**), 3,4-dimethoxybenzaldehyde (**7**), 3,4,5-trimethoxybenzaldehyde (**8**), terephthalaldehyde (**9**), phenol, 4-fluorobenzaldehyde, dimethylsulfoxide (DMSO), ethyl acetate (AcOEt), potassium carbonate and sodium hydroxide were purchased to Sigma–Aldrich and used without purification.

2.2. Characterizations

¹H and ¹³C NMR spectra were recorded in DMSO-*d*₆ on a Bruker Avance 400 MHz spectrometer. ¹H chemical shifts are expressed in ppm/TMS.

Conversion of aldehyde functions during resol syntheses reactions, C15 min and C30 min, were measured with ¹H NMR titration of t0, t15 min and t30 min resol samples using 2,4,6-trimethylphenol as a standard. All the measurements were performed five times; results are an average of those five measurements and uncertainty ranges were measured with the standard deviation of the measurements [38].

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