European Polymer Journal 68 (2015) 488–502

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Feature Article

Vanillin, a key-intermediate of biobased polymers

Maxence Fache, Bernard Boutevin, Sylvain Caillol *

Institut Charles Gerhardt, UMR CNRS 5253, Equipe Ingénierie et Architectures Macromoléculaires, ENSCM, 8 rue de l'Ecole Normale, 34296 Montpellier, France

ARTICLE INFO

Article history:
Received 16 October 2014
Received in revised form 20 February 2015
Accepted 7 March 2015
Available online 28 March 2015

Keywords:
Vanillin
Lignin
Biobased
Phenolic
Polymers

ABSTRACT

The use of vanillin for the preparation of renewable polymers is reviewed in this work. The synthesis of polymers from renewable resources is a burning issue that is actively investigated. Vanillin is currently one of the only biobased and aromatic compounds that are industrially available. For this reason, vanillin recently gained much attention from the polymer community. The first part of this work aims at giving an overview of the different existing sources of vanillin, and of their relevance in the context of a potential use in polymer science. The second part of this work sums up the efforts of the scientific community to prepare a wide range of vanillin-based polymers, e.g. phenolic, epoxy and benzoxazine resins, polyesters, acrylate and methacrylate polymers. The interest in the use of vanillin to prepare renewable polymers is recent but the number of contributions on this subject is growing fast.

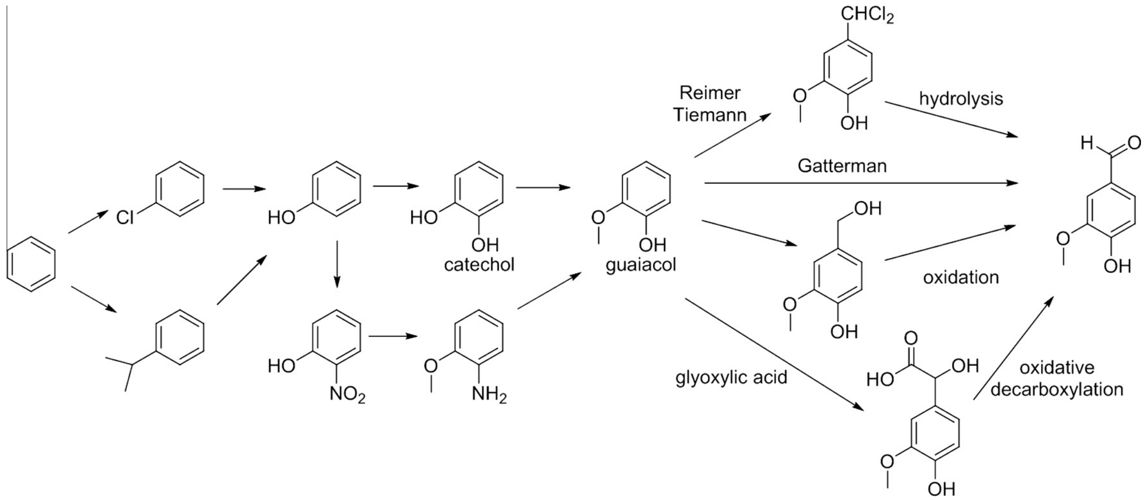
Contents

1. Introduction

Vanillin (4-hydroxy-3-methoxybenzaldehyde), a plant metabolite, is the main component of natural vanilla extract and is responsible for its flavoring properties. Natural vanilla is originally extracted from vanilla orchid pods. The composition of natural vanilla extract is complex and contains many more compounds than only vanillin. Also, vanilla orchid growing and harvesting is a costly process. For these reasons, vanillin from natural extract accounts for less than 1% of the total vanillin production

* Corresponding author. Tel.: +33 4 67144327.
E-mail address: sylvain.caillol@enscm.fr (S. Caillol).

http://dx.doi.org/10.1016/j.eurpolymj.2015.03.050
0014-3057/



Scheme 1. Outlines of petrochemical synthesis of vanillin adapted from [2].

worldwide [1]. This sourcing is not adapted to an industrial use of vanillin.

As a flavoring and fragrance ingredient, the current global demand for vanillin is estimated to be roughly 20,000 tons per year [1]. To satisfy constantly increasing markets, new chemical routes for the synthesis of vanillin were developed. Today, 85% of the vanillin is produced from the petroleum-based raw material guaiacol [2] (Scheme 1). Solvay-Rhodia dominates the vanillin market using the catechol–guaiacol process.

However, vanillin produced through this process cannot be labeled as "natural vanilla flavor". According to EU regulations, vanillin can be sold as "natural vanilla aroma" only if the base material and the process are natural. This led to the development of other ways of producing vanillin using biotechnology, improving the scientific knowledge and financial investment in this field along the way.

Numerous strategies have been envisaged to produce vanillin by biotechnology processes. Literature reports can be classified in plant-based and microorganism-based approaches. Plant-based strategies [3] consist in growing plant tissues or cells to make use of their biosynthetic pathways for the conversion of various substrates to vanillin. This approach consistently suffers from low and inconsistent yields. Microorganism-based approaches have been extensively reviewed [4–6] and consist in using biotransformation reactions from native or genetically-modified fungi [7,8], yeast [9] or bacteria [10] to produce vanillin (or a derivative in a different oxidation state) from a structurally close substrate. The most available and promising substrates include, ferulic acid extracted from sugar beet pulp [7] or waste of rice bran oil processing [8], glucose [11,12], and even lignin fragments [5]. Separation technologies are maturing [13] and play a key role for the industrial-scale production of vanillin from biotechnologies. Recently, Solvay-Rhodia and Evolva entered a pre-production phase from yeast fermentation of rice bran oil processing waste and glucose respectively [1]. These processes are still emerging technologies producing high-cost vanillin, which is suitable for the aroma and fragrances field for marketing reasons, but not for potential use in renewable resources-based polymers.

One last production method might however suit this purpose. The production of vanillin from wood actually accounts for about 15% of the total vanillin production and Borregaard, the second largest vanillin producer worldwide, produces vanillin from lignin [14]. Indeed, chemical depolymerization of lignosulfonate by-products from the paper industry was historically the first industrial synthetic process for vanillin production [15]. However, vanillin-from-lignin plants raised environmental concerns [2]. Recently, this process regained attention thanks to the understanding of lignin depolymerization mechanism [16–18], better yields through process improvement and catalysis [18–22], and better separation and purification techniques [14,23–25].

These advances promoted the lignin-to-vanillin process to one of the most promising in terms of sustainability and economical relevance. Indeed, lignin is the second most available renewable raw material with around 50 million tons per year produced [26]. Vanillin is currently one of the only aromatics industrially available from lignin. The production of other biobased aromatics from lignin depolymerization, although under intense investigation, is not a mature technology yet [27]. The production of vanillin from lignin is not in the scope of this review and more details are available elsewhere [28]. However, the fact that processes to produce vanillin from wood exist, at an industrial scale, and with high sustainability, leads us to consider vanillin as a top-priority renewable building block. Its use for the synthesis of biobased polymers is reviewed in this work.

2. Polymers based on vanillin and derivatives

2.1. Context

The investigation of vanillin as a biobased building block has been very dependent on its sourcing. Indeed,