Cite this: Green Chem., 2012, 14, 2395

www.rsc.org/greenchem

## COMMUNICATION

## Vanillin based polymers: I. An electrochemical route to polyvanillin<sup>†</sup>

Ananda S. Amarasekara,\* Bernard Wiredu and Ashfaqur Razzaq

Received 27th April 2012, Accepted 3rd July 2012 DOI: 10.1039/c2gc35645g

Electrochemical reductive polymerization of divanillin in aqueous sodium hydroxide using a lead cathode gives polyvanillin in 91% yield. The product was characterized by elemental analysis, UV-Vis, FT-IR, <sup>1</sup>H, <sup>13</sup>C NMR, TGA-DTGA, and GPC.

Current interest in the development of renewable resources based polymeric materials has opened up a new area of research into abundant natural products that can be utilized as monomers or monomer precursors for the polymer industry.<sup>1</sup> Vanillin (4-hydroxy-3-methoxybenzaldehyde, **1**, Fig. 1) is one of these renewable resources based building blocks gaining increasing attention in this area of research as a potential monomer or precursor,<sup>2</sup> in addition to its present applications in the food and pharmaceutical industries. Currently, approximately half of the vanillin produced in the world is used as a flavoring material in the food industry, and the remaining half is utilized as an intermediate in the chemical and pharmaceutical industries for the production of herbicides, antifoaming agents or drugs such as papaverine, L-dopa, L-methyldopa and the antimicrobial agent trimethoprim.<sup>3</sup>

This eight carbon phenolic-aldehyde was initially isolated from the vanilla bean extract derived from orchids of the genus *Vanilla*, and primarily from the Mexican species, *Vanilla planifolia*. Until the 1920s, vanillin was commercially produced from another natural product eugenol. Later it was synthesized from the lignincontaining paper industry by-product called "brown liquor". Even though this process uses industrial waste materials, the "brown liquor" based process is no longer popular because of environmental concerns, and today most of the vanillin is produced from the petroleum based raw material guaiacol.<sup>3</sup> However the recent advancements<sup>4</sup> in the production of vanillin by catalytic air oxidation of abundant lignin have made this an easily accessible material, and have promoted the status of this flavor chemical to another promising feedstock material.

Alternative biotechnology-based approaches applying fungi, bacteria, plant cells, and genetically engineered microorganisms are also currently under study<sup>5</sup> for the large scale production of this highly functionalized versatile building block.

The related dimer of vanillin, or divanillin (6,6'-dihydroxy-5,5'-dimethoxy-(1,1'-biphenyl)-3,3'-dicarboxaldehyde, **2**, Fig. 1),



Fig. 1 Synthesis of polyvanillin (3). a = 3% H<sub>2</sub>O<sub>2</sub>, 1% w/w horseradish peroxidase, pH = 4.0, b = electrolysis in 1 M aqueous NaOH, Pb electrodes, 1.1 A, 12 V, 3 h.



Fig. 2 meso-Hydrovanilloin (4).

is also a flavor chemical found in roasted vanilla beans at very low concentrations. Fortunately, this symmetrical dimer of vanillin can be easily prepared by FeCl<sub>3</sub><sup>6</sup> or enzyme<sup>7</sup> catalyzed oxidative dimerization of vanillin, and the polyfunctional divanillin is a very attractive molecule as a monomer due to its symmetrical arrangement of functional groups.

In addition to the free radical promoted oxidative dimerization to produce divanillin, vanillin can be reductively dimerized at the aldehyde function using low-valent titanium generated via TiCl<sub>4</sub>-Mn<sup>8</sup> or by electrochemical<sup>9</sup> methods. In 1952 Pearl first reported<sup>9</sup> this electrochemical dimerization of vanillin to hydrovanilloin (1,2-bis-(4-hydroxy-3-methoxy-phenyl)-ethane-1,2-diol, 4, Fig. 2) in basic media; later, Grimshaw and Ramsey showed<sup>10</sup> that electrochemical coupling is a highly stereoselective reaction, and gives the meso compound. Our interest<sup>11,12</sup> in the synthesis of novel polymeric materials from biomass derived monomers has led us to examine the application of vanillin (1) and divanillin (2) as building blocks for the preparation of new renewable polymeric materials. While reinvestigating this classical electrochemical coupling reaction, we envisioned that a combination of oxidative and reductive couplings of vanillin could be used to produce polyvanillin (3), and in this communication we report the first preparation of polyvanillin (3) by electrochemical polymerization of the vanillin dimer, divanillin (2) prepared by enzymatic dimerization of vanillin.

During this study *meso*-hydrovanilloin (4) (m.p. 232–233 °C, lit.<sup>9</sup> 233–234 °C) was prepared as a model compound to collect spectroscopic data that can be used as tools in the

Department of Chemistry, Prairie View A&M University, Prairie View, Texas 77446, USA. E-mail: asamarasekara@pvamu.edu; Fax: +1 936 261 3117; Tel: +1 936 261 3107

<sup>†</sup>Electronic supplementary information (ESI) available: Procedures, characterization data, spectra. See DOI: 10.1039/c2gc35645g

characterization of polyvanillin. The <sup>1</sup>H NMR spectrum of *meso*-hydrovanilloin (4) recorded in DMSO-d<sub>6</sub> showed a singlet at 4.44 ppm, and was assigned to the hydrogens attached to secondary alcohol carbons. In the <sup>13</sup>C NMR spectrum, these carbons are observed as one signal at 77.4 ppm, confirming that a pure *meso* stereoisomer is formed as reported earlier.<sup>10</sup> Furthermore, aromatic ring carbon signals of *meso*-hydrovanilloin at 112.1(C-3,3'), 114.7(C-6,6'), 120.3(C-4,4'), 134.6(C-5,5'), 145.6 (C-2,2'), 147.1(C-1,1') could be assigned with help from published NMR data<sup>13</sup> of the related compound divanillin.

Polyvanillin was prepared by reductive coupling of divanillin (m.p. > 300 °C) at the aldehyde groups using an electrochemical polymerization cell as shown in Fig. 3. The polymer is insoluble in water, alcohols and common organic solvents, slightly soluble in warm DMSO and DMF, and soluble in aqueous sodium hydroxide.

Proton and carbon NMR spectra of polyvanillin recorded in DMSO-d<sub>6</sub> are shown in Fig. 4a and b. The broad peaks at 3.78, and 4.43 ppm in the <sup>1</sup>H NMR (**4a**) were assigned to methoxy groups, and CH–O hydrogens of the repeating unit of the polymer. These values are comparable to the 3.65 and 4.44 ppm peaks of OCH<sub>3</sub> and CH–O groups of the model compound *meso*-hydrovanilloin (**4**). The aromatic hydrogens of the polymer are seen as a broad signal in the 6.65–6.80 ppm region, whereas

12 V

Pb Cathode

Pb Anode

Porous cup





**Fig. 4**  $^{1}$ H (a) and  $^{13}$ C (b) NMR spectra of polyvanillin (3) recorded in DMSO-d<sub>6</sub>, \*solvent.

 $D_2O$  exchangeable broad peaks at 3.60 and 8.30 ppm were assigned to alcoholic and phenolic OH groups of the polymer (Fig. 4a).

Additionally, the unreacted aldehyde end groups of the polymer can be seen as a very small peak at 9.88 ppm. The  $^{13}$ C NMR spectrum of polyvanillin (3) in Fig. 4b shows eight peaks, further confirming the symmetrical repeating unit of the polymer. The peaks at 56.1 and 78.2 ppm are assigned to OCH<sub>3</sub> and CH–O carbons of the polymer which are comparable to peaks at 55.9 and 77.4 ppm for related carbons of the model compound *meso*-hydrovanilloin (4). The remaining six peaks at 110.4, 123.7, 125.0, 126.3, 143.1, and 148.0 ppm were assigned to aromatic ring carbons.

The FT-IR spectrum of polyvanillin shows the major peaks expected for the proposed structure. For instance, peaks observed at 1140 and 1270 cm<sup>-1</sup> could be assigned to the C-O stretching of alcohol and methoxy groups respectively, and peaks at 1049, 1460, 1499, and 1596  $\text{cm}^{-1}$  are assigned to the aromatic rings in the structure. Furthermore, alcohol and phenol OH groups of the polymer were seen as a broad absorption at 3400 cm<sup>-1</sup>. UV-Vis spectral data ( $\lambda_{max}$  and  $\varepsilon_{max}$ ) for polyvanillin (3) and divanillin (2) recorded in 0.01 M aqueous sodium hydroxide are shown in Table 1. Divanillin shows two absorptions at 273 and 336 nm, whereas the polymer sample showed two absorptions at 217 and 280 nm indicating the truncated chromophore in the polymer. Furthermore, it is interesting to note that the UV-Vis absorption spectrum of the polymer is similar to the spectrum reported<sup>9</sup> for meso-hydrovanilloin (222, 280 nm), suggesting a twisted arrangement of the two aromatic rings in divanillin units of the polymer.

Thermogravimetric analysis of polyvanillin showed a decomposition onset temperature at 300 °C, and 50% weight loss at 440 °C, indicating good thermal stability of the polymer. DSC analysis failed to give a  $T_g$  value as the DSC trace showed no identifiable peaks. GPC molecular weight determinations of polymer samples were carried out using DMF as the solvent. Molecular weight data for polyvanillin samples prepared in six polymerization trials are shown in Table 2, demonstrating reasonable reproducibility of the polymerization method.

We have shown that polyvanillin can be prepared in 93% overall yield from vanillin by peroxidase catalyzed enzymatic

**Table 1** UV-Vis spectral data ( $\lambda_{max}$  and  $\varepsilon_{max}$ ) for polyvanillin (3) and divanillin (2). A 1.1 × 10<sup>-4</sup> M solution in 0.01 M aqueous sodium hydroxide was used

Compound	$\lambda_{\max}$ (nm), $\varepsilon_{\max} \times 10^4$ (L mol <sup>-1</sup> cm <sup>-1</sup> )
Polyvanillin (3)	217(1.76), 280(0.45)
Divanillin (2)	273(1.47), 336(1.42)

 Table 2
 GPC molecular weight data of polyvanillin samples prepared in six polymerization trials

Entry	$\overline{M_{ m n}}$	DP	PD
1	10 950	36	1.47
2	11 200	37	1.55
3	11 784	39	1.42
4	10 622	35	1.44
5	9850	32	1.58
6	9967	33	1.54

dimerization followed by electrochemical reductive polymerization in aqueous sodium hydroxide medium at a lead cathode. This efficient, green, all aqueous medium synthesis provides easy access to a totally renewable resources based functionalized polymer with potential applications like chelating metal ions from aqueous solutions.

The authors would like to acknowledge American Chemical Society-PRF grant UR1-49436, NSF grant CBET-0929970, and USDA grant CBG-2010-38821-21569 for financial support. The NMR spectrometer used in this study was obtained through an NSF MRI grant CHE-0421290.

## References

 (a) V. Mittal, *Renewable Polymers*, Scrivener Publishing, Salem, Massachusetts, 2012; (b) A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, 107, 2411.

- 2 L. Mialon, A. G. Pemba and S. A. Miller, Green Chem., 2010, 12, 1704.
- 3 M. B. Hocking, J. Chem. Educ., 1997, 74(9), 1055.
- 4 (a) J. D. P. Araújo, C. A. Grande and A. E. Rodrigues, *Chem. Eng. Res. Des.*, 2010, **88**(8), 1024; (b) T. Voitl and P. Von Rohr, *Ind. Eng. Chem. Res.*, 2010, **49**(2), 520; (c) V. E. Tarabanko, D. V. Petukhov and G. E. Selyutin, *Kinet. Catal.*, 2004, **45**(4), 569.
- 5 H. Priefert, J. Rabenhorst and A. Steinbüchel, Appl. Microbiol. Biotechnol., 2001, 56(3–4), 296.
- 6 H. Yamamoto, T. Hoshino and T. Uchiyama, Biosci., Biotechnol., Biochem., 1999, 63(2), 390.
- 7 R. T. Nishimura, C. H. Giammanco and D. A. Vosburg, J. Chem. Educ., 2010, 87(5), 526.
- 8 X-F. Duan, J-X. Feng, G-F. Zi and Z-B. Zhang, Synthesis, 2009, 277.
- 9 I. A. Pearl, J. Am. Chem. Soc., 1952, 74(17), 4260.
- 10 J. Grimshaw and J. S. Ramsey, J. Chem. Soc. C, 1966, 653.
- 11 A. S. Amarasekara, D. Green and L. D. Williams, *Eur. Polym. J.*, 2009, 45(2), 595.
- 12 A. S. Amarasekara and S. Hawkins, Eur. Polym. J., 2011, 47(12), 2451.
- 13 G. E. Hawkes, C. Z. Smith, J. H. P. Utley, R. R. Vargas and H. Viertler, *Holzforschung*, 1993, 47, 302.