

Research Article

Vanillin-Based Polymers—part II: Synthesis of Schiff Base Polymers of Divanillin and Their Chelation with Metal Ions

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Condensation of renewable resources-based monomer divanillin with alkyl diamines gives Schiff base polymers with degree of polymerization (DP) ~25–32 in 88–95% yield. These yellow polymers are insoluble in water and common organic solvents, slightly soluble in warm DMSO, DMF and dissolves in aqueous NaOH. The polymers were characterized using FT-IR, ^1H , and ^{13}C NMR spectroscopy and by comparison with the model compound *N,N'*-bis(vanillidene)-1,3-propanediamine. Polymer prepared by condensation of divanillin and 1,6-diaminohexane is shown to chelate with Cu(II), Fe(II), and Co(II) metal ions in basic aqueous methanol.

1. Introduction

Synthesis of polymeric and composite materials from renewable resources-based feedstock has attracted an increasing attention over the last two decades due to concerns over dwindling petroleum resources [1, 2]. Some of the renewable resources-based monomers currently under study are triglycerides [3, 4], 1,3-propanediol [5], furfural [6, 7], 2,5-furandicarboxylic acid or its derivatives [8–10], lactic acid [11], and levulinic acid [12, 13]. Vanillin (**1**, Figure 1) is another biomass-derived compound that can be considered as a potential renewable feedstock chemical. This phenolic-aldehyde was first isolated from vanilla extract used as a common food flavoring, which is derived from orchids of the genus *Vanilla*, and primarily from the Mexican species, *Vanilla planifolia*. Recent advancements in the production of vanillin by metal catalyzed air oxidation of abundant lignin have promoted the status of this old world flavor chemical to another promising renewable feedstock material for the chemical and polymer industries [14–16]. Alternative biotechnology-based approaches applying fungi, bacteria, plant cells, and genetically engineered microorganisms are also currently under study [17] for the large scale production of this highly functionalized versatile building block. Even though the lignin derived vanillin is becoming

relatively easily accessible, still there are only a handful of reports on attempts to utilize vanillin or vanillin derivatives as monomers for the renewable resources-based polymer synthesis. In one example, Gosling et al. have recently reported [18] the preparation of 3-carboxy muconate as a monomer by an enzymatic transformation of vanillin. Furthermore, as a proof of the principle, they demonstrated that trimethyl ester derivative of 3-carboxy muconate can be copolymerized with styrene to give novel polyesters. In another recent example, vanillin-derived dihydroferulic acid has been used in the preparation of a polyester [19]. In these experiments, vanillin was subjected to the Perkin reaction with acetic anhydride and then hydrogenation to afford acetyl dihydroferulic acid. Polymerization of this monomer produced *poly*(dihydroferulic acid), which exhibits thermal properties similar to those of polyethylene terephthalate (PET). Additionally, the related compound *ortho*-vanillin has been used in the synthesis of organometallic polymers as well, where a Schiff base polymer derived from *ortho*-vanillin has been shown to complex with various metal ions [20].

6,6'-Dihydroxy-5,5'-dimethoxy-(1,1'-biphenyl)-3,3'-dicarboxaldehyde (**2**, Figure 1) or the compound commonly known as divanillin is the symmetrical dimer of vanillin and can be easily prepared from vanillin by FeCl_3 [21] or enzyme catalyzed [22] oxidative dimerization. This symmetrical

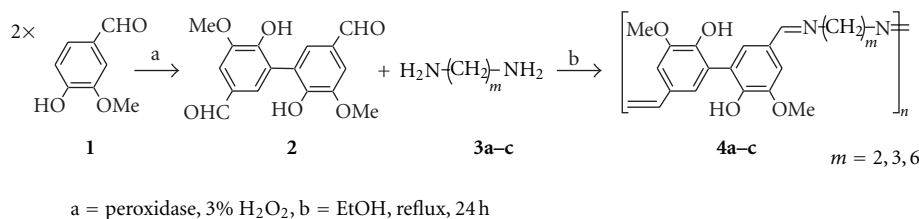


FIGURE 1: Synthesis of divanillin Schiff base polymers(4a-c).

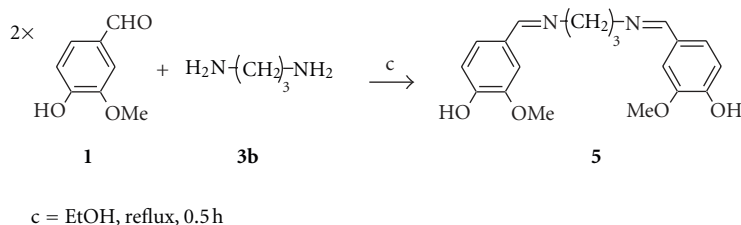


FIGURE 2: Synthesis of the model compound *N,N'*-bis(vanillidene)-1,3-propanediamine (5).

dimer is a reactive polyfunctional molecule, hence, very attractive as a monomer, and we recently reported the preparation of polyvanillin using divanillin as the building block. In this experiment, divanillin was polymerized in aqueous sodium hydroxide at a lead cathode to produce polyvanillin in 91% yield [23]. As an extension of our interests in the use of renewable resources based monomers for the synthesis of novel polymeric materials [13, 23, 24] and application of divanillin as a polymer precursor [23], we have studied the synthesis of divanillin Schiff base polymers, and their chelation properties with metal ions.

2. Experimental

2.1. Materials and Instrumentation. Vanillin, ethylenediamine, 1,3-propanediamine, 1,6-hexanediamine, 3% hydrogen peroxide, peroxidase (from horseradish, 59 units/mg), CuCl₂·2H₂O, FeCl₂·4H₂O, and CoCl₂·6H₂O were purchased from Aldrich Chemical Co. ¹H NMR Spectra were recorded in DMSO-*d*₆ on a Varian Mercury plus spectrometer operating at 400 MHz, and chemical shifts are given in ppm downfield from TMS ($\delta = 0.00$). ¹³C Chemical shifts were measured relative to DMSO-*d*₆, using δ (DMSO) = 39.5. FT-IR spectra were recorded on a Thermo Nicolet IR 200 spectrometer using KBr pellets. Elemental analysis was performed at QTI laboratories, NJ, USA. Thermogravimetric analysis was carried out in air on a Perkin Elmer Diamond TG/DTA system in 25–800°C temperature range, 10°C/min, and using Pt crucibles.

2.2. Synthesis of Divanillin (2). Divanillin (2) was prepared by horseradish peroxidase catalyzed oxidative dimerization of vanillin (1) using 3% hydrogen peroxide as the oxidant, as a gray powder in 95% yield, following the literature procedure [22].

IR (KBr) 744, 848, 1044, 1151, 1260, 1400, 1423, 1450, 1587, 1675, 3310 cm⁻¹.

¹H NMR (DMSO-*d*₆) δ 3.91 (s, 6H, 2X-OCH₃), 7.41 (bs, 4H, Ar), 9.78 (s, 2H, CHO), 9.95 (bs, 2H, OH); ¹³C NMR (DMSO-*d*₆) 56.5(OCH₃), 109.6(Ar), 124.9(Ar), 128.1(Ar), 128.6(Ar), 148.6(Ar), 150.9(Ar), 191.7(CHO).

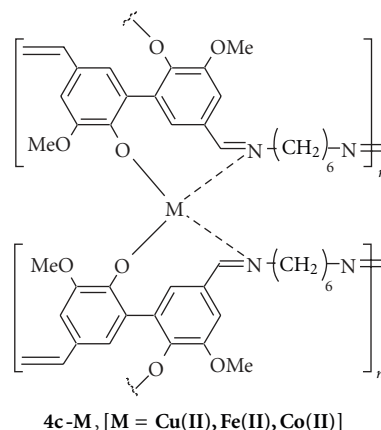
2.3. General Procedure for the Synthesis of Divanillin Schiff Base Polymers (4a-c). A mixture of divanillin (0.302 g, 1.00 mmol), and diamine 3a-c (1.00 mmol) in 60 mL of ethanol was heated under reflux for 24 h. Then the reaction mixture was cooled, filtered, and washed with cold ethanol (2X 10 mL) to give divanillin Schiff base polymers (4a-c) as yellow powders. Degree of polymerization (DP) of polymers was calculated by end-group analysis method, using ¹H NMR (DMSO-*d*₆) peak area ratios of -HC=N- of polymer (~8.2 ppm) and unreacted-CHO end groups (~9.7 ppm).

4a: 88% yield. Anal. Calc. for (C₁₈H₁₈N₂O₄)_n: C, 66.25; H, 5.56; N, 8.58%. Found: C, 66.61; H, 5.38; N, 8.39%. DP = 25.

4b: 92% yield. Anal. Calc. for (C₁₉H₂₀N₂O₄)_n: C, 67.05; H, 5.92; N, 8.23%. Found: C, 67.41; H, 5.88; N, 8.15%. DP = 28.

4c: 95% yield. Anal. Calc. for (C₂₂H₂₆N₂O₄)_n: C, 69.09; H, 6.85; N, 7.35%. Found: C, 69.31; H, 6.78; N, 7.15%. DP = 32.

2.4. Synthesis of the Model Compound *N,N'*-bis(vanillidene)-1,3-propanediamine (5). A mixture of vanillin (1.52 g, 10.0 mmol) and 1,3-propanediamine (0.37 g, 5.0 mmol) in 10 mL of ethanol was heated under reflux for 30 min. Then the solution was cooled to room temperature and allowed to stand at room temperature overnight. Evaporation of the solvent gave *N,N'*-bis(vanillidene)-1,3-propanediamine (5) as a yellow viscous oil, 1.60 g, 99% yield.

FIGURE 3: Proposed structure for metal complexes **4c-M** [M = Cu(II), Fe(II), Co(II)].TABLE 1: ^1H and ^{13}C NMR data of divanillin Schiff base polymers (**4a–c**) in DMSO- d_6 .

Polymer	^1H (ppm)	^{13}C (ppm)
4a	3.50 (OH), 3.64 (2XCH ₂), 3.75 (OCH ₃), 7.28 (Ar), 7.48 (Ar), 8.14 (CH=N)	55.7 (2XCH ₂), 57.5 (OCH ₃), 107.8 (Ar), 126.2 (Ar), 128.3 (Ar), 130.0 (Ar), 151.6 (2XC, Ar), 164.2 (CH=N)
4b	2.03 (CH ₂), 3.50 (OH), 3.58 (2XCH ₂), 3.75 (OCH ₃), 7.28 (Ar), 7.48 (Ar), 8.15 (CH=N)	29.5 (CH ₂), 56.7 (2XCH ₂), 58.3 (OCH ₃), 107.2 (Ar), 126.1 (Ar), 128.3 (Ar), 130.0 (Ar), 151.6 (2XC, Ar), 164.5 (CH=N)
4c	1.24 (2XCH ₂), 1.56 (2XCH ₂), 3.50 (OH), 3.52 (2XCH ₂), 3.75 (OCH ₃), 7.15(Ar), 7.38 (Ar), 8.20 (CH=N)	26.6 (2XCH ₂), 30.5 (2XCH ₂), 55.6 (2XCH ₂), 55.7 (OCH ₃), 107.7 (Ar), 128.1 (Ar), 128.6 (Ar), 129.8 (Ar), 151.0 (Ar), 151.5 (Ar) 162.0 (CH=N)

TABLE 2: Decomposition onset temperature (T_{onset}) and derivative thermogravimetric analysis (DTG) peaks data of divanillin Schiff base polymers (**4a–c**).

Polymer	$T_{\text{onset}}/^\circ\text{C}$	DTG/ $^\circ\text{C}$
4a	255	345, 492
4b	245	375, 478
4c	250	350, 475

Anal. Calc. for $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_4$: C, 66.65; H, 6.48; N, 8.18%. Found: C, 66.95; H, 6.56; N, 7.89%. IR 3432, 2935, 1651, 1593, 1512, 1467, 1430, 1127, 1026, 826 cm^{-1} . ^1H NMR (DMSO- d_6) δ 1.89 (m, 2H, CH₂), 3.52 (t, J = 6.4 Hz, 4H, 2XCH₂), 3.56 (s, 6H, 2X-OCH₃), 4.50 (bs, 2H, 2xOH), 6.79 (d, J = 8.4 Hz, 2H, Ar), 7.08 (d, J = 8.4 Hz, 2H, Ar), 7.31 (s, 2H, Ar), 8.15 (s, 2H, CH=N). ^{13}C NMR (DMSO- d_6) δ 32.6, 55.8, 58.6, 110.2, 115.6, 123.1, 128.1, 148.3, 149.9, 160.9.

2.5. General Procedure for Synthesis of Metal Chelates 4c-M. Polymer **4c** (0.382 g, 1.0 mmol of repeating unit) was dissolved in minimum volume of a 1 : 1 mixture of methanol and 0.1 M aqueous sodium hydroxide, and a solution of metal chloride (0.5 mmol) in 5 mL of water was added. The resulting solution was heated at 60°C for 3 h and cooled, and precipitate formed was isolated by centrifugation (1700 \times g, 6 min) and dried under vacuum at 50°C to give metal-chelated divanillin Schiff base polymers: **4c-Cu(II)** brown powder, 91% yield; **4c-Fe(II)** yellowish-brown powder 92%

yield; **4c-Co(II)** dark brown powder 95% yield. FT-IR spectra data of these metal chelated polymers are shown in Table 3.

3. Results and Discussion

3.1. Synthesis and Characterization of *N,N'*-bis(vanillidene)-1,3-propanediamine (5). Model compound *N,N'*-bis(vanillidene)-1,3-propanediamine (**5**) (Figure 2) was prepared to collect spectroscopic data that can be used as tools in the characterization of polymeric Schiff bases of divanillin. The ^1H NMR of **5** showed imine hydrogens as a singlet at 8.15 ppm, and the imine carbons were observed in ^{13}C NMR at 160.9 ppm. The C=N imine absorption in the IR spectrum was observed as a strong peak at 1651 cm^{-1} .

3.2. Synthesis of Divanillin Schiff Base Polymers (4a–c). Condensation divanillin (**2**) with three diamines (**3a–c**) produced three divanillin Schiff base polymers (**4a–c**) as shown in Figure 1. These brightly yellow polymers are insoluble in water, and all common organic solvents, slightly soluble in warm DMSO and DMF, however, readily dissolve in dilute aqueous NaOH. ^1H , ^{13}C NMR data, thermogravimetric analysis data, and FT-IR data of polymers **4a–c** are shown in Tables 1, 2, and 3, respectively. All three polymers showed strong –C=N– absorptions in the IR spectra in the 1654–1656 cm^{-1} range. This value is comparable to the 1651 cm^{-1} –C=N– absorption in the model compound *N,N'*-bis(vanillidene)-1,3-propanediamine (**5**). ^1H NMR spectra of polymers **4a**, **b**, and **c** showed imine

TABLE 3: FT-IR data of divanillin Schiff base polymers (**4a–c**), metal chelated divanillin Schiff base polymers **4c-Cu(II)**, **4c-Fe(II)**, and **4c-Co(II)**.

Polymer	–O–H (cm^{-1})	–CH=N– (cm^{-1})	–C=C– (Ar) (cm^{-1})	–C–O (cm^{-1})	Metal-O (cm^{-1})	Metal-N (cm^{-1})
4a	3402 b	1656 s	1594 s, 1463 s	1274 s	—	—
4b	3397 b	1654 s	1591 s, 1462 s	1270 s	—	—
4c	3409 b	1656 s	1593 s, 1462 s	1276 s	—	—
4c-Cu(II)	3408 b	1643 s	1586 s, 1463 s	1268 s	611 m	704 m
4c-Fe(II)	3389 b	1645 s	1589 s, 1458 s	1265 s	588 m	660 m
4c-Co(II)	3382 b	1642 s	1590 s, 1459 s	1266 s	601 m	701 m

b: broad, s: sharp, m: medium.

hydrogen peaks at 8.14, 8.15, and 8.20 ppm, respectively, whereas similar –HC=N– peak of the model compound **5** was observed at 8.15 ppm. The imine carbon resonances of polymers **4a**, **b**, and **c** were observed at 164.2, 164.5, and 162.0 ppm (Table 1), and corresponding signal in the model compound **5** was seen at 160.9 ppm, confirming the Schiff base structure in these polymers. Thermogravimetric analysis showed (Table 2) that all three polymers **4a–c** are stable up to about 250°C.

3.3. Synthesis of Metal Chelated Polymers 4c-M(II). The metal ion chelating ability of the representative polymer prepared from 1,6-diaminohexane was tested by treatment of the sodium salt of the polymer with chloride salts of Cu(II), Fe(II), and Co(II) in aqueous methanol medium. The resulting metal-chelated polymers were yellow-brown powders that are completely insoluble in water and all common organic solvents. The chelation of metal is evident from characteristic shift of –CH=N– IR absorption band to lower wave numbers by 11–14 cm^{-1} and C–O band by 8–11 cm^{-1} . Similar shifts are known in the complexation of metal ions with salen-type ligands as well [20, 25, 26]. Additionally, the appearance of two moderate peaks around 600 and 700 cm^{-1} due to metal-O and metal-N absorptions confirms the chelation of metal to imine nitrogen and phenolic oxygen of the polymer. Based on the shifts in IR absorptions and similar Schiff base organometallic polymers reported in the literature [20, 26], general structure **4c-M(II)** shown in Figure 3 is proposed for these novel metal chelated polymers.

4. Conclusion

We have shown that condensation of renewable resources based monomer divanillin with alkyl diamines gives low molecular weight Schiff base polymers in excellent yields. The Schiff base as well as phenolic binding sites in the polymer are shown to complex with **Cu(II)**, **Fe(II)**, and **Co(II)** metal ions. This class of vanillin-based polymers can be used to chelate and remove metal ions from aqueous solutions.

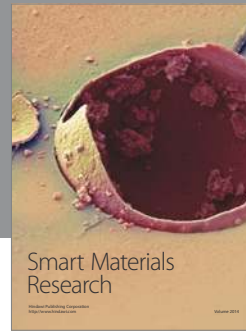
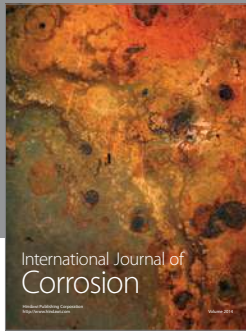
Acknowledgments

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