Copper(II)-Catalyzed Reactions of Activated Aromatics

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Received September 27, 1999

The catalytic reaction of *cis*-bisglycinato copper(II) monohydrate in the presence of hydrogen peroxide leads to hydroxylation of phenol to give catechol and hydroquinone (1:1.2 ratio) in good yield. 2,6-Dimethylphenol can be hydroxylated by hydrogen peroxide and a catalytic amount of *cis*-bisglycinato copper(II) monohydrate to give an aggregate of 1,4-dihydroxy-2,6-dimethylbenzene and 2,6-dimethylphenol. A similar reaction of *o*-cresol gives 2,5-dihydroxytoluene. The reactivity of *cis*-bisglycinato copper(II) monohydrate in hydrogen peroxide with *o*-cresol is 4.5 times faster than that of a similar reaction by *trans*-bisglycinato copper(II) monohydrate. A catalytic reaction of *cis*-bisglycinato copper(II) monohydrate with aniline in aqueous hydrogen peroxide gives polyanilines in the form of pernigraniline with different amounts of $Cu(OH)_2$ attached to them. The two major components of polyanilines obtained have M_n values of 1040 and 1500, respectively. Resistance of films of these polyanilines increases with temperatures from 40 °C to a maximum value at 103 °C and then decreases in the region of 103−150 °C, showing the property of a thermoelectric switch. The aggregate prepared from hydroxylation of 2,6-dimethylphenol shows a similar property in the region of 30−180 °C.

Introduction

Aromatic hydroxylation finds important place in biological chemistry.[1] Such a hydroxylation process can be achieved by transition metal complexes.[2] Preparation of model compounds for selective catalytic hydroxylation constitutes the backbone of this research.[3] Biochemical processes such as tyrosinase[4a] activity and biosynthesis of lignin[1] involve copper(II)-catalyzed aromatic hydroxylation. The cleavage of DNA by copper(II) complexes having phenolic groups as a part of the ligand is well established.[4b] Oxidative polymerization[5] and biochemical methods[6] are commonly used methods for the synthesis of polyphenols. Recently, success has been made in mimicking galactose oxidase by radical-containing copper(II) phenoxo complexes.[7] Copper(I) catalyst together with nitrogen bases in the presence of oxygen gives linear polymer of 2,6-dimethylphenol having an ether-type of linkage.[8] Oxidation of copper(I) phenoxides passes through hydroxylation.[9] In stoichiometric reactions copper(II) complexes can effectively cause selective hydroxylation on aromatic rings.[10] In contrast to these, the anilinic compounds easily oligomerize under oxidative conditions by transition metal catalysts to give polyanilines.[11] These oxidative oligomerizations are usually performed with the anilinium salts.[11d,e] There are different types of polyanilines such as leucoemeraldine, emeraldine, and pernigraniline, depending on the extent of oxidation of the chain.[12] Thus, the properties of the polyanilines are dependent on the method of preparation. From the foregoing discussion it is clear that there is a need to develop biorelated mild, catalytic, efficient methods for the oxidative transformation of aromatic com-

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10.1021/jo991509j CCC: $19.00
Published on Web 03/22/2000

pounds. Glycine is a basic amino acid which forms stable *cis*-bis and *trans*-bis chelates with copper(II).[13] We designed our study to elucidate the reactivity of *cis*- and *trans*-bisglycinato copper(II) complexes with activated aromatics under neutral conditions and also to exploit the material properties of the products from these reactions. This article describes the results of hydroxylation of phenols and oligomerization of anilinic compounds catalyzed by *cis*-bisglycinato copper(II) complex. A new property of thermoelectric sensor from the polynanilines as well as from dihydroxy aggregates prepared by this method is also described.

Results and Discussion

Phenol reacts with hydrogen peroxide in the presence of a catalytic amount of *cis*-bisglycinato copper(II) monohydrate [abbreviated as Cis-Cu] to give hydroquinone and catechol (eq 1). The products of this reaction, hydroquinone (**1**), catechol (**2**), and unreacted phenol were obtained in the form of a stable hydrogen-bonded aggregate. Phenolic compounds are known to form aggregates,[17] and we had confirmed such aggregation by recording GPC and MALDI spectra of the products. The MALDI spectra with high laser gain showed a broad *m/e* signal ranging from 602 to 1298 with maximum intensity mass at 864. The ^{1}H NMR had three sets of hydroxy signals appearing at δ 8.5, 8.0, and 7.8 arising from hydroquinone, catechol, and phenol, respectively. The ^{13}C{^{1}H} NMR signals of the aggregate of a freshly prepared sample at room temperature (Figure 1a) showed a lesser number of signals. However, the same sample upon heating resulted in degradation of the aggregate and gave the ^{13}C{^{1}H} NMR signals from each individual entity, namely phenol, catechol, and hydroquinone (Figure 1b). The hydroquinone and catechol from these aggregates could be purified by column chromatography, but the recovery of the compounds was <10%. In these reactions further oxidation of hydroxylated compounds was not significant. The yields of hydroxylated derivative were found to be dependent on the catalyst concentration. The results are listed in Table 1. It also includes a comparison of the results of a few other well-established procedures on similar hydroxylations by other catalysts. The reaction of 2,6-dimethylphenol with hydrogen peroxide and a catalytic amount of Cis-Cu gives hydroxylated compound along with 2,6-dimethylbenzoquinone (~5%). The hydroxylated product was obtained as an aggregate of 2,6-dimethylphenol and 1,4-dihydroxy-2,6-dimethylbenzene (**3**); it had six ^{13}C{^{1}H} NMR signals of which the signals at δ 115, 122, and 151 were assigned to **3**. The 2,6-dimethylphenol could also be hydroxylated by aqueous hydrogen peroxide with a catalytic amount of copper(II) acetate monohydrate.

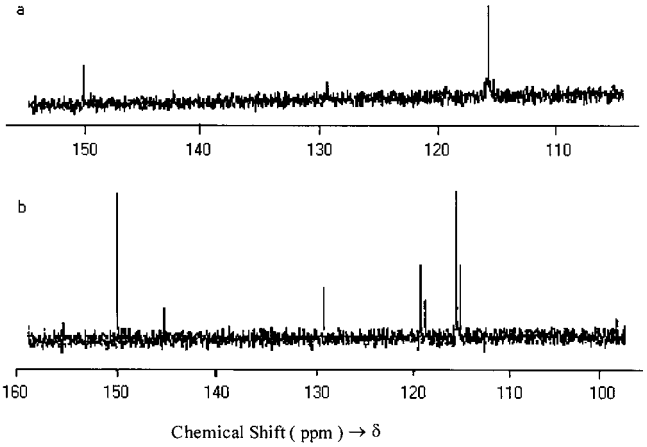

Figure 1. (a) ^{13}C{^{1}H} NMR of the aggregate obtained from phenol by hydroxylation. (b) ^{13}C {^{1}H} NMR of the same aggregate that was heated to 100 °C prior to recording NMR.

Table 1

name of catalyst	phenol/ catalyst (mmol)	hydroquinone: catechol	phenol convn, %
cis-bisglycinato copper(II)	10/0.125	54:46	29
cis-bisglycinato copper(II)	10/0.23	54:46	47.4
cis-bisglycinato copper(II)	10/0.38	54:46	44
$Pt(CF_3)(P-P)(OPh)$[18]	6/0.006	7:55	–
P−P = diphosphenoethane $(C)_4PMo_{11}VO_{40}$[19a]	–	84:16	12
C = cetylpyridinium cation zirconium phosphate/ acetic acid[19b]	–	1.4:1	26
titanium silicate[20]	–	1:1	26.8
ketone/acid[21]	–	1:1.5	5
$H_3PO_4/HClO_4$[21]	–	1:1.5	5

A solution containing phenol with *cis*-bisglycinato copper(II) monohydrate and hydrogen peroxide showed formation of an isosbestic point at 304 nm in UV−visible spectroscopy. A lack of any well-defined absorption maxima had prevented us from making further kinetic study. However, a solution containing *o*-cresol, Cis-Cu, and H_2O_2 showed growth of a well-defined peak at 412.4 nm. This absorption initially grew to a maximum value and decayed slowly as the hydrogen peroxide got consumed in the reaction (Figure 2). The final products obtained from *o*-cresol did not possess absorption at this wavelength. Thus, the origin of the absorbance at 412.4 nm could be from an intermediate species that took part in the reaction. Linear increase in the rate of formation of the intermediate species upon increase in [H_2O_2] as well as [Cis-Cu] were observed (Figure 3).

There was a significant difference in the reactivity in *cis*-bisglycinato copper(II) and *trans*-bisglycinato copper-(II) complex in these hydroxylation reactions. A solution comprising *o*-cresol, *trans*-bisglycinato copper(II) monohydrate, and H_2O_2 in water upon reaction also showed growth of absorbance at λ_{max} 412.4 nm. All these factors

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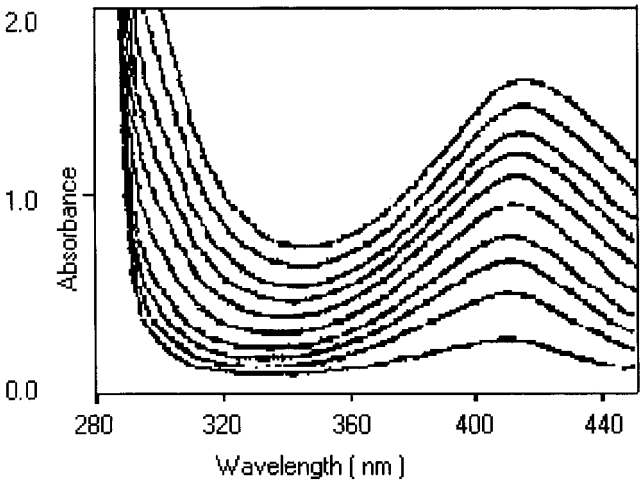


Figure 2. The growth of absorption maximum at 412.4 nm in a solution of *o*-cresol, hydrogen peroxide, and a catalytic amount of Cis-Cu.

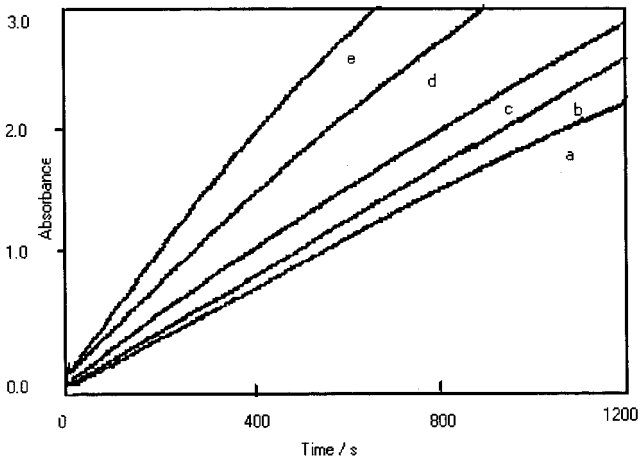


Figure 3. The change of absorbance vs time at 450 nm in the reaction of *o*-cresol (0.093 mmol) with Cis-Cu (0.0018 mmol) in 3 mL of water and H_2O_2 (30%, 100 vol). [H_2O_2] in (a) = 1 μL, (b) = 2 μL, (c) = 3 μL, (d) = 4 μL, (e) = 5 μL.

suggested that both reactions passed through a similar intermediate. Attempts were made to know about the existence of two different absorption maxima for intermediates in the reactions of *cis* and *trans* isomer from two independent experiments. The UV−visible spectra of a reaction mixture having both *cis* and *trans* complexes together did not give separate peaks. Taking the rate of increase in the absorption at 412.4 nm as the index of formation of the catalytic species for hydroxylation, we found that the rate of Cis-Cu-catalyzed reaction was 4.5 times faster than the *trans* counterpart under identical reaction conditions. The rate of a equimolar mixture of *cis* and *trans* isomer was 1.8 times faster than the *trans* isomer (Figure 4). The isomerization of *trans*-bisglycinato copper(II) in solution to Cis-Cu is a well-known phenomenon.[13] The active center of tyrosinase contains *cis*-histidines as ligands in the active site.[14] The phenoxy-linked galactose oxidase[7] also contains *cis*-histidines present in the active site. Generation of a dimeric oxo-bridged copper core having nitrogen ligands as the surrounding ligands is also established.[4a,16,22] Species

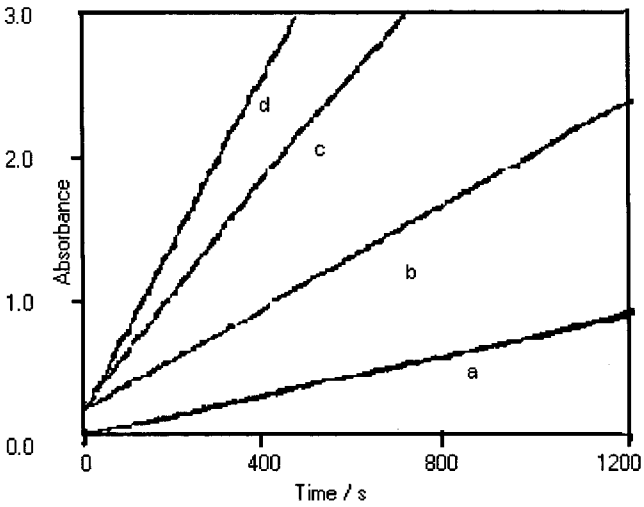
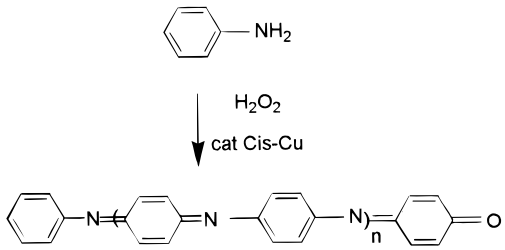


Figure 4. The change in absorbance vs time at 450 nm in the reaction of *o*-cresol (0.093 mmol) and H_2O_2 (30%, 100 vol, 5 μL) in 3 mL of water with Cis-Cu. [Cis-Cu] in (a) = 0.0045 mmol, (b) = 0.003 mmol, (c) = 0.0015 mmol, (d) = same as 1e but with 0.25 mL of acetonitrile.

containing phenolic groups attached at an axial position possess a characteristic absorption maximum in the region of 400−450 nm.[4a,16,22] Thus, the growth of the absorbance at 412.4 nm in the reaction of *o*-cresol with *cis*-bisglycinato copper(II) could be due to generation of a dimeric core of Cu_2O_2.[22] This kind of intermediate probably participates in hydroxylation of activated aromatic compounds and gets degraded after the reaction.

Reaction of aniline with hydrogen peroxide with a catalytic amount of *cis*-bisglycinato copper(II) gave polyanilines through C−N bond formation (eq 2). Several side



products were formed in the reaction, but only two major components of polyanilines were isolated. They were found to contain different amounts of $Cu(OH)_2$, which was formed during the reaction of the catalyst with hydrogen peroxide. The extent of oxidation of the rings to form C═N-bonded compounds in these cases was also different. The 400 MHz ^{1}H NMR of the two major components of polyaniline is shown in Figure 5. The other major component had a different number of $Cu(OH)_2$ molecules

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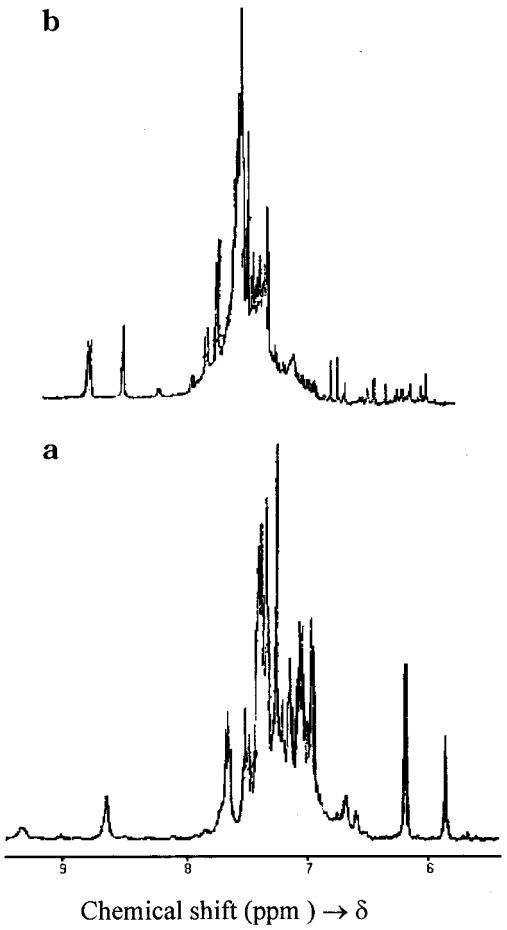


Figure 5. The 400 MHz ^{1}H NMR of two polyanilines: (a) = of **A**, (b) = of **B**.

attached per polyanilinic chain. The M_n and M_w values determined by GPC for these two polyanilines were 1040, 1250 and 1500, 1900, respectively. The mass spectra determined by MALDI suggest that the aggregate has a broad mass distribution from 1438 to 2134 in one case and from 1491 to 2503 in another. A clear difference in the IR spectra (Figure 6) of these two components of polyanilines in the region of 3300 cm^{-1} and also in the region of 1500−1700 cm^{-1} was observed. Due to C=O, C=N, and C=C stretching, several strong absorptions appear in the 1500−1700 cm^{-1} region. It is worth noting that polyanilines prepared by dehalogenative coupling reactions by catalytic reactions of nickel complexes have very simple absorption patterns[11b] in this region. This suggests oxidation of the C−NH linkages of the polyanilines to the C=N bond, leading to pernigraniline-type structures during oxidative coupling reactions. The nitrogen contents in the oligomers were lower than the calculated analytical value of polyaniline having an amino group at one end of the chain. But in both polyanilines they were close to the analytical values of a structure having carbonyl as an end group with residual

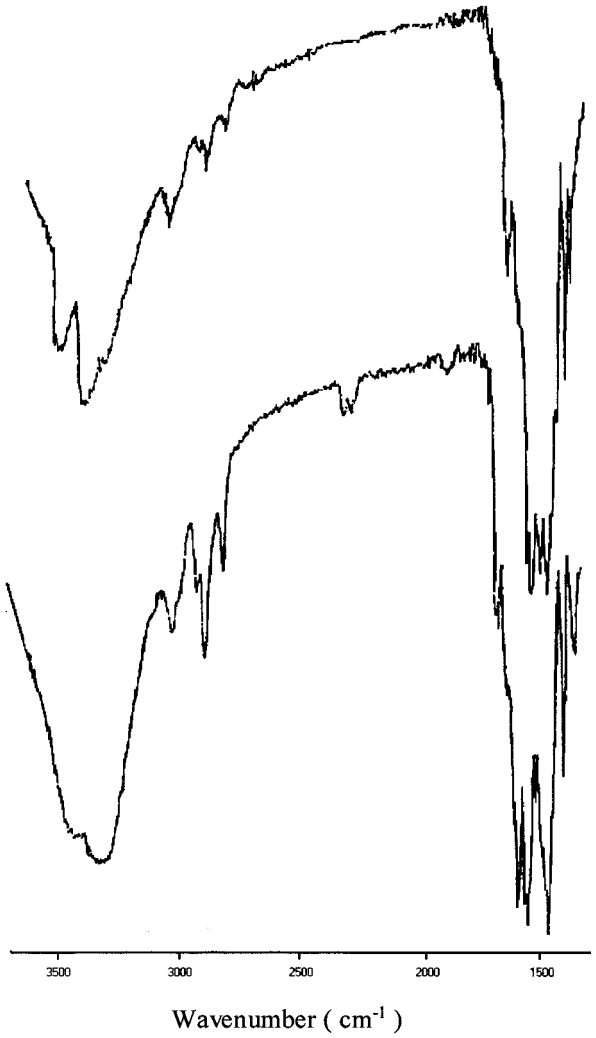
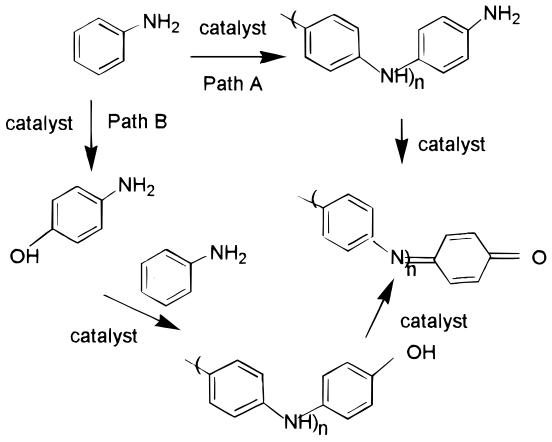


Figure 6. IR spectra of the polyanilines (a) = of **A**, (b) = of **B**.

$Cu(OH)_2$. This can occur through an oxidative hydrolysis of the NH_2 group to form a C=O group via a C=NH bond[26] (path A of eq 3). Another path can be through a



competitive hydroxylation and oxidative polymerization of aniline (path B of eq 3). Path A is preferred, as we had observed earlier that *p*-aminophenol itself did not

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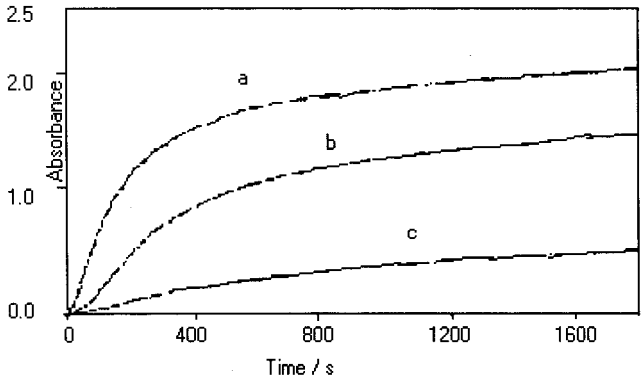

Figure 7. The change of absorbance vs time at 440 nm of solutions containing aniline (1 mg, 1.1 mmol) and H_2O_2 (3%, 100vol, 1 μL) in water (2 mL) and Cis-Cu. [Cis-Cu] in (a) = 1.04 mmol, (b) = 0.52 mmol, (c) = 0.10 mmol.

oligomerize under similar conditions but gave a copper-(II)-containing aggregate.[23a]

An absorption peak at 440.5 nm in the UV−visible spectra was observed in a solution of aniline and *cis*-bisglycinato monohydrate in water. The change of absorbance at this wavelength with different catalyst concentrations and by variation in the amount of hydrogen peroxide showed that as the copper concentration was increased the rates were enhanced (Figure 7). The absorption at 440 nm was increased to a maximum value after which the absorbance did not change significantly. This kind of variation on absorbance shows that the reaction involves consecutive reactions and involves an intermediate that decomposes to give product. They also indicate that an optimum concentration of hydrogen peroxide is required to accelerate the polyaniline formation. The preparation of polyaniline by hydrogen peroxide and anilinic compounds are known to be catalyzed by copper salts such as copper(II) sulfate, but the difference of our reaction from the reported one is the mild reaction conditions and the performance of the reactions without converting to the anilinium salt[11d,e] in which polyaniline was formed in the form of emeraldine base.

Polyanilines and polyphenolic aggregates described above have interesting electrical properties. The films prepared from each of them had a resistance profile which increased with temperature to a maximum value and then decreased to the original value, showing the property of a thermoelectric sensor.[23] The plot of resistance normalized to room-temperature resistance vs temperature of polyaniline (**B**) and that of the aggregate of the hydroxylated product of 2,6-dimethylphenol are shown in Figure 8. These profiles can be explained in terms of proton conductivity arising from extensive hydrogen bonding in the aggregates. These aromatic compounds can have significant π-interaction through a cation present[24] in the system. Although we do not have a quantitative picture on this, we have evidence that such an interaction can also lead to metallic properties in related systems. A system possessing inherent semiconducting properties competes with the proton conductivity present in the system. In polyaniline it can occur due to the proton conductivity present from the extended hydrogen bonding with a hydroxyl group attached to Cu-(II). Such hydrogen bonding gets disrupted upon supply of thermal energy, and the proton conductivity decreases. Above a particular temperature the proton conductivity

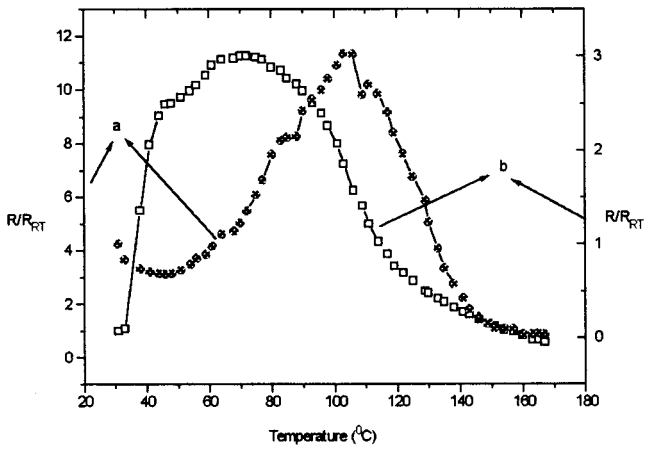

Figure 8. Plot of resistance (R) normalized to resistance at room temperature (R_{RT}) vs temperature of the (a) polyaniline **B**, and (b) aggregate obtained from the hydroxylation of 2,6-dimethylphenol.

becomes less significant, and the inherent semiconducting properties present[26] in the system due to delocalization of π-electron predominate.

In conclusion, this study demonstrates a mild, environmentally friendly method for hydroxylation of phenols as well as for oligomerization of anilines. The hydroxylated phenols and polyanilines form aggregates containing copper ions, and these aggregates have properties of a thermoelectric sensor.

Experimental Section

cis-Bisglycinato copper(II) monohydrate and *trans*-bisglycinato copper(II) monohydrate[13] were prepared by a published procedure. The kinetic studies were carried out by mixing a requisite amount of Cis-Cu and phenolic compound in water or acetonitrile followed by adding hydrogen peroxide to the reaction mixture in a quartz cell (cap. 3 cm^3) and carrying out the time and wavelength scan of the solutions at ambient condition. In the reaction where *o*-cresol was used as one of the reactants, the kinetics at 450 nm were recorded in a time scan mode with a variation of concentration of Cis-Cu and hydrogen peroxide to make the study uniform.

Reaction of Phenol with Hydrogen Peroxide Catalyzed by Cis-Cu. *cis*-Bisglycinato copper(II) monohydrate (50 mg, 0.225 mmol), phenol (473 mg 5.32 mmol), and H_2O_2 (1 cm^3, 30%) were mixed together in a flask and stirred at room temperature. The white paste obtained slowly turned brown, and the color intensified with time. After 24 h of continuous stirring, the reaction mixture was washed several times with petroleum ether (4 × 20 cm^3) to obtain a paste, and this paste was washed with water (1 cm^3) and dried in evacuated desiccator to obtain a black solid (0.24 g). IR (film) 3297 (s), 2930 (s), 1749 (s), 1618 (s), 1593 (s), 1456 (s), 1357 (s), 1214 (s), 1090 (s), 835 (s), 741 (s) cm^{-1}. ^1H NMR (DMSO-d_6) δ 8.5 (s), 8.0 (s), 7.8 (s), 6.7−7.5 (m). $^{13}C\{^1H\}$ NMR (DMSO-d_6) δ115, 116, 119, 120, 129, 145, 150, 155. Anal. Found: C, 54.63, H, 3.74, N, 1.24, ash 4.7.

Reaction of *o*-Cresol. Similar reaction of *o*-cresol (540 mg, 5 mmol) with hydrogen peroxide (1 cm^3, 30%) and *cis*-bisglycinato copper(II) monohydrate (50 mg, 0.225 mmol) gave 2,5-dihydroxytoluene in 98% yield. ^1H NMR (acetone-d_6) δ 2.4−2.2 (m, 3H), 6.5−7.5 (m, 3H), 8.3 (broad s, 1H); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 15.02, 114.47, 119.19, 126.46 130.48, 148.10, 155.70; IR (neat) 3390 (bs), 2918 (w), 1730 (m),1612 (s), 1512 (s), 1214 (s), 810 (s). GPC average (M_n, M_w) 1380, 2175. Anal. Calcd for $C_7H_8O_2$: C, 67.74, H, 6.4. Found: C, 67.29, H, 5.93.

Reaction of 2,6-Dimethylphenol. Similar reaction to that described above but carried out at 70 °C for 4 h with 2,6-dimethylphenol (5 mmol) yielded a mixed aggregate of 1,4-

dihydroxy-2,6-dimethylbenzene and 2,6-dimethylphenol in a yield of 31%. IR (KBr) 3472 (bs), 2919 (s), 1719 (s), 1659 (s), 1600 (s), 1480 (s), 1200 (s), 1029 (s), 886 (m) cm^{-1}. ^1H NMR δ (DMSO-d_6) 7.9 (s, 2H), 7.2 (s, 2H), 2.6 (s, 6H) from the dihydroxy compound, and 7.15−7.3 (m), 2.4 (s) from the monohydroxy part. $^{13}C\{^1H\}$ NMR δ 151, 139, 133, 130, 127, 122, 115. Anal. Found: C, 62.49, H, 4.84, ash, 9.4.

Reaction of Aniline. A well-stirred reaction mixture containing aniline (930 mg, 10 mmol), *cis*-bisglycinato monohydrate (50 mg, 0.225 mmol), and hydrogen peroxide (1 cm^3, 30%) was stirred at room temperature for 4 h. The reaction mixture turned black. Concentration of the reaction mixture under vacuum at room temperature gave a black paste. The paste was washed with petroleum ether (2 × 15 cm^3) (60−80 °C). The residue (368 mg, 40%) thus obtained was purified by column chromatography to afford major components polyaniline **A** and **B** in a ratio 2:1.6.

The analytical and spectral data of polyaniline **A**: Anal. Found: C, 73.97, H, 5.38, N,10.87. Anal. Calcd for $[(-C_6H_4N-)_5(-C_6H_4O)\cdot 0.4\{Cu(OH)_2\}]_n$ C, 73.02, H, 4.62, N, 11.35. ^1H NMR ($CDCl_3$) δ 5.8 (s), 6.8 (d, J = 8 Hz), 6.6−7.8 (m), 8.7 (s), 9.4 (s); IR (neat film) 3341 (bs), 3072 (m), 2931 (m), 1641 (s), 1601 (s), 1507 (s), 1447 (s), 1393 (m), 1299 (m), 761 (s), 694 (s) cm^{-1}. MALDI mass (m/z) 1438 to 2134.

The analytical and spectral data of polyaniline **B**: Anal. Found: C, 65.5, H, 4.95, N, 11.86. Anal. Calcd for $[(-C_6H_4N-)_5(-C_6H_4O)\cdot Cu(OH)_2]_n$ C, 65.27, H, 4.35, N, 10.15. ^1H NMR ($CDCl_3$) 6.8−7.8 (m), 8.4 (s), 8.7 (s). IR (neat film) 3308 (bs), 2925 (s), 2851 (m), 1689 (s), 1608 (s), 1541 (s), 1501 (s), 1313 (s), 762 (s), 702 (s) cm^{-1}. MALDI mass (m/z) 1491−2503.

Acknowledgment. We are thankful to Prof. P. Balaram of Indian Institute of Science, Bangalore, for mass spectra, Prof. K. Osakada of Tokyo Institute of Technology for gel permeable chromatography, Dr. A. Srinivasan of our Institute for help with resistivity measurement, and Sophisticated Instrumentation Facility, Indian Institute of Science, Bangalore, for use of the NMR facility.

JO991509J