

Catalytic Effects of Selected Transition Metal Ions in the Synthesis of Lignosulfonic Acid Doped Polyaniline

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ABSTRACT: Lignosulfonic acid doped polyaniline (LIGNO-PANI) is a water-dispersible conducting polymer. The incorporation of dopants to achieve higher conductivities in addition to lignosulfonates during the polymerization process results in prohibitively long initiation times. A variety of transition metal ions including silver and ferrous ions were studied as potential catalysts for the reaction. Silver nitrate was found to have superior catalytic properties followed closely by ferrous sulfate heptahydrate. The effects of these ions on the synthesis of LIGNO-PANI with methanesulfonic acid (HMSA) as an additional dopant (MSA-LP) and on the synthesis of MSA-PANI were studied via poten-

tial profile monitoring. The LIGNO-PANI derivatives produced by the catalyzed reaction demonstrated no negative effects on the conductivity (10–15 S/cm) or dispersibility. In addition, residual metal analysis indicated that, although not much iron remained (<0.01%) in the product, a large amount of silver was present (1.8%) in the final product. X-ray diffraction analysis was used to determine the identity of the silver containing moieties in the products. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 29–33, 2005

Key words: lignosulfonic acid; polyaniline; transition metals; catalysts; potential profile; water dispersible

INTRODUCTION

The synthesis of inherently conducting polymers (ICPs) has become an appealing area of research since the discovery of electrically conducting conjugated polymers.¹ Polyaniline (PANI) is an ICP that has been widely explored because it is relatively cheap and easy to synthesize. Although applications of PANI are imminent in many fields, a disadvantage in the use of PANI is the insolubility of most emeraldine salts in water as well as most organic solvents.² Lignosulfonic acid doped PANI (LIGNO-PANI)³ is one of the only water- and solvent-dispersible PANIs commercially available on a mass scale in the United States. The synthesis of LIGNO-PANI is environmentally friendly because lignosulfonates are a derivative of the paper industry and represent an abundant renewable resource. The incorporation of the highly soluble lignosulfonate macromolecule provides dispersibility in a wide range of solvents and resins without significantly decreasing the conductivity (3–4 S/cm).

Although lignosulfonic acid functions as both a template for polymerization and a dopant, properties such as conductivity may be improved by the use of an additional dopant [e.g., methanesulfonic acid (HMSA) and

p-toluenesulfonic acid (pTSA)] added prior to polymerization. These additional dopants may also lead to improved compatibility in host solvents and resins.⁴ However, the time required for bulk polymerization in the presence of lignosulfonates and some additional dopants is prohibitively long (more than 2 h in some cases). This is significantly longer than the typical time required for bulk polymerization in the absence of additional dopants, which is less than 30 min. Although bulk polymerization time can be shortened by increasing the temperature, previous studies have shown that increased temperature results in lower molecular weight PANIs with more defect sites.⁵

Persulfate is the most common oxidant used for the synthesis of PANI. In some unrelated studies, Ag(I) has been found to exhibit catalytic effects in the presence of persulfate for the decarboxylation of acids.⁶ The Ag(II) ion has also been shown to form reactive intermediates during reactions involving persulfate.^{6,7} In addition, the Ag(III) ion formed from a 2e⁻ transfer in the dissociation of persulfate may be stabilized by the formation of complexes. These complexes have also been shown to possess oxidative capabilities in the decarboxylation of acids.⁷ Other studies have shown that ferrous ions promote oxidation when used in conjunction with hydrogen peroxide (Fenton reagent)⁸ and have demonstrated catalytic effects in the polymerization of methyl methacrylate.⁹ Catalytic effects using iron ions for the polymerization of aniline have also been observed in conjunction with ozone¹⁰

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and persulfate, a more traditional oxidant.¹¹ In some instances a transition metal has been shown to impede the polymerization of aniline.¹² Therefore, in this study, several transition metal ions were explored as possible catalysts in the polymerization of aniline by sodium persulfate.

EXPERIMENTAL

Synthesis of PANIs

LIGNO-PANI with HMSA as an additional dopant (MSA-LP) was synthesized by dissolving 0.25 g of sodium lignosulfonate (Reax 825E from Westvaco) in 25 mL of 1M HMSA. One milliliter (0.011 mol) of distilled aniline was then added to the reaction mixture. The reaction was cooled to $\sim 0^{\circ}\text{C}$. Then, 0.0011 mol of the different metal salts dissolved in water was added followed by 2.62 g (0.011 mol) of sodium persulfate (Aldrich). The reaction was carried out overnight and then vacuum filtered through a Whatman #4 filter paper. The wet cake was washed with distilled water until the filtrate was clear. Two successive washings of the cake with 1M HMSA were performed. The cake was dried under a vacuum. HMSA doped PANI (MSA-PANI) was synthesized in a similar manner in the absence of lignosulfonates. Dedoping of the PANIs was accomplished by stirring the solids in 1M NaOH, filtering through a Whatman #4 filter paper, and washing with distilled water until the filtrate was neutral. The resulting solids were dried under a vacuum.

Electrochemical monitoring during chemical polymerization

A two electrode system was employed for the electrochemical measurements. A glassy carbon electrode was used as the working electrode and a silver/silver chloride electrode (SSCE) was used as the reference. In order to ensure that the chemical polymerization products did not affect the porosity of the frit, the SSCE was placed in a separate vessel containing a saturated KCl solution and connected to the system via a Luggin capillary capped with a semipermeable membrane. The electrodes were connected to an EG&G PAR 283 potentiostat. The software used to collect the data was an open circuit monitoring program within the SoftCORR corrosion measurement software. Potential measurements were collected at 30-s intervals starting 5 min before the addition of persulfate. The reactions were monitored for a total of 24 h. Control profiles were obtained for persulfate in the presence of catalytic amounts of silver and iron ions under the same reaction conditions prescribed above with and without lignin. The time at which the maximum potential was achieved was shortly after the addition of persulfate (at 5 min). The maximum potentials of the controls with no catalyst, ferrous sulfate heptahy-

drate, and silver nitrate without lignin were approximately 0.81 (~ 9 min), 0.85 (~ 9 min), and 1.55 V (~ 9 min), respectively. The maximum potentials of the controls with no catalyst, ferrous sulfate heptahydrate, and silver nitrate with lignin were approximately 0.62 (~ 13 min), 0.71 (~ 18 min), and 1.05 V (~ 75 min), respectively. The control potential profile for silver nitrate in the presence of lignin continued to rise and was stopped at 75 min because the polymerization of aniline would have occurred during this time.

Conductivity measurements

The conductivity values were obtained for pressed pellets (1.3-cm diameter, <1-mm thickness) using an Alessi 4-point conductivity probe connected to a Keithley electrometer and a Keithley programmable current source.

Spectroscopic analysis

A Nicolet MAGNA-IR 550 Series 2 spectrometer was used to acquire the FTIR spectra of the doped and dedoped samples as pressed pellets in KBr. A Perkin-Elmer UV-visible-near IR Lambda 19 spectrometer was used to acquire the spectrum of the doped samples in distilled water and dedoped samples in DMSO.

X-ray diffraction (XRD) analysis

Powder XRD patterns were obtained using a Rigaku Geigerflex X-ray generator equipped with a goniometer of $2\theta/2\theta$ geometry, a graphite monochromator, and a spinning sample holder. Data were collected in step scan mode (step size $0.05^{\circ} 2\theta$, 2 s/step, range = $10\text{--}75^{\circ} 2\theta$) using Cu $K\alpha_1$ radiation.

Analysis of residual metals

The dry samples catalyzed with silver nitrate and ferrous sulfate heptahydrate were digested using HCl/HNO₃ in a CEM microwave digestion system. The metal content was analyzed using a Perkin-Elmer Optima 4310 DV ICP-OES.

RESULTS AND DISCUSSION

The effect of the catalyst was initially evaluated based on the first appearance of an observable green color, which is indicative of the formation of PANI. Although this gave an approximate time for the initiation of polymerization, it was later realized from the electrochemical measurements that there was a significant time lag between the observable color change and the actual bulk polymerization. Bulk polymerization was defined by Manohar et al. as the rapid polymerization of aniline accompanied by an exotherm.¹³

TABLE I
Times Required for Observable Color Change and Conductivity of MSA-LP for Various Transition Metal Salt Catalysts

Transition metal salt	Time color change (min)	Conductivity (S/cm)
CuSO ₄ · 5H ₂ O	245	9.8
Ce(NO ₃) ₃ · 6H ₂ O	225	11.1
Co(NO ₃) ₂ · 6H ₂ O	225	9.8
Cu(NO ₃) ₂ · 2.5H ₂ O	210	6.7
CuBr	135	9.2
No catalyst	130	10.8
FeCl ₃ · 6H ₂ O	30	9.7
Fe(NO ₃) ₃ · 6H ₂ O	30	11.8
FeCl ₂ · 4H ₂ O	15	10.7
FeSO ₄ · 7H ₂ O	15	9.0
AgNO ₃	10	9.9

Table I lists the time required for an observable color change from brown to a deep green during the synthesis of MSA-LP in the presence of several transition metal salts. Of the metal salts listed in Table I, only the iron and silver salts were found to significantly decrease the time required for a color change. Even though ferrous and ferric ions reduced the time required for a color change to occur, the former was twice as effective as the latter. Silver nitrate was found to be the most effective catalyst. The conductivities of the products (Table I) were not significantly affected by any of the metal salts.

The mechanism of catalysis in the synthesis of LIGNO-PANI has not yet been elucidated. Previous studies by Fong et al. indicate that the mechanism of catalysis is the formation of a more efficient oxidizing species (i.e., the metal cation) by the persulfate.¹⁴ However, the study by Fong et al.¹⁴ is significantly different than the study being reported here. They focused only on varying the ratio of ceric ions to persulfate while keeping the total concentration of oxidant steady.¹⁴ Other studies using metals for catalytic effects kept the amount of persulfate constant while varying the amount of the cation.^{6,7} Based on the results from these studies, all catalysts were initially added in a 1 : 10 molar ratio of catalyst to a constant amount of persulfate. Varying molar ratios of silver nitrate to persulfate were also studied to identify the optimum ratio for the catalysis of the synthesis of MSA-LP. Figure 1 is a graph of the time required for color change in the reaction as a function of the molar ratio of silver nitrate to persulfate. The results indicate that a 1 : 10 ratio is optimal because no significant decrease in initiation time is seen at higher ratios. All potential profile studies were conducted using this molar ratio of catalyst/persulfate.

Results from electrochemical monitoring

Although an approximation of the initiation time can be obtained visually, the exact time of bulk polymerization

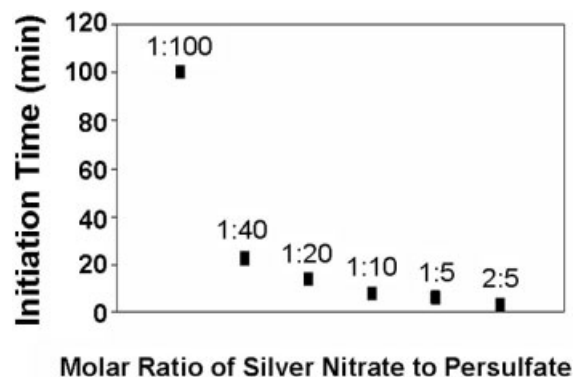


Figure 1 The time required for color change for MSA-LP as a function of the molar ratio of silver nitrate to sodium persulfate.

can be clearly seen in the potential profile. Both silver nitrate and ferrous sulfate heptahydrate exhibited significant catalytic effects in the preparation of LIGNO-PANI. A more accurate analysis of the effect of these salts on the MSA-LP reaction and the MSA-PANI reaction was accomplished via potential profile monitoring. Previous studies of the electrochemical reaction of aniline polymerization have offered help in the dissection of the potential profiles.^{15,16} The potential profiles for this study can be seen in Figures 2 and 3.

The first rise in potential can be labeled as the induction period during which time the sodium persulfate quickly dissociates to form sulfate radicals that oxidize the aniline species.^{15,16} The induction period is followed by a period labeled as the plateau period during which time the oxidized form of PANI (also known as pernigraniline) begins to form. During bulk polymerization the remaining aniline in solution is oxidized by pernigraniline to form PANI in the emeraldine state. The reduction of the pernigraniline to the emeraldine state results in a sharp decrease in potential.^{16,17}

When lignosulfonates are used as the dopant/tem-plate, the time required for the bulk solution to begin

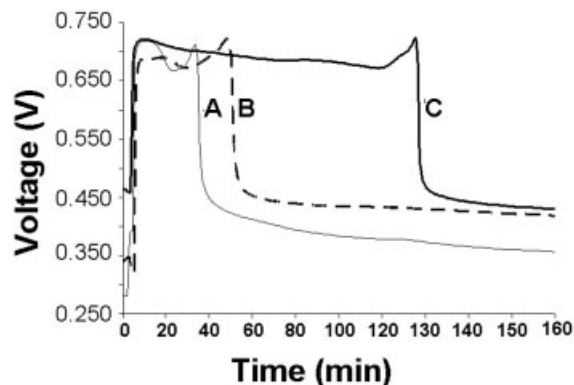


Figure 2 The potential profile of silver nitrate catalyzed MSA-LP (curve A), ferrous sulfate heptahydrate catalyzed MSA-LP (curve B), and MSA-LP with no catalyst (curve C).

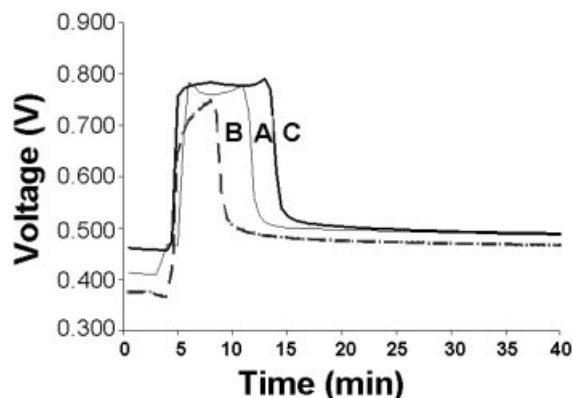


Figure 3 The potential profile of silver nitrate catalyzed MSA-PANI (curve A), ferrous sulfate heptahydrate catalyzed MSA-PANI (curve B), and MSA-PANI with no catalyst (curve C).

polymerization (~27 min) is longer than traditional reactions such as the synthesis of HCl-PANI (~2–3 min). The increase in time required for bulk polymerization is acceptable because the product has superior processibility. A possible explanation for the increased time is the attraction of the anilinium salt to the polyaromatic lignosulfonate macromolecule, which results in increased steric hindrance. This may delay the oxidation of the anilinium salt via persulfate and subsequent formation of a dimer, which has been shown to be the rate limiting step.¹⁷ In addition, it is also known that lignosulfonates are radical scavengers.¹⁸ This could result in a lower effective concentration of persulfate and therefore decrease the concentration of anilinium radical cations.

The time required for bulk polymerization of aniline in the presence of lignosulfonates and some additional dopants (i.e., HMSA and pTSA) is prohibitively long (~130 min). In addition to the steric hindrance of the lignosulfonate previously discussed, the sulfonic acid groups of the additional dopants, which themselves may associate with lignin species and which protonate the amine, may further impede the oxidation of aniline. Further studies may indicate that, as the functionality of the acid is varied, the initiation time may vary.

As indicated by the potential profiles, the addition of silver nitrate or ferrous sulfate heptahydrate significantly shortens the plateau period. This appears to support the idea that the metal cation is a more effective oxidant because of its smaller size. Building on ideas previously published by Fong et al.,¹⁴ Scheme 1 illustrates the mechanism by which the metal cation can act as an oxidant in the polymerization of aniline. As the persulfate dissociates, metal cations are promoted to a higher oxidation state (M_{ox}). The cations (M_{ox}) begin to oxidize the aniline to dimers and/or oligomers, resulting in a reduced form of the metal cation (M_{red}). M_{ox} can be regenerated from M_{red} via

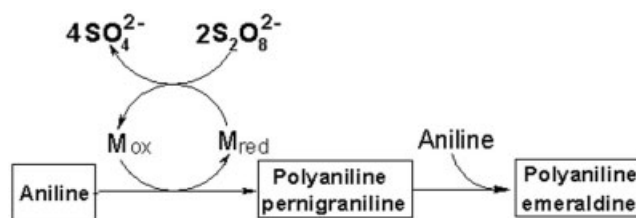
persulfate. Once the dimers or oligomers are present, further oxidation can occur via M_{ox} , resulting in the pernigraniline species. Once the persulfate is consumed, and the metal oxidant can no longer be regenerated, the remaining aniline in solution can be oxidized by the pernigraniline and results in PANI in the emeraldine state. This mechanism of polymerization has been labeled reactivation chain polymerization by Wei.¹⁹

The effect of the metal salts on the polymerization of aniline in the absence of lignosulfonates was also studied. The dopant used in this study was MSA, the same additional dopant used in the MSA-LP studies. As seen in the MSA-PANI reactions (Fig. 3), ferrous sulfate heptahydrate is more effective in decreasing the time for bulk polymerization than silver nitrate. The difference in catalytic effects may be attributed to steric factors because the nonhydrated atomic radius of an iron ion is smaller than a silver ion. Although this is true, ferrous sulfate heptahydrate did not exhibit better catalytic effects than silver nitrate in the synthesis of MSA-LP (Fig. 2). Lignosulfonates have been shown to easily form complexes with iron species.²⁰ This would result in a lower concentration of free catalyst, affecting the time required to reach bulk polymerization. Work is ongoing to confirm this hypothesis.

Spectroscopic characterization of PANIs

The PANIs synthesized in this study were characterized by UV-visible and FTIR spectroscopy. The UV-visible spectra of the doped MSA-PANI and MSA-LP samples in water exhibited absorption peaks at ~460 and ~850 nm that are characteristic of the bipolaron and polaron transitions of doped PANI, respectively. The UV-visible spectra of the dedoped samples in DMSO also exhibited expected peaks characteristic of an emeraldine base at ~320 ($\pi-\pi^*$) and ~600 nm (quinoid unit). The dedoped silver and iron catalyzed MSA-LP spectra displayed peaks that are consistent with a PANI base in a slightly higher oxidation state according to Masters et al.²¹

Further FTIR characterization of the dedoped products supported the presence of PANI in a slightly higher oxidation state when silver and iron catalysts



Scheme 1 The proposed mechanism of metal catalyzed polymerization of aniline.

were used. The peaks at $\sim 1500\text{ cm}^{-1}$ (benzenoid ring stretch) and $\sim 1600\text{ cm}^{-1}$ (quinoid ring stretch) can be used to estimate the degree of oxidation of the polymer; the benzenoid stretch is generally more intense in the emeraldine oxidation state.²² When compared to the FTIR of PANI synthesized by conventional means, both silver and iron catalyzed MSA-PANI and MSA-LP samples showed increased absorption at 1600 cm^{-1} relative to 1500 cm^{-1} . The presence of an overoxidized contaminant is most likely a result of the increased reaction rate.

Elemental metal formation

At the end of the reactions catalyzed by silver nitrate, the formation of a metallic silver precipitate within the reaction vessel was observed. Lignosulfonates contain some *ortho*-catechol moieties that are known to complex metal species readily and aid in the recovery of metals from metal sulfate, nitrate, and oxide containing compounds.^{15,23} The redox capability of the PANI chain can also aid in the recovery of precious metals.^{15,24} Future studies will focus on the effectiveness of lignosulfonate doped ICPs for precious metal recovery.

XRD analysis

The XRD patterns were analyzed to determine if any silver moieties were being incorporated into the polymer as well as the identity of the precipitate. The three major peaks observed in the precipitate correspond to the (111), (200), and (220) planes of metallic silver. The peaks present in both the dry MSA-LP and MSA-PANI products indicate the presence of elemental silver as well as some unidentified silver salts.

Residual metal analysis

As mentioned, there is a dramatic difference between the amount of silver and iron in the respective products. Residual metal analysis was performed on polymer products allowed to stir for approximately 17 h after bulk polymerization. Only a trace amount of iron was left in the final polymer matrix ($<0.01\%$) compared to about 1.8% silver. Because silver has a favorable reduction potential, it is more likely to exist in the solid elemental state but may also exist as insoluble silver salts that can be occluded in the polymer matrix. As the contact time between the ICP product and silver cations increases, it appears that more silver is incorporated into the polymer matrix. However, because the formation of elemental iron is not favorable, iron cations will remain in the more stable and soluble Fe(II) state. The majority of these soluble species are removed during the washing process. The small amount of iron that remains as indicated by residual metal analysis is most likely in the form a ferrous-

lignosulfonate complex. Although silver is highly conducting, no effect on the conductivity of the resulting polymer can be observed, presumably because of the extremely low volume content of the silver particles.

CONCLUSION

The catalytic effects observed in this research proved useful in the reduction of reaction times for the synthesis of LIGNO-PANI in the presence of additional dopants. The data suggested that both silver and iron function effectively as catalysts. The catalysts reduced the time required for bulk polymerization up to 10-fold. The results from the MSA-PANI studies indicated that ferrous sulfate heptahydrate was more effective than silver nitrate. This supports the hypothesis that the steric hindrance of the anilinium salt is the inhibiting factor when large oxidants, such as sulfate radicals, are used. Because of their smaller sizes, Fe(II) and Ag(I) were shown to overcome these steric factors and act as effective catalysts in the oxidative synthesis of LIGNO-PANI.

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