

SYNTHESIS OF CONDUCTIVE POLYANILINE VIA OXIDATION BY MnO_2

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Abstract A unique process of chemical oxidation polymerization of aniline using manganese dioxide (MnO_2) as the oxidizing agent in an aqueous medium is described. The reaction between aniline and MnO_2 follows a mechanism by which the organic monomer is oxidized while the metal oxide undergoes reductive dissolution. The effects of the amount of oxidizing agent and aniline, pH and temperature of the reactive system, type of acid on the yield and conductivity of polyaniline are discussed. The resulting polyaniline was characterized by IR and UV-Vis spectrometry. Polyaniline with a conductivity of 12.5 S/cm was obtained using 0.033 mol of aniline oxidized by 0.023 mol MnO_2 in the presence of 100 mL of 2.7 mol/L HCl at 25°C for 4 h.

Keywords Conducting polymers, Heteroatom-containing polymers, Manganese oxide, Oxidation polymerization, Polyaniline

INTRODUCTION

Among intrinsically conductive polymers (ICPs), polyaniline (PANI) is regarded as one of the most promising practicable materials because of its environmental and thermal stability, its high electrical conductivity and its easy preparation from low-cost raw materials and reagents. A number of publications^[1–9] has appeared concerning the synthesis, structure, properties and applications of PANI. After more than twenty years of extensive research on PANI, many important advances^[10–13] have been made with respect to molecular design and materials synthesis, doping method and doping mechanism, solubility and processability. Conductive, optical, electronic, and magnetic properties and their mechanisms together with the investigation of its potential applications in technology have received a lot of attention^[14, 15].

The preparation methods of PANI can be classified into two categories: chemical and electrochemical oxidative polymerization. In the chemical oxidation^[16], aniline is oxidized by chemical oxidants, such as $(\text{NH}_4)_2\text{S}_2\text{O}_8$, H_2O_2 and FeCl_3 , in an aqueous acidic medium (HCl, H_2SO_4 , HClO_4). The properties of obtained PANI are directly affected by reaction conditions.

MnO_2 is a strong oxidant in acidic conditions with an electrochemical potential of 1.23 V and is widely used as chemical energy source. In the synthesis of conductive polymers, Gemeay *et al.*^[17] used the oxidative ability of MnO_2 in an acidic medium to synthesize composites of polypyrrole (PPy) and MnO_2 , and also used it as the cathode active material for a secondary lithium battery. In this composite, polypyrrole not only acts as an electrochemically active material but also as the conducting network for MnO_2 . The electrochemical efficiency of MnO_2 is higher than that of carbon black powder as conductive material in the battery.

However, whether MnO_2 can oxidize aniline to make it polymerize and the conductive properties of the obtained product are still a matter of debate. In an earlier report by Mazeikiene *et al.*^[18], it was stated that MnO_2

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could oxidize aniline to make it polymerize, but finally only a small amount of thus-prepared PANI has the structure of emeraldine type due to the strong oxidizability of MnO_2 . A large amount of the product is an alternative PANI with poor conductivity. Biswas *et al.*^[19] had a different opinion and stated in their article that MnO_2 can not directly induce pyrrole or aniline to polymerize. In order to improve the processability of conductive polymer PPy and PANI, they used colloidal MnO_2 (10–60 nm) as particulate dispersant and the conventional oxidants FeCl_3 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$ respectively for water dispersible conducting nanocomposites of PPy- MnO_2 and PANI- MnO_2 . MnO_2 was regarded as inert towards the oxidative polymerization of aniline. A result it was considered to combine totally with the conductive polymer.

In this paper, MnO_2 was chosen as the oxidant in the chemical oxidative polymerization of aniline because of its cheapness and its non-toxic, safe properties. Also MnO_2 has some interesting properties in the synthesis of conductive polymer. Indeed, MnO_2 is found to be a strong oxidant in acidic solution, which can induce aniline to polymerize. The reaction between aniline and MnO_2 follows the well-known mechanism by which MnO_2 undergoes reductive dissolution and the organic monomer is oxidized. The resulting content of MnO_2 in the PANI is low. This result is quite different from that of Biswas's nanocomposites^[19]. The electronic conductivity of our final product is similar to that of PANI prepared by $(\text{NH}_4)_2\text{S}_2\text{O}_8$.

EXPERIMENTAL

Materials

Aniline (Aldrich, 99%) was purified by distillation under vacuum and kept in a closed container in the dark before use. MnO_2 (A.R., China), hydrochloric acid (A.R., Merck, 32%) and ammonium peroxodisulfate (APS, Merck, extra pure) were used without purification. Deionized water was employed throughout the synthesis.

Synthesis of Polyaniline (PANI)

PANI was prepared by chemical oxidative polymerization of aniline in an aqueous acidic medium with MnO_2 as the oxidant. The molar ratio of MnO_2 to aniline ranges from 0.70 to 3.50, and the concentration of acidic medium ranges from 1 mol/L to 5 mol/L. Typically, 0.023 mol MnO_2 was suspended in 80 mL of 2.7 mol/L HCl aqueous medium with constant stirring, and the aniline acidic solution of 0.033 mol of aniline in 20 mL of 2.7 mol/L HCl was injected slowly into the reaction system. The reaction was performed at 25°C for 4 h. The resulting greenish black mixture was filtered, washed with 1 mol/L HCl solution till the filter liquor is colorless and no Mn^{2+} ion could be detected. The product was dried under vacuum at 50–60°C for more than 12 h.

PANI emeraldine base (EB) powder was prepared by dedoping the resulting PANI-HCl in an aqueous ammonium hydroxide solution, washed with water and dried under vacuum at 60°C.

Determination of the Residual MnO_2 in the PANI and of the Yield of PANI

The content of MnO_2 in the product (c_{MnO_2} %) was determined gravimetrically. The sample was heated under vacuum at 60°C to remove H_2O till constant weight (W_1) was obtained. Then, the sample was heated in an oven at 400°C to decompose the polymer until the weight (W_2) of residual MnO_2 was constant.

The content of MnO_2 in the product is calculated by Eq. (1) and the yield of PANI is calculated using Eq. (2):

$$c_{\text{MnO}_2} (\%) = \frac{W_2}{W_1} \times 100 \quad (1)$$

$$\text{PANI yield} (\%) = \frac{\text{Mass of product} \times (1 - c_{\text{MnO}_2} \%) }{\text{Mass of aniline}} \times 100 \quad (2)$$

Conductivity, IR and UV Measurements

PANI was powdered and pressed into a disk with diameter of 13 mm under a pressure of 300 kg/cm² for 1–2 min using the IR mould press instrument. The electrical conductivity of the specimens was measured at room

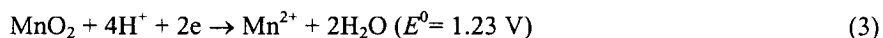
temperature by the standard four-point method using a SZ-85 electrometer (made in Suzhou, China). The IR spectrum of PANI in a KBr pellet was recorded on a Nicolet Magna IR 500 spectrometer. UV-Vis spectra were obtained from a JASCO 7800 UV-Vis spectrophotometer. The spectra were determined from 200 to 1100 nm. The samples were dissolved in formic acid, tetrahydrofuran, dimethyl sulfoxide, *N,N*-dimethylformamide, respectively.

RESULTS AND DISCUSSION

The chemical oxidative polymerization of aniline is usually carried out in the presence of oxidant, acid and water. Because the structure and properties of PANI are greatly affected by the reaction medium, such as acid type and its acidity, oxidant type, and reaction temperature, PANI with better conductivity can only be prepared under optimal reactive conditions. In this research work, MnO₂ was chosen as the oxidant and hydrochloric acid as the acidic medium to polymerize aniline. So far there is no detailed report about the synthetic conditions of polymerization of aniline by using MnO₂ as the oxidant and the properties of the obtained product. In contrast with the report of Biswas^[19], the results obtained from our experiments show that MnO₂ oxidation polymerization of aniline does take place.

Effect of Amount of MnO₂ on the Yield and Conductivity of PANI

It was described in the literature^[16] that oxidants (NH₄)₂S₂O₈, H₂O₂, KIO₃ and FeCl₃, could be used in the chemical oxidation polymerization of aniline. Owing to their standard chemical potential at the oxidation (E^0) (S₂O₈²⁻/SO₄²⁻ = 2.010 V, H₂O₂/H₂O = 1.776 V, IO₃⁻/I⁻ = 1.085 V, Fe³⁺/Fe²⁺ = 0.771 V) higher than that of aniline (*ca.* 0.7 V versus saturated calomel electrode), aniline is initiated and leads to polymerization. For MnO₂ in an acidic medium, the following semi-reaction occurs with the standard chemical potential of 1.23 V:



Because the condition of higher E^0 is satisfied, MnO₂ is able to oxidize aniline and leads to polymerization.

The mechanism of polymerization for aniline is a cation-radical oxidative polymerization^[16]. Aniline oligomers such as dimer and trimer are first produced in the initiation step. Subsequently, the reaction is significantly accelerated spontaneously, resulting in release of heat in the chain propagation reaction step. Finally the reaction proceeds quickly into the chain termination step. Oxidation reaction of aniline occurs at the interface between solid MnO₂ and the aniline-HCl aqueous solution when MnO₂ is used as the oxidant in contrast to chemical oxidative polymerization of aniline by water-soluble oxidant. MnO₂ accepts two electrons to become water-soluble Mn²⁺ salt while it initiates aniline. This salt can be washed away in the subsequent treatment process whereas the unreacted part of MnO₂ remains in PANI.

In general, the yield and conductivity of the obtained PANI depend upon the molar ratio of oxidant to aniline. The relation between initial molar ratio of oxidant/aniline and the yield and conductivity of the resulting polymer are shown in Table 1. As the molar ratio goes from 0.7 to 1.4, the yield of PANI increases from 72.8% to 97.4% and above this molar ratio it decreases (Fig. 1). The conductivity of PANI decreases gradually and finally becomes difficult to detect. Table 1 also shows that the residual MnO₂ in PANI increases with the ratio of MnO₂ to aniline.

Table 1. Effect of ratio of oxidant to aniline on the yield and electrical conductivity of PANI^a

Oxidant (g)	Molar ratio of MnO ₂ to aniline	MnO ₂ consumption in the reaction (%)	Residual of MnO ₂ in PANI (%)	Yield of PANI (%)	Conductivity (S/cm)
2	0.70	98.5	1.42	72.8	12.5
4	1.40	99.0	1.13	97.4	8.5
6	2.10	99.2	1.72	93.5	2.2
8	2.80	96.0	11.14	82.0	Undetected
10	3.50	81.8	42.45	80.6	Undetected

^a Reaction condition: aniline, 0.033 mol; 100 mL HCl of 2.7 mol/L, ~25°C; 4 h

On the other hand, the consumption of MnO_2 in the reaction varies with the same amount of aniline. When the MnO_2 /aniline molar ratio is increasing, the consumption of MnO_2 remains constant or slightly increasing until the value of the ratio is 2.10 and then it decreases rapidly. Almost complete consumption occurs at a ratio of 2.10. In this case, the residual MnO_2 in the PANI is very low. At the same time, the conductivity of the obtained PANI decreases greatly. This indicates that the molar ratio should be reasonably chosen so that the optimal ratio would induce the lowest residue of MnO_2 in the products, which leads to high yield and high conductivity. High molar ratio of MnO_2 to aniline is not favorable for obtaining high conductivity of PANI because of the insulating properties of residual MnO_2 in the polymer.

It was known^[13] that PANI exists in three well-defined oxidation states: leucoemeraldine, emeraldine and pernigraniline. Leucoemeraldine is the fully reduced state, with all the nitrogen atoms belonging to amine groups, denoted as $(1\text{S})_n$, whereas pernigraniline is the fully oxidized state, with all the nitrogen atoms belonging to imine groups, denoted as $(2\text{S})_n$. In emeraldine, both reduced and oxidized states exist together with the nitrogen atom ratio ~ 0.5 for amine to imine, denoted as $[(1\text{S})(2\text{S})]_n$, where 1S and 2S represent $(-\text{B}-\text{NH}-\text{B}-\text{NH}-)$ and $(-\text{B}-\text{N}=\text{Q}=\text{N}-)$, respectively. Here B represents a $-\text{C}_6\text{H}_4-$ ring in the benzenoid form and Q represents a $-\text{C}_6\text{H}_4-$ ring in the quinoid form. The emeraldine base $[(1\text{S})(2\text{S})]_n$ can be fully reduced to the leucoemeraldine $(1\text{S})_n$, and fully oxidized to the pernigraniline $(2\text{S})_n$. The conductive structure is the emeraldine salt (ES) which is obtained by protonation of the emeraldine base.

Mazeikiene^[18] reported that the product of aniline oxidized by MnO_2 is mainly an alternate polymer without the emeraldine structure. However, he did not explain the alternate polymer, either from the directly oxidized aniline polymerization or from the subsequent oxidation of emeraldine by an excess of MnO_2 . Indeed, our experiments show that the conductivity of the product is greatly dependent on the amount of MnO_2 which means that when the amount of MnO_2 is higher, the produced emeraldine in PANI is subsequently oxidized by the excessive MnO_2 , resulting with a drop of the conductivity of PANI. If the alternative PANI was formed during the polymerization instead of deoxidization from emeraldine, the conductivity of PANI would be kept at a low value without any drop with the enhanced molar ratio of MnO_2 /aniline.

Effect of Acidity of the Reaction System on the Yield and Conductivity of PANI

In general, the polymerization of aniline needs an acidic medium in order to obtain PANI with good properties and low defects with the aniline linked in the 1,4-coupling manner. If the medium is of low acidity, or is neutral, or alkaline, the conductivity of PANI is low. A certain pH is necessary for obtaining highly conductive products. In addition, the protons in the medium play an important role in the polymerization process. The acidic medium provides the H^+ for the reaction and meanwhile it protonates the backbone of PANI to make it conductive. Finally, it should be noted that the concentration of HCl has an effect on the chemical potential of $\text{MnO}_2/\text{Mn}^{2+}$, when MnO_2 is used as oxidant. The reduction of MnO_2 in an acidic medium is shown in Eq. (3). The relationship between the electrochemical potential for the redox couple $\text{MnO}_2/\text{Mn}^{2+}$ and the acidity is given by the Nernst equation:

$$E_{\text{MnO}_2/\text{Mn}^{2+}} = E^0_{\text{MnO}_2/\text{Mn}^{2+}} + \frac{0.0592}{2} \times \lg \frac{[\text{H}^+]^4}{[\text{Mn}^{2+}]} = 1.23 - 0.118 \text{ pH} \quad (4)$$

As predicted by Eq. (4), the higher the concentration of HCl is, the higher the oxidizing power of MnO_2 will be. The effect of concentration of HCl on the yield and conductivity of resulting PANI is presented in Table 2. On increasing the concentration of HCl from 1.0 to 5.4 mol/L, the yield of PANI decreases from ca. 72% to 46%. The conductivity reaches a maximum value of 12.5 S/cm at 2.7 mol/L HCl. The conductivity and yield of PANI show the same trend with the variation of acidity (Fig. 2). Because the chemical oxidative polymerization of aniline depends on both the amount of MnO_2 and the concentration of HCl, the yield and conductivity of the resulting PANI are affected by both of them. The optimal concentration of HCl ranges from 1.00 to 2.70 mol/L corresponding to the oxidant/aniline molar ratio 0.7. Out of this range, the conductivity would become lower. The trial experiments with low concentration of HCl (pH = 1, 2, 3, 4) indicate that in this case, the yield is low

and the conductivity of PANI is only 10^{-2} S/cm. In the lowest acidic medium, by-products such as azo-compounds are produced while at high acidity, the hydrochloric acid causes the substitution of chlorine atom on the phenyl ring of PANI, which affects the properties of PANI^[16]. In the meantime, the high oxidizability of MnO_2 induces the decrease of the yield and conductivity.

Table 2. Influence of pH on yield and electrical conductivity of PANI^a

Acid	Concentration (mol/L)	Consumption of MnO_2 in the reaction (%)	Percent of MnO_2 in PANI (%)	Yield of PANI (%)	Conductivity (S/cm)
HCl	1.0	96.0	3.50	71.8	5.3
HCl	1.35	96.5	3.18	71.2	5.2
HCl	2.7	98.5	1.42	72.8	12.5
HCl	4.05	99.5	0.31	59.0	5.2
HCl	5.4	100	0.11	45.8	2.1
HClO_4	1.0	-	-	82.7	12.0

^a Reaction condition: aniline, 3 mL; MnO_2 , 2 g; MnO_2 /aniline molar ratio = 0.7; aqueous acid 100 mL; $\sim 25^\circ\text{C}$; 4 h

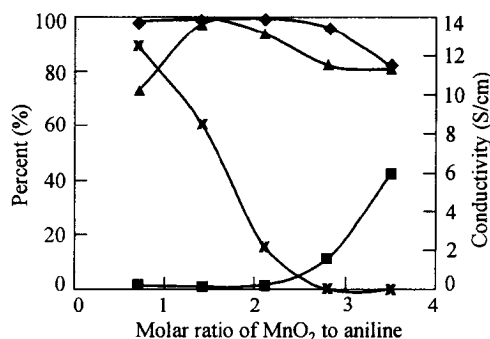


Fig. 1 Variation of consumption (◆) and residual (■) of MnO_2 and conductivity (×) and yield (▲) of PANI with molar ratio of MnO_2 to aniline

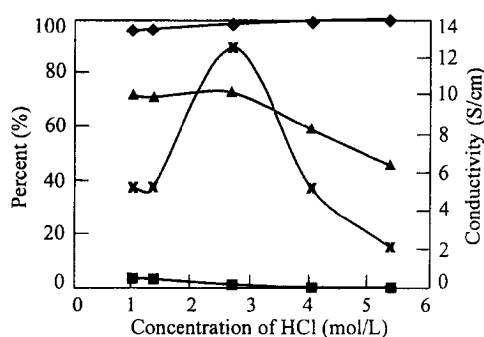


Fig. 2 Variation of consumption (◆) and residual (■) of MnO_2 and conductivity (×) and yield (▲) of PANI with concentration of HCl

Effect of Kind of Acid on the Yield and Conductivity of PANI

The polymerization of aniline can occur in different acids, such as HCl, H_2SO_4 , HClO_4 , HBr, CH_3COOH , HBF_4 , NH_2SO_3 and *p*-toluene sulfonic acid. HCl is usually used as the acid medium for its simplicity and attainable purity. PANI can be used as the cathode material of a rechargeable Li^+ -ion battery, in which the anion ClO_4^- is introduced into the backbone of doped PANI as the counter-ion. The synthesis of PANI in 100 mL of 1 mol/L HClO_4 with the MnO_2 /aniline molar ratio of 0.7 was also performed. The yield of 82.7% and conductivity of 12 S/cm were obtained which shows little difference from that of PANI synthesized in 1 mol/L HCl medium (Table 2). This indicates that HClO_4 is also a selected acid medium for the polymerization of MnO_2 and aniline.

Effect of Aniline Amount on the Yield and Electrical Conductivity of PANI

The effect of aniline amount on the yield and electrical conductivity of PANI is presented in Table 3 with a reaction condition of 2 g MnO_2 and 2.7 mol/L HCl. With increasing aniline contents from 2 mL (2.194×10^{-2} mol) to 6 mL (6.582×10^{-2} mol), the yield of PANI decreases from 91.2 to 53.5% (Fig. 3). This is because the polymerization of aniline is dependent on the amount of oxidant that is limited. With a large amount of aniline, there is not enough MnO_2 to oxidize it, therefore the yield of PANI is lowered. In contrast, the conductivity of the resulting PANI increases from 10.6 to 27.0 S/cm, which indicates more emeraldine PANI in the system^[20]. It is evident that a small amount of MnO_2 cannot oxidize the emeraldine structure and enables the PANI to keep its high conductivity.

Effect of Reaction Temperature on the Yield and Electrical Conductivity of PANI

The influence of reaction temperature on the yield and conductivity of PANI is given in Table 4. Comparing the yield and electrical conductivity at reaction temperatures of 10°C and 25°C, it is evident that the higher the temperature is, the more efficient the synthesis of PANI is. The polymerization of aniline is an exothermal and temperature activated process. However, according to the literature, the optimal reaction temperature of chemical oxidative polymerization of aniline should lie within −5 to 0°C because the per-oxidative reaction and the reverse hydrolysis reaction are stimulated at higher temperature and this will affect the yield and conductivity of the resulting PANI. Nevertheless, the experiment at lower temperature is more difficult than that at ambient temperature and, surprisingly, the yield and conductivity in our experiment at ambient temperature are better than that at lower temperature.

Table 3. Effect of amount of aniline on the yield and electrical conductivity of PANI^a

Aniline (mL)	2	3	4	5	6
Yield of PANI (%)	91.2	72.8	55.2	43.5	53.5
Conductivity (S/cm)	10.6	12.5	22.7	25.0	27.0

^a Reaction condition: MnO₂, 2 g; 2.7 mol/L HCl, 100mL; ~25°C; 4 h

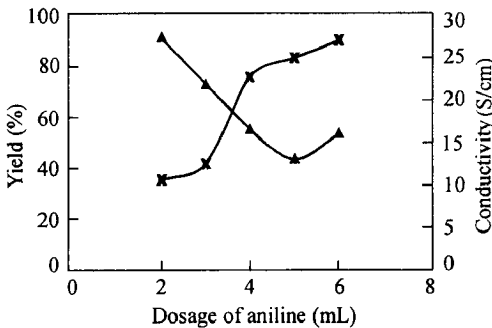


Fig. 3 Relationship between yield (▲) and conductivity (✕) of PANI and amount of aniline

Table 4. Effect of reaction temperature and oxidant on the yield and conductivity of PANI^a

Oxidant	Temperature (°C)	Yield of PANI (%)	Conductivity (S/cm)
MnO ₂	10	65.7	11
MnO ₂	25	72.8	12.5
(NH ₄) ₂ S ₂ O ₈	25	72.1	21.7

^a Reaction condition: aniline, 0.033 mol; oxidant/aniline molar ratio = 0.7; 100 mL HCl of 2.7 mol/L; 4 h

Comparison of the PANI Properties for Oxidation by MnO₂ or Ammonium Peroxydisulfate

Ammonium peroxydisulfate (APS) is a common oxidant for the chemical oxidative polymerization of aniline. In order to compare the yield and conductivity of PANI prepared by the manganese oxidant with that prepared using APS, both PANI were synthesized under similar conditions. The products are denoted by PANI (APS) and PANI (MnO₂) thereafter. The yield of PANI is almost the same but the conductivity of PANI (APS) (21.7 S/cm) is higher than that of PANI (MnO₂) (12.5 S/cm) though of the same order of magnitude (Table 4).

PANI is highly intractable because of its aromatic nature, interchain hydrogen bonding, and charge delocalization effects^[21]. Both PANI are available in a powder form of emeraldine salt doped with mineral acids, and are non-soluble except in strong acids such as concentrated sulfuric acid and formic acid. However, the emeraldine base form of PANI is soluble in dimethyl sulfoxide, dimethylformamide, tetrahydrofuran, *m*-cresol, and generally in strong or moderately polar organic solvents. However, it is still not soluble in nonpolar organic

solvents such as xylene and chloroform. It is interesting to note that the dissolution speed of PANI (MnO_2) is faster than that of PANI (APS).

IR and UV-Vis Spectroscopy

The IR spectra shown in Fig. 4 exhibit characteristic absorption peaks for PANI emeraldine base (PANI EB). Both spectra of PANI (MnO_2) EB and PANI (APS) EB are shown for comparison. The absorption peaks of two kinds of PANI EB are assigned as follows and the wave number in parentheses is that of PANI (APS) EB. The peak at 1593 cm^{-1} (1591 cm^{-1}) is the $\nu_{\text{C}=\text{C}}$ of the quinoid ring, and 1499 cm^{-1} (1498 cm^{-1}) is the $\nu_{\text{C}=\text{C}}$ of the benzenoid ring. The 1379 cm^{-1} (1379 cm^{-1}), the strong 1302 cm^{-1} (1305 cm^{-1}) and the shoulder 1242 cm^{-1} (1243 cm^{-1}) are attributed to the $\nu_{\text{C}-\text{N}}$ in QB_tQ , in QB_tQ , QBB , BBQ and in BBB , respectively^[11, 22]. Here the symbols Q, B, t and c represent quinoid ring, benzenoid ring, *trans* and *cis*, respectively. The 1166 cm^{-1} (1165 cm^{-1}) is a vibration of $\text{N}=\text{Q}=\text{N}$, and 831 cm^{-1} (830 cm^{-1}) are assigned to $\delta_{\text{C}-\text{H}}$ of 1,4 ring. This spectrum indicates that PANI (MnO_2) has a structure similar to that of PANI (APS).

UV-Vis spectroscopy has been widely used to characterize PANI. The UV-Vis spectra of the two kinds of PANI (oxidized by MnO_2 and APS) in tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and formic acid were recorded. In THF, DMF and DMSO, both PANI emeraldine bases display two characteristic absorption peaks in the range 320–329 nm and 605–633 nm (Table 5) which can be attributed to $\pi-\pi^*$ transition of benzenoid rings and $\pi-\pi^*$ transition of quinoid rings^[11, 23], respectively. The typical absorption spectra of PANI (MnO_2) EB and PANI (APS) EB in DMF are depicted in Fig. 5 and their shapes are similar in THF and DMSO. The absorption curves of PANI (MnO_2) and PANI (APS) in the same solvent show no evident differences.

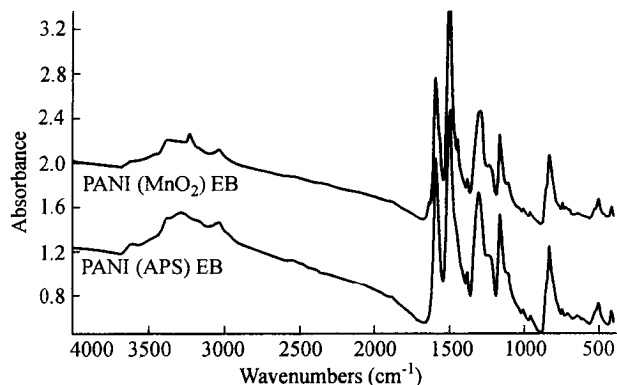


Fig. 4 IR spectrum of PANI(MnO_2) EB and PANI(APS) EB

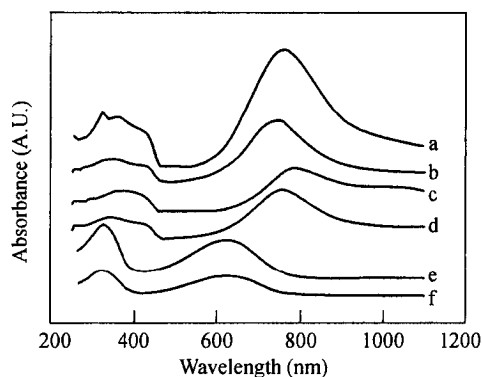


Fig. 5 UV-Vis spectra of PANI in various solvents

- a) PANI(MnO_2) EB in formic acid;
- b) PANI(APS) EB in formic acid;
- c) PANI(MnO_2) ES in formic acid;
- d) PANI(APS) ES in formic acid;
- e) PANI(MnO_2) EB in DMF;
- f) PANI(APS) EB in DMF

Differences in absorption only appear in different solvents, especially for the exciton band of quinoid ring for which the absorption is attributed to a charge-transfer excitation-like transition from the highest occupied energy level to the lowest unoccupied energy level that may be influenced by the solvent. From THF, DMF to DMSO the solvent polarity increases, and the polymer chain may exist in a more stretched form in the solvent, which results in a shift of the absorption peak towards longer wavelength.

UV-Vis spectra of PANI emeraldine base dissolved in formic acid shows that the polymer undergoes protonation by the solvent. Comparing the spectra of PANI in formic acid and in DMF reveals that the exciton

band of quinoid ring disappears and two new absorption bands appear, at 428–439.5 nm and 739–789 nm, which are characteristic of protonated PANI with localized charge carriers (polarons)^[11, 23]. Anyway, the absorption spectra of PANI EB and PANI emeraldine salt (PANI ES) in the formic acid are similar to each other, meaning that PANI EB is completely doped by the formic acid.

Table 5. UV-Vis absorption bands of PANI in difference solvents and their band

Sample	Solvent	Absorption peaks (nm) and their assignments		
		π - π^* Transition of benzenoid rings	π - π^* Transition of quinoid rings	Localized charge carriers (polarons)
PANI(MnO ₂) (EB)	Formic acid	327.5	-	437.5; 759
PANI(APS) (EB)	Formic acid	328.5	-	439.5; 739
PANI(MnO ₂) (ES)	Formic acid	363.5	-	428; 789
PANI(APS) (ES)	Formic acid	351.5	-	430; 756.5
PANI(MnO ₂) (EB)	DMF	329	621	-
PANI(APS) (EB)	DMF	326	624	-
PANI(MnO ₂) (EB)	THF	327	605	-
PANI(APS) (EB)	THF	320	606	-
PANI(MnO ₂) (EB)	DMSO	329	633	-
PANI(APS) (EB)	DMSO	327	626	-

PANI(MnO₂): PANI using MnO₂ as the oxidant; PANI(APS): PANI using APS as the oxidant

EB: emeraldine base, ES: emeraldine salt; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide;

THF: tetrahydrofuran

There are some differences between PANI EB and PANI ES because PANI EB is protonated only by formic acid, while PANI ES is doped by HCl during polymerization of aniline. For the polaronic bands above 739 nm, the PANI doped with HCl has higher conjugation length than that of PANI doped by formic acid.

Compared with the spectra of PANI (APS), the polaronic bands above 739 nm of PANI (MnO₂) are seen at higher wave number, indicative of a higher conjugation length.

CONCLUSIONS

The chemical oxidation polymerization of aniline using MnO₂ as the oxidizing agent in an aqueous acid medium can be carried out. The effects of reaction conditions on the conductivity of PANI such as the amount of MnO₂, acidity of medium, reaction temperature and type of acid are discussed. From the conductivity and yield point of view, optimal reaction conditions are identified, namely, the molar ratio of MnO₂ to aniline is 0.7–1.4 and the acidic concentration is 1.0–2.7 mol/L. There is no evident influence of the kind of acid on the conductivity and yield of the resulting PANI. The reaction can be carried out at room temperature.

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