Catalytic Oxidization Polymerization of Aniline in an H_2O_2 —Fe²⁺ System

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ABSTRACT: Polyaniline is prepared by chemical polymerization of aniline in an acidic solution using H_2O_2 as an oxidant and ferrous chloride as a catalyst. A wide variety of synthesis parameters are studied, such as the amount of the catalyst, reaction temperature, reaction time, initial molar ratio of oxidant, monomer and catalyst, and aniline and HCl concentrations. The polymerization of aniline can be initiated by a very small amount of catalyst. The yield and the conductivity of product depend on the initial molar ratio of the oxidant and monomer. The polyaniline with a conductivity of about 10° S/cm and a yield of 60% is prepared under optimum conditions. The process of polymerization was studied by *in situ* ultraviolet–visible spectroscopy and open-circuit potential technology. Compared to the polymerization process in a $(NH_4)_2S_2O_8$ system, the features of the H_2O_2 —Fe²⁺ system are pointed out, and the chain growth mechanism is proposed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1077–1084, 1999

Key words: H_2O_2 —Fe²⁺ system; catalytic oxidization polymerization; polyaniline; *in situ* ultraviolet–visible spectra; open-circuit potential.

INTRODUCTION

During the past decade, the synthesis and characterization of conducting polymers became one of the most important research areas in polymer science. Conducting polymers have attracted considerable attention due to their potential applications.¹ Among them, polyaniline (PAn) has been of particular interest because of its cheap monomer, simple synthesis technology,^{1,2} unique electrochemical characterization,³ reversibility in the doping/dedoping process,⁴ and environmental and chemical stability.^{2,4}

PAn is generally prepared by the oxidative polymerization of aniline by ammonium persulfate (APS) in 1*M* HCl. However, the PAn obtained is often neither soluble nor fusible, and, thus, its applications are limited. APS is a strong oxidant, and the polymerization of aniline is an exothermal reaction, so the reaction heat is difficult to control, leading to a wide molecular weight distribution. Posttreatments become complicated because the inorganic by-product (ammonium sulfate) exists in the product. So, the cost of PAn is increased. A. Pron et al. compared the electrical conductivity and the reaction yield of PAn, polymerized with four different oxidizing agents, $(NH_4)_2S_2O_8$, $K_2Cr_2O_7$, KIO_3 , and H_2O_2 . They concluded that the redox potential of the oxidants was not a determining factor in the chemical polymerization of aniline; most might be used to polymerize aniline, but H₂O₂ was not a good oxi-

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dant for preparing PAn.⁵ Yasuda and Shimidzu synthesized PAn with $FeCl_3$, but the yield and the conductivity of PAn was so low that they could not be given in the article.⁶ Other oxidants are not satisfactory because they lead to worse product property and do not simplify the posttreatment compared to APS system.

 H_2O_2 is an important oxidant, which is used widely in industry. Its redox potential is 1.77 V versus SCE, high enough for aniline polymerization, but not so high that the reaction will take place vigorously. Its reduction product is only H_2O , thus greatly simplifying the posttreatment. Another advantage is the possibility of recycling the reaction medium because it does not contain any harmful components to aniline polymerization. Therefore, the H_2O_2 approach is easy to industrialize. But when H₂O₂ alone is used as oxidant, the reaction rate is extremely low. In order to obtain high-quality PAn, the reaction activity of H₂O₂ must be improved. D. K. Moon et al.⁷ synthesized PAn at $30-35^{\circ}$ C using H₂O₂ as the oxidant and $FeSO_4$ as the catalyst. However, the reaction yield and electrical conductivity were not satisfactory. On the basis of our earlier work,⁸ this article studied the chemical polymerization of aniline in the H_2O_2 —Fe²⁺ system. The reaction conditions were optimized for the reaction yield, electrical conductivity, and viscosity of PAn. The process of polymerization was followed by in situ ultraviolet-visible (UV-vis) spectra and open-circuit potential measurements. The differences in the polymerization process between H_2O_2 —Fe²⁺ and $(NH_4)_2S_2O_8$ systems were found. Chain growth mechanism in the H_2O_2 —Fe²⁺ system was proposed.

EXPERIMENTAL

Polymerization of Aniline

Aniline was purified by vacuum distillation prior to use. 5 mL of aniline (54.8 mmol) and 10 mL of 2 mg/mL FeCl₂ in H₂O were added into 150 mL of 2.0 mol/L HCl. When it was cooled to about 0°C in an ice bath, 36 mL of H₂O₂ (6%) was dropped in 30 min. The temperature remained 0–5°C throughout the entire polymerization reaction. After 48 h, the reaction mixture was filtered, washed with a large amount of 0.5 mol/L HCl and acetone, dedoped with 0.5 mol/L NH₃·H₂O and neutralized with much water. The resulting PAn powder was dried under vacuum to constant weight.

In Situ UV-Vis Spectroscopic Studies

The UV–vis spectra were recorded by a UVIKON 922 spectrometer from Kontron Instruments. 0.5 mL of 6% H_2O_2 in 2 mol/L HCl was added with a syringe to a 10 mm quartz cell, which contained 2.0 mL of a reaction solution without H_2O_2 . The reference cell contained 2.0 mL of original reaction solution and 0.5 mL of 2 mol/L HCl.

Open-Circuit Potential Technology

The open-circuit potential of the reaction system was continuously measured using an electrochemical technique described in literature.⁹ Saturated calomel electrode (SCE) was used as reference electrode, and a platinum plate was used as measuring electrode.

Measurements of Solubility, Intrinsic Viscosity, and Conductivity

Solubility of the product was measured by following method. 0.1 g PAn was added in 20 mL solvent (THF, DMSO, DMF, or NMP) at room temperature under moderate stirring for 2 h; after filtration and washing with solvent, the insoluble part was dried and weighed.

Electrical conductivity of the PAn was measured on pressed pellets employing a standard four-probe method after PAn samples were doped with 1 mol/L HCl for 24 h and dried in vacuum.

Intrinsic viscosity of the as-polymerized polymers was determined at 30°C in 0.1 g/dL solutions in 0.5 wt % LiCl–NMP, using an Ubbelohde viscometer.

RESULTS AND DISCUSSION

Optimization of Reaction Conditions

Amount of Catalyst

When polymerization of aniline is carried out using H_2O_2 as the oxidant without a catalyst, PAn is hardly obtained at room temperature in 24 h. If the reaction temperature is increased to 60°C, the reaction occurs at once. But the properties of the product are bad. The reaction occurs as soon as a little FeCl₂ (the molar ratio of FeCl₂ to H_2O_2 is 1/500) is added at room temperature. The properties of the product are obviously improved. The product has similar conductivity and better solubility compared to that from the $(NH_4)_2S_2O_8$ system. It can be seen that when H_2O_2 alone is used as oxidant, its conversion into radical ions is slow,

No.	Molar Ratio of H ₂ O ₂ / Aniline/Fe ²⁺	Yield (%)	σ (S/cm)	$\begin{array}{c} [\eta]_{0.1} \\ (\mathrm{dL/g}) \end{array}$
Z-01 Z-02 Z-03	100:100:1 200:200:1 500:500:1	57 50 56	$1.5 \\ 1.0 \\ 1.3$	$0.28 \\ 0.24 \\ 0.33$

Table IThe Effect of the Amount of Catalyston the Properties of Polyaniline

Reaction conditions: [aniline] = 0.2 mol/L; [HCl] = 0.7 mol/L; temperature, room temperature; time, 24 h.

while polymerization of aniline by the radical ions is rapid. The former is a controlling step. Addition of Fe^{2+} into the system speeds up the decomposition of H_2O_2 and formation of the radical ions. Table I shows the effect of amount of the catalyst on the properties of PAn. The properties, such as yield, conductivity, or viscosity, are almost invariant when the initial amount of catalyst is 1/100 and 1/500 of the oxidant (molar ratio). After the PAn is separated, the reaction medium may be used in later polymerization. If the concentrations of aniline, oxidant, and HCl are properly adjusted, the polymerization product shows as good properties as that obtained in the first polymerization. During the reaction, ferrous ion is oxidized and exists in ferric ion as detected with NH_4SCN .

Reaction Temperature and Time

The reaction temperature has an effect on the polymerization of aniline because it is exothermal. Figure 1 shows the yields and conductivity as a function of aniline concentration and reaction temperature. At a given aniline concentration, the reaction at room temperature (RT) for 24 h gives a higher yield than that in an ice water bath for 48 h, but the latter results in higher conductivity. If the reaction temperature decreases to -10° C, the yield and conductivity are 37% and 7.2 S/cm for 72 h, respectively. These results indicate that decomposition rate of H₂O₂ falls at lower temperature, and, thus, aniline is polymerized slowly. When the temperature rises, the reaction rate increases; meanwhile, the side reactions also increase so that the regularity of the

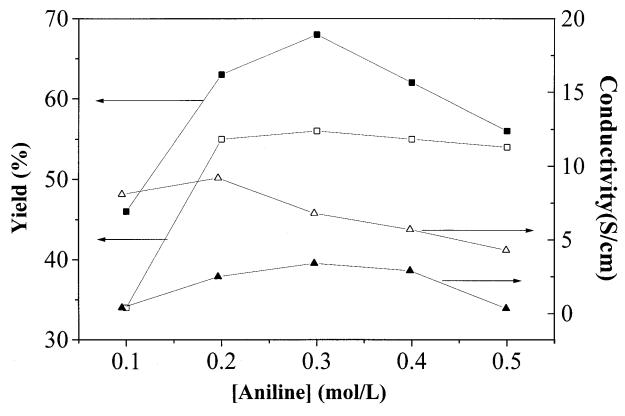


Figure 1 The influence of aniline concentration on the yield (\Box, \blacksquare) and conductivity $(\triangle, \blacktriangle)$ of polyaniline at different reaction temperatures: $(\Box, \triangle) 0-5^{\circ}C$, 48 h; $(\blacksquare, \blacktriangle) 15-20^{\circ}C$, 24 h.

No.	Time (h)	Yield (%)	σ (S/cm)	$\begin{array}{c} [\eta]_{0.1} \\ (\text{dL/g}) \end{array}$
Z-04	12	18	4.5	0.25
Z-05	24	39	7.9	0.30
Z-06	40	51	9.0	0.34
Z-07	48	56	6.8	0.26
Z-08	68	67	5.0	0.24
Z-09	90	65	4.0	0.28

Table IIThe Effect of Reaction Time on theProperties of Polyaniline

Reaction conditions: [aniline] = 0.3 mol/L; ratio of oxidant to monomer to catalyst = 500/500/1; temperature, $0-5^{\circ}$ C; [HCl] = 1.2 mol/L.

polymer chain becomes worse, and its conductivity decreases.

Generally, chemical polymerizations of aniline in the APS system can be completed in 4-8 h.^{1,2} In the H_2O_2 system, a reaction time of 4–8 h is not sufficient to achieve high yield. Table II shows the effect of the reaction time. The yield and intrinsic viscosity of PAn increases with increasing time in the first 40 h. After 68 h, the yield does not increase any longer, while viscosity slightly decreases. At this stage, if the oxidant is added into the filtrate, more products are obtained, indicating that the amount of oxidant in the reaction system is not sufficient. That is why the yield remains constant at the last stage of the polymerization. The intrinsic viscosity decreases after 40 h, probably due to hydrolysis and degradation of PAn. The electrical conductivity of the PAn obtained, in the same order of magnitude (10° S/ cm), does not show obvious dependence on the polymerization time.

Concentration of Aniline

Table III summarizes the effect of aniline concentration. A low aniline concentration (<0.1 mol/L) results in a low yield (35%). In the range of 0.3 to 1.0 mol/L, the reaction yield is between 50 and 60%, and the electrical conductivity is in the order of 10° S/cm. When aniline concentration exceeds 1.5 mol/L, both the reaction yield and the conductivity drop (for example, 44% and 0.9 S/cm, respectively, at an aniline concentration of 1.5 mol/L). The viscosity of PAn obtained reaches its maximum at 0.5 mol/L. Therefore, it can be concluded that 0.5–1.0 mol/L may be the best concentration range for aniline polymerization. Higher aniline concentration is not suitable because it leads to more side reactions and, thus, to more irregular-

Table IIIThe Influence of AnilineConcentration

No.	[Aniline] (mol/L)	Yield (%)	σ (S/cm)	$ \begin{array}{c} [\eta]_{0.1} \\ (dL/g) \end{array} $
Z-10	0.1	35	8.2	0.19
Z-11	0.3	56	6.8	0.24
Z-12	0.4	52	4.0	0.35
Z-13	0.5	54	4.3	0.38
Z-14	0.8	55	5.2	0.28
Z-15	1.0	54	2.6	0.30
Z-16	1.5	44	0.9	0.19
Z-17	2.0	47	0.2	0.19

Reaction conditions: ratio of oxidant to monomer to catalyst = 500/500/1; temperature, 0-5°C; [HCl] = 1.2 mol/L; time, 48 h.

ity in PAn molecular chains. At the same time, more termination reactions may occur by the chain transfer or coupling mechanism, leading to lower molecular weight and viscosity.

HCl Concentration

In the reaction, HCl has a few effects, as follows: it reacts with the monomer to form aniline chlorides; it provides an acidic environment for the polymerization; it serves as a dopant for PAn; and it participates in the redox reaction of H_2O_2 and makes its redox potential increase. Therefore, the influence of acidity is systematically studied, and the results are shown in Table IV. No product is obtained under a neutral condition. The yield, electrical conductivity, and the viscosity remained unaffected over the range of HCl concentration of 0.7 to 2.0 mol/L within experimental error. When the concentration of HCl exceeds 2.0

Table IV	The	Influence	of	the	Acid
Concentra	tion				

No.	[HCl] (mol/L)	Yield (%)	σ (S/cm)	
Z-18	0.0	_	_	
Z-19	0.7	58	2.9	0.43
Z-20	0.9	64	3.2	0.40
Z-21	1.3	70	10	0.37
Z-22	2.0	69	6.0	0.26
Z-23	4.0	41	0.58	0.18
Z-24	8.0	10	0.08	Undetermined

Reaction conditions: [aniline] = 0.3 mol/L; molar ratio of oxidant to monomer to catalyst = 500 : 500 : 1; temperature, $0-5^{\circ}$ C; time, 48 h.

No.	Ratio ^a	K	Yield (%)	σ (S/cm)	
Z-25	500:500:1	0.8	52	7.8	0.28
Z-26	625:500:1	1.0	64	4.3	0.16
Z-27	750:500:1	1.2	78	4.0	0.14
Z-28	875:500:1	1.4	85	0.66	0.12
Z-29	1000:500:1	1.6	90	0.39	0.08

Table V The Effect of the Molar Ratio of Oxidant to Monomer

Reaction conditions: [aniline] = 0.3 mol/L; [HCl] = 1.2 mol/L; temperature, 0–5°C; time, 48 h. ^a Molar ratio of oxidant to monomer to catalyst $(H_2O_2/aniline/Fe^{2+})$.

mol L, the properties of PAn all decrease. When the HCl concentration is 4.0 mol/L, some changes appear in the Fourier transform infrared (FTIR) spectra of PAn obtained, corresponding to chlorine substitution, similar to the case of the $(NH_4)_2S_2O_8$ system.¹⁰ The absorptions at 1590, 1308, 1165 cm⁻¹ are obviously weakened, indicative of less an amount of quinone units. New peaks emerging at 1073, 1041, and 1010 cm⁻¹ may be assigned to chlorine substitution on the PAn rings. With increasing HCl concentration, the yield and conductivity decrease further. At an HCl concentration of 8.0 mol/L, the yield is only 10%, and the conductivity is 0.08 S/cm.

The intrinsic viscosity depends on the HCl concentration: it decreases along with increasing HCl concentration. It means that the hydrolysis of PAn is enhanced at high acid concentration. There exist two competing reactions, polymerization and hydrolysis, and their coexistence and competition determine the polymerization of PAn.⁵ At a high acid concentration, the hydrolysis becomes dominant, and, thus, the molecular weight of PAn decreases.

Initial Molar Ratio of Oxidant to Aniline

Considering the number of electrons involved in the reaction,⁵ the oxidant-to-aniline molar ratio is converted into a normalized K number: $K = M_{\rm ox}$ $iN_e/2.5 M_{\rm ani}$, where $M_{\rm oxi}$ is the number of moles of oxidizing agent, N_e is the number of electrons necessary to reduce one molecule of oxidizing agent, and $M_{\rm ani}$ is the number of moles of aniline. It is assumed that oxidation of aniline to polyemeraldine involves, on average, 2.5 electrons for each aniline unit. The reduction reaction of H_2O_2 occurs according to $H_2O_2 + 2H^+ + 2e^- = 2H_2O$, so Ne = 2. As shown in Table V, the yield is low when K < 1. The reaction yield obviously increases with increasing oxidant, but the electrical conductivity and viscosity rapidly drop. For example, when K = 1.6, the yield is 90%, but the electrical conductivity is only 0.39 S/cm, and intrinsic viscosity is only 0.08 dL/g. It should be pointed out that although the molecular weight of the PAn prepared at high oxidant concentration is low, its solubility is not improved. For example, sample Z-25 shows solubility 50% in THF, 95% in DMF and DMSO, and 100% in NMP, whereas Z-29 shows solubility only 31% in THF. Therefore, the rational conclusion is that high concentration of free radicals and, thus, low molecular weight. At the same time, it brings about hydrolysis and crosslinking of PAn molecular chains, leading to less conductivity and solubility.

In Situ UV–Vis Spectrum and Open-Circuit Potential Technology

Huand and MacDiarmid et al.¹¹ and Cao et al.^{12,13} assign the UV–vis spectra of polymers and oligomers of aniline in different states. The doped PAn has three absorption bands at 330 (3.8 eV), 430 (2.7 eV), and 820 nm (1.5 eV), respectively.

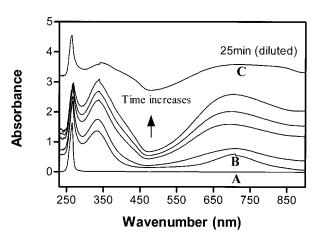


Figure 2 In situ UV–vis spectra recorded during the aniline polymerization.

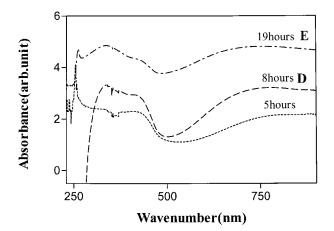


Figure 3 The UV spectra of the polyaniline deposited on the quartz cell wall at different reaction times.

The protonated pernigraniline has two peaks at 270 (4.6 eV) and 565 nm (2.2 eV). In situ UV–vis spectroscopy is used to follow the reaction process in H_2O_2 —Fe²⁺ system, and the spectra recorded before the precipitation occurs are shown in Figure 2. Before the addition of H_2O_2 , the mixture solution of aniline and FeCl₂ do not show significant absorption in the range of 300–900 nm. Upon addition of H_2O_2 , polymerization occurs,

and two new absorption peaks appear at 330 and 700 nm, respectively. The reaction solution is light blue at first and becomes dark blue, and the absorption intensities of UV-vis spectra increase, but their peak positions remain unchanged. That indicates the polymer is not in the form of pernigraniline. The peak at 425 nm appears after 15 min. At 25 min, flocculent precipitation appears in the reaction system, and the absorption band at 425 nm becomes appreciable. This means the existence of emeraldine salt. Precipitate is formed at the latter stage of the reaction; the UV-vis spectra of the PAn deposited on the wall of quartz cell are measured at different reaction times and shown in Figure 3. The main absorption bands are located at 330, 425, and 700 nm, and the latter peak is very broad and may be assigned to emeraldine salt.¹¹ The above UV-vis observations therefore show that the PAn prepared in the reaction process is not pernigraniline, but emeraldine salt, even at the presence of H₂O₂ at the early stage of the reaction.

Open-circuit potential (OCP) measurements were performed by Manohar and MacDiarmid⁹ to follow the polymerization process of aniline in APS system. The measured potential of 0.1 mol/L APS solution in aqueous 1 mol/L HCl is 1.05 V;

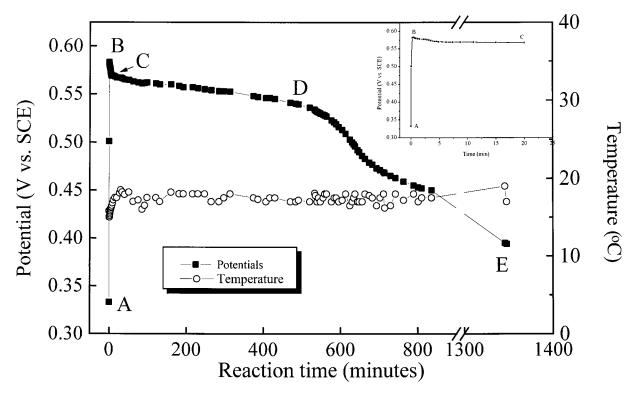
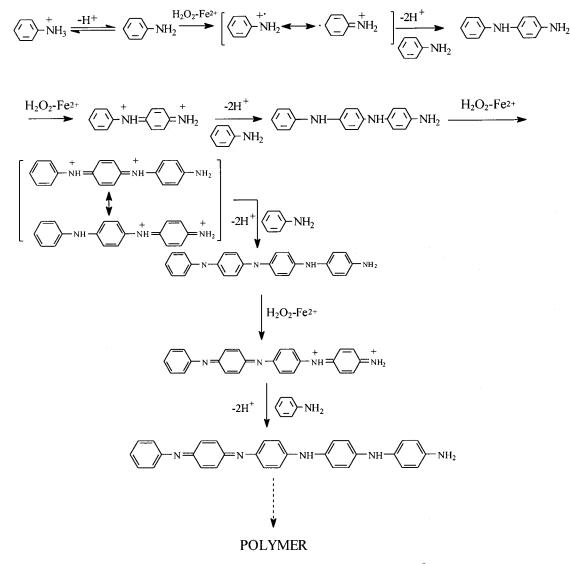


Figure 4 Open-curcuit potential and temperature variation during aniline polymerization.



Scheme 1 The chain-growing of polyaniline in the H_2O_2 —Fe²⁺—HCl system.

that of pernigraniline and emeraldine base in 1 mol/L HCl are 0.83 and 0.43 V, respectively. During the polymerization of aniline, a high potential (near 0.8 V) is measured until the oxidant APS is used up. Therefore, it is concluded that aniline is converted into pernigraniline at the presence of APS and pernigraniline is reduced to emeraldine by the remainder aniline after APS is consumed up.

The same measurements are carried out for the H_2O_2 —Fe²⁺ system. Figure 4 shows the variation of the measured OCP and temperature in the reaction mixture during the polymerization. When H_2O_2 is added, OCP jumps to 0.59 V [Fig. 4(A–B)] rapidly, and then decreases to 0.56 [Fig. 4(C)] slowly in 20 min. After that, it keeps almost constant in 12 h [Fig. 4(C–D)], then declines a

little, then keeps constant at 0.43 V until the end [Fig. 4(E)]. During the whole process of polymerization, the temperature is almost unchanged. Corresponding UV–vis spectra [Fig. 4(A–E)] are shown in Figure 2(A–C) and Figure 3(D, E). Spectra (C)–(E) looks alike over the range of 300–900 nm.

Figures 2–4 show that the polymerization of aniline in H_2O_2 —Fe²⁺ system is much slower than that in the APS system.⁹ H_2O_2 is consumed within 12 h. At the presence of H_2O_2 , the polymerization product is not in a pernigraniline form but in an emeraldine form, as evidenced by UV– vis spectra (C) and (D). This may be ascribed to the low OCP of H_2O_2 (0.59 V versus SCE), which is much lower than that of pernigraniline. After 12 h, $\rm H_2O_2$ does not exist in the system any longer. The measured OCP (0.43 V) is due to PAn in emeraldine form.

Based on our previous results,⁸ the polymerization of aniline in the H_2O_2 —Fe²⁺ system may follow a different mechanism from that of APS system: PAn in emeraldine form is directly formed from aniline monomer, not converted from the PAn in pernigraniline form. Scheme 1 is proposed to elucidate the formation of the emeraldine units. In the H_2O_2 —Fe²⁺ system, H_2O_2 reacts with Fe²⁺ to form radicals, which initiate the formation of an aniline dimer. The dimer is oxidized by H_2O_2 —Fe²⁺ and reacts with the monomer to form a trimer. The trimer is oxidized by oxidant and converted into an oxidized state (the quinoid ring maybe located in the middle or end ring). Tetramer is obtained similarly. When the number of the phenyl ring unit is greater than four, the polymer chain is oxidized in the middle. This process is repeated to form polyaniline in the emeraldine form. From the results of studying oligoaniline, it is known that the fully reduced tetramer is necessary to polymerization. And the octamer is not obtained through the oxidation of middle-oxidized tetramer, but it could be obtained when tetramer is fully reduced.

CONCLUSIONS

A composite oxidizing agent is used for aniline polymerization. It is composed of H_2O_2 and a catalytic amount of Fe²⁺. Optimized polymerization conditions are as follows: aniline concentration, 0.5–1.0 mol/L; HCl concentration, 1.0–3.0 mol/L; initial molar ratio of H_2O_2 /aniline/Fe²⁺, 750–500/ 500/1; reaction temperature, 0–5°C; and reaction time, 48 h. Under these conditions, a polymerization yield of 60% may be achieved. The polymer obtained shows a conductivity of 10° S/cm and a

solubility of 50% in THF, 95% in DMF and DMSO, and 100% in NMP. The reaction medium may be reused for further polymerization without special treatment. Therefore, this approach may lower the cost of polyaniline and is suitable to industrialization. The *in situ* UV–vis spectroscopic study and open-circuit potential measurement show that the direct product of aniline polymerization is not in pernigraniline form but in the emeraldine form at the presence of the oxidant. Thus, a polymerization mechanism is proposed in which a trimer of aniline containing a middle quinoid ring is the mediate reaction product.

REFERENCES

- Geniès, E. M.; Boyle, A.; Lapkows, M.; Tsintavis, C. Synth Met 1990, 36, 139.
- MacDiarmid, A. G.; Chiang, J.-C.; Halpern, M.; Huang, W. S.; Mu, S. L.; Samasiri, N. L. D.; Wu, W. Q.; Yaniger, S. Z. Mol Cryst Liq Cryst 1985, 121, 173.
- Kobayashi, T.; Yoneyama, H.; Tamura, H. J Electroanal Chem 1984, 161, 419.
- Chiang, J.-C.; MacDiarmid, A. G. Synth Met 1986, 13, 193.
- Pron, A.; Genoud, F.; Menardo, C.; Nechtschein, M. Synth Met 1988, 24, 193.
- 6. Yasuda, A.; Shimidzu, T. Polym J 1993, 25, 329.
- Moon, D. K.; Osakada, K.; Maruyama, T.; Yamamoto, T. Makromol Chem 1992, 193, 1723.
- Sun, Z.; Geng, Y.; Li, J.; Jing, X. B.; Wang, F. S. Synth Met 1997, 84, 99.
- Manohar, S. K.; MacDiarmid, A. G.; Epstein, A. J. Synth Met 1991, 41–43, 711.
- Tang, J.-S.; Jing, X. B.; Wang, B. Ch.; Wang, F. S. Synth Met 1988, 24, 231.
- Huand, W. S.; MacDiarmid, A. G. Polymer 1993, 34, 1833.
- Cao, Y.; Li, S. Z.; Xue, Z. J.; Guo, D. Synth Met 1986, 16, 305.
- 13. Cao, Y. Synth Met 1990, 35, 319.