Chemical Oxidative Polymerization of Aniline with Ferric Chloride

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ABSTRACT: Aniline was chemically oxidized and polymerized in water with FeCl_3 , with emphasis on molecular weight and yield. Reaction conditions, including reaction temperature, electrochemical equivalent ratio ($\text{FeCl}_3/\text{aniline}$), reaction time, aniline and HCl concentrations, and atmosphere (in air and in N_2) were investigated and optimized. At an optimum condition, 20400 of number average molecular weight and 51% of yield were obtained. The product was assumed emeraldine by elemental analysis, solid state ^{13}C NMR and IR spectroscopy. The effects of the reaction condition are discussed on the basis of the mechanisms which are proposed for electrochemical polymerization of aniline.

KEY WORDS Aniline / Polyaniline / Chemical Oxidation / Ferric Chloride
/ Molecular Weight Distribution /

Conducting polymers have attracted much scientific and technological interest in recent years. A considerable portion of these studies has been devoted to polyaniline since MacDiarmid *et al.*¹ reinvestigated this material as a conducting polymer. Polyaniline is unique among conducting polymers in that its electrical properties can be reversibly controlled both by charge-transfer doping and by protonation. In addition, the wide range of associated electrical, electrochemical and optical properties, coupled with good stability, make polyaniline potentially attractive for application as an electronic material.

As Geniès² described in his review, both electrochemical and chemical oxidative syntheses of polyaniline have been studied.³ Considerable efforts were devoted to electrochemical polymerization,^{4–6} especially to develop relationships between synthesis conditions and properties of the products. By contrast, a few papers describe chemical polymerization. The chemical synthesis is of

particular importance since this synthesis is the most feasible route for the production of polyaniline on a large scale.

Polyaniline was chemically synthesized by oxidation of aniline in scheme 1 and employed also in this study. Polyaniline is called emeraldine when Y is *ca.* 0.5 and leucoemeraldine when Y is 1.

Hand *et al.*^{7,8)} described the chemical oxidation of aniline and aniline derivatives with $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and $\text{Ce}(\text{SO}_4)_2$. After MacDiarmid *et al.*¹ described the polymerization of aniline with $(\text{NH}_4)_2\text{S}_2\text{O}_8$, it has been mainly employed as an oxidant for chemical oxidative polymerization. Recently, Ragimov *et al.*⁹ described the chemical oxidation of aniline with NaClO and showed that oligomer of aniline was obtained. Pron *et al.*¹⁰ described the chemical oxidative polymeriza-

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tion with $(\text{NH}_4)_2\text{S}_2\text{O}_8$, H_2O_2 , $\text{K}_2\text{Cr}_2\text{O}_7$ and KIO_3 . The authors concluded that the redox potential of oxidants was not a dominant parameter; most oxidants gave similar results. Armes *et al.*¹¹ described the chemical oxidative polymerization with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and concluded that conductivity, yield, elemental composition and degree of oxidation were essentially independent of oxidant/monomer initial ratio when its value was below 1.15. On the basis of elemental analysis, over-oxidation occurred at high oxidant/monomer mole ratios. Cao *et al.*¹² extensively studied the chemical oxidative polymerization of aniline with $(\text{NH}_4)_2\text{S}_2\text{O}_8$, $\text{K}_2\text{Cr}_2\text{O}_7$, KIO_3 , FeCl_3 , KMnO_4 , KBrO_3 , and KClO_3 . The authors concluded that $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and $\text{K}_2\text{Cr}_2\text{O}_7$ resulted in high polymerization yield and high molecular weight; KIO_3 and FeCl_3 resulted in low molecular weight. Inoue¹³ described that aniline was chemically oxidized with CuClO_4 in acetonitrile.

Polyaniline has been synthesized electrochemically from 0.9 to 1.4 V *versus* NHE². From the view point of redox potential, most oxidants employed for chemical oxidation have higher potential than that for electrochemical oxidation: $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 1.94 V; H_2O_2 , 1.776 V; $\text{Ce}(\text{SO}_4)_2$, 1.74 V; KMnO_4 , 1.695 V; KBrO_3 , 1.52 V; KClO_3 , 1.44 V; $\text{K}_2\text{Cr}_2\text{O}_7$, 1.29 V; CuClO_4 , 1.23 V; KIO_3 , 1.219 V; NaClO , 0.89 V; FeCl_3 , 0.771 V.

The authors commenced chemical oxidative polymerization of aniline under mild conditions. For this purpose, FeCl_3 was employed as an oxidant. In this paper, we present results on the effects of reaction temperature, time, electrochemical equivalent ratio ($\text{FeCl}_3/\text{aniline}$), aniline and HCl concentration, and atmosphere (in air and in N_2), with special emphasis on yield and molecular weight. The results are discussed on the basis of the polyaniline growth mechanisms, which are proposed for electrochemical polymerization of aniline.

EXPERIMENTAL

Synthesis

Reagent-grade aniline (Nakalai) was vacuum distilled three times prior to use. Reagent-grade FeCl_3 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$, N-methyl-2-pyrrolidinone (NMP), HCl, and NH_3 (Nakalai) were used as received.

Preparations were carried out in aqueous HCl or water. The concentrations of aniline, FeCl_3 and HCl were widely varied. The FeCl_3 solution was added dropwise to the aniline solution, which was adjusted at the specific temperature. The rate of addition was controlled to prevent any increase of temperature. The mixture was vigorously stirred and kept at the temperature during a specific period of time. The pristine polymer was recovered and washed successively with aqueous 1 mol l^{-1} HCl, aqueous 1 mol l^{-1} NH_3 , NMP, methyl alcohol, and diethyl ether. After washing, the polymer was dried under vacuum until constant mass was reached. Yield was calculated assuming that the polymer was deprotonated emeraldine.

For washing, special attention was paid to avoid contamination of Fe cation. Fe possibly forms a complex with polyaniline. To decompose the complex, the polymer was washed in aqueous 1 mol l^{-1} HCl. Moreover the polymer was washed in NMP as follows. Deprotonated polyaniline was dissolved in NMP and aqueous 3 mol l^{-1} HCl was added dropwise to precipitate protonated polyaniline. In the course of precipitation, the complex decomposed and Fe cations dissolved in the acidic solvent.

For comparison, emeraldine was synthesized with $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The reaction and washing conditions described by Cao *et al.*¹² were employed.

Characterization

Deprotonated polyaniline was dissolved in NMP and the molecular weight was measured with gel permeation chromatography: main

column (TOSOH, KD80M); pump (Shimadzu, LC-3A); oven (Shimadzu, SPD-6AV); UV-VIS detector (Shimadzu, 6PA); integrator (Shimadzu, C-R4A). 0.01 mol l^{-1} LiBr NMP solution was employed for eluent. A calibration curve was obtained with polystyrene standard (TOSOH, TSK standard polystyrene).

Solid state ^{13}C NMR spectra were obtained with deprotonated polyaniline powder on an NMR spectrograph (JEOL, GSX270WB). ^{13}C cross polarization (CP) measurement was carried out at 67.5 MHz with magic angle spinning (MAS) from 3.5 to 3.7 kHz. IR spectra were obtained with a KBr tablet of deprotonated polyaniline on a FT-IR spectrograph (BIO-RAD, FTS-30).

RESULTS AND DISCUSSION

Various transition metal compounds, specifically Fe^{3+} and Cu^{2+} complexes, were shown to function as polymerization initiators for pyrrole by Bjorklund¹⁴ and Myers.¹⁵ Bjorklund proposed a mechanism in which the rate-limiting step is the oxidation of pyrrole to a radical cation by an outer-sphere, activated-complex mechanism.¹⁶ The mechanism can be possibly applied to aniline polymerization and the effects of reaction temperature on molecular weight and yield were investigated. Following solutions were prepared: 25 mmol of FeCl_3 in 100 ml of aqueous 1 mol l^{-1} HCl; 10 mmol of aniline in 100 ml of aqueous 1 mol l^{-1} HCl. Electrochemical equivalent ratio ($\text{FeCl}_3/\text{aniline}$) was kept at 2.5. Reactions were carried out from 20 to 50°C for 1 day in air.

The reaction was sensitive to temperature and showed the highest yield and molecular weight at 35°C , as shown in Figure 1. At that temperature, the number average molecular weight was 3700, while yield was 17.7%. When $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was employed as an oxidant, soluble and high molecular weight polyaniline was obtained at -4°C .¹⁷ Even though the

Figure 1. Number average molecular weight and yield of polyaniline synthesized at from 20 to 50°C .

reaction with FeCl_3 was carried out at 0°C , the reaction did not proceed. The difference between the optimum reaction temperatures suggests the possibility to form an activated complex of water- FeCl_3 -aniline. Therefore, the outer-sphere activated-complex mechanism for pyrrole is to be applied to aniline.

Hand *et al.*^{7,8} studied the degradation of polyaniline in aqueous media. Similar work was carried out by Kobayashi *et al.*,¹⁸ who proposed a degradation mechanism that occurs via the imine form of polyaniline which subsequently hydrolyses to form quinone-hydroquinone structure. These products are soluble in aqueous solution. Park *et al.*¹⁹ studied the polymerization reaction of aniline electrochemically and reached the conclusion that polyaniline growth reaction competes with degradation reaction paths. Molecular weights with FeCl_3 at more than 35°C were lower than that at 35°C . This suggests that degradation by the hydrolysis becomes dominant at more than 35°C . Therefore, 35°C of reaction temperature was used for further study.

Molecular weight distribution with FeCl_3 was bimodal at every investigated temperature, as shown in Figure 2. Number average molecular weight of a high molecular weight fraction at 35°C was around 10000, while that of a low molecular weight fraction was around 1000. Molecular weights of both high and low molecular weight fractions were highest from

Figure 2. Molecular weight distribution of polyaniline: (a) synthesized at 25°C; (b) 35°C; (c) 45°C.

35 to 40°C. The following two mechanisms for the bimodal distribution can be assumed.

First, there are two kinds of reaction species, cation radicals of aniline monomer and oligomer. Park *et al.*¹⁹ assumed an autocatalytic reaction mechanism for the growth of polyaniline, where aniline oligomer whose oxidation potential is lower than aniline monomer is predominantly oxidized to form a radical cation. Sasaki *et al.*²⁰ proposed the incorporation mechanism for the growth of polyaniline, where monomeric aniline is incorporated in an oxidized aniline oligomer and chain growth takes place by the insertion of the neutral monomer at the end of the oligomer. On the other hand, the dimerization of cation radical aniline and successive dimerization result in low-molecular-weight polyaniline. A similar reaction mechanism was assumed also by Geniès *et al.*²¹ Therefore, the lower molecular weight fraction in Figure 2 would occur by the dimerization of cation radical aniline, while the higher molecular weight fraction by the incorporation mechanism.

Figure 3. Number average molecular weight and yield of polyaniline synthesized with from 2.5 to 10 of electrochemical equivalent ratio ($\text{FeCl}_3/\text{aniline}$).

Second, as already mentioned, hydrolysis of polyaniline takes place and competes with the growth reaction. The lower molecular weight fraction would consist of fragments of the hydrolysis. The authors assume that the two mechanisms contribute, more or less, to the bimodal molecular weight distribution.

As the hydrolysis takes place parallel to the growth of polyaniline, electrochemical equivalent ratio ($\text{FeCl}_3/\text{aniline}$) is an important factor for molecular weight. When cation radicals of the aniline oligomer are in excess and the rate of the insertion is relatively small, the hydrolysis of the aniline oligomer takes place before insertion. This reaction is dominant when the concentration of FeCl_3 is in large excess and the effects of electrochemical equivalent ratio ($\text{FeCl}_3/\text{aniline}$) on molecular weight and yield were investigated. Reactions were carried out at 35°C in air with the equivalent ratio from 2.5 to 10.0. The following solutions were prepared: From 25 to 100 mmol of FeCl_3 in 100 ml of aqueous 1 mol l^{-1} HCl; 10 mmol of aniline in 100 ml of aqueous 1 mol l^{-1} HCl.

At a ratio of 2.5, the highest molecular weight was obtained, as shown in Figure 3. On the other hand, yield was lowest at this ratio. This result is due to the competition reaction mechanism of growth and hydrolysis. When the equivalent ratio is higher than 2.5, hydrolysis becomes dominant and results in low molecular weight, although yield is high.

Figure 4. Number average molecular weight and yield of polyaniline synthesized with from 1 to 3 days of reaction time.

For further study, 2.5 as the electrochemical equivalent ratio was employed.

Molecular weight distribution was bimodal also in this series. As the equivalent ratio increased, both molecular weight and yield of the high molecular weight fraction decreased. This suggests that the hydrolysis takes place at a more than 2.5 equivalent ratio.

On the basis of the competition reaction mechanism of growth and hydrolysis, reaction time also plays an important role. At the end of the reaction, the concentration of monomeric aniline decreases and the rate of the insertion of aniline monomer into cation-radical aniline oligomer becomes small. At that time, hydrolysis of the oligomer proceeds much more than growth. To prevent hydrolysis, the reaction should be stopped in an appropriate period of time. The effects of reaction time on molecular weight and yield were investigated with reaction time from 1 to 3 days. The following solutions were prepared: 25 mmol of FeCl_3 in 100 ml of aqueous 1 mol l^{-1} HCl; 10 mmol of aniline in 100 ml of aqueous 1 mol l^{-1} HCl. Reactions were carried out at 35°C in air with 2.5 of the electrochemical equivalent ratio.

Yield was almost the same at any reaction time, while molecular weight decreased as reaction time increased, as shown in Figure 4. Molecular weight distribution was bimodal also in this series, while the molecular weights of both high and low molecular weight fractions decreased as reaction time increased.

Figure 5. Number average molecular weight and yield of polyaniline synthesized with from 50 to 750 mmol l^{-1} of aniline concentration.

This suggests that polymerization finished in 1 day and hydrolysis took place afterward. For further study, 1 day of the reaction time was employed.

Both the incorporation reaction mechanism and the competition reaction mechanism of growth and hydrolysis are related to the transport of monomeric aniline and Fe^{3+} . When the cation radical of aniline oligomer reacts with the incorporated aniline monomer as soon as possible, growth of aniline oligomer is preferable to hydrolysis. To attain this condition, a high concentration of aniline and FeCl_3 would be desirable and the effects of aniline concentration on molecular weight and yield were investigated. The following solutions were prepared: From 25 to 375 mmol of FeCl_3 in 100 ml of aqueous 1 mol l^{-1} HCl; 10 to 150 mmol of aniline in 100 ml of aqueous 1 mol l^{-1} HCl. Chemical equivalent ratio ($\text{FeCl}_3/\text{aniline}$) was kept at 2.5. Reaction temperature of 35°C and reaction time of 1 day were employed.

Molecular weight and yield were sensitive to concentration, as shown in Figure 5. Number average molecular weight showed highest at 750 mmol l^{-1} of aniline concentration. Because FeCl_3 solution was saturated at that concentration, more than 750 mmol l^{-1} of aniline concentration was not investigated. Molecular weight distribution was the single mode at 750 mmol l^{-1} of aniline concentration, while bimodal at lower concentration, as shown in Figure 6. This is consistent with

Figure 6. Molecular weight distribution of polyaniline: (a) synthesized with 50 mmol l^{-1} of aniline concentration; (b) 100 mmol l^{-1} ; (c) 500 mmol l^{-1} ; (d) 750 mmol l^{-1} .

the incorporation and the competition reaction mechanisms and a high concentration of aniline gave a high molecular weight. For further study, 750 mmol l^{-1} of aniline concentration was employed.

Even when single mode molecular weight distribution is obtained, dispersion (weight average molecular weight/number average molecular weight) is considerably high (4.4). The high dispersion would be related to the heterogeneous reaction mixture. In the course of the reaction, polyaniline precipitated, and formed insoluble small particles. Because of the poor transport of monomeric aniline and Fe^{3+} , a high molecular weight polymer was given on the surface of the particles. In contrast, a low molecular weight polymer was given at the center of the particles. This would be the mechanisms for the high dispersion.

Figure 7. Number average molecular weight and yield synthesized with from 0 to 4 mol l^{-1} of HCl concentration.

Hand *et al.*^{7,8} described that an acid is necessary for head-to-tail coupling of aniline. For the growth of polyaniline, elimination of H^+ must follow the coupling. Aniline is believed to work both as monomer and a H^+ acceptor. On the other hand, proton concentration was held essentially constant throughout the reaction because the increase from polymerization was balanced by the corresponding decrease when Fe^{3+} was converted into Fe^{2+} .²² From the view point of the mechanism, the polymerization of aniline is affected by pH of the reaction mixture and the effects of HCl concentration on molecular weight and yield were investigated. The following solutions were prepared: 75 mmol of FeCl_3 in 50 ml of aqueous from 0 to 4 mol l^{-1} HCl; 187.5 mmol of aniline in 50 ml of aqueous from 0 to 4 mol l^{-1} HCl. In case of 0 mol l^{-1} HCl, aniline did not dissolve and was dispersed. Chemical equivalent ratio ($\text{FeCl}_3/\text{aniline}$) was kept at 2.5. Reaction temperature of 35°C and reaction time of 1 day were employed.

Both molecular weight and yield were sensitive to HCl concentration, as shown in Figure 7. At low HCl concentration, high molecular weight and yield were obtained. At 0 mol l^{-1} , number average molecular weight was 20400, while yield was 51.0%. Cao *et al.*¹² studied synthesis condition of polyaniline with $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The authors showed that the highest molecular weight was obtained at 1.5 mol l^{-1} of HCl. The result with FeCl_3 was in contrast to that with $(\text{NH}_4)_2\text{S}_2\text{O}_8$. FeCl_3

was supposed to work as both an oxidant and acid.

At more than 2 mol l^{-1} of HCl, molecular weight was low. From the view point of H^+ elimination, monomeric aniline does not work as a H^+ acceptor under this condition, since it forms, to a considerable extent, a salt. When H^+ is not eliminated from the cation radical oligomer, the oligomer not only does not grow but also decomposes by hydrolysis. The molecular distribution also showed this clearly, as shown in Figure 8. It was the single mode when HCl concentration was less than

1 mol l^{-1} . By contrast, at more than 1 mol l^{-1} HCl, the distribution came bimodal. This suggests the possibility of a slow H^+ elimination rate and concomitant hydrolysis. Polyaniline synthesized at 0 mol l^{-1} HCl was employed for chemical analysis.

In addition, the effects of O_2 on molecular weight and yield were investigated. The following solutions were prepared: 25 mmol of FeCl_3 in 100 ml of aqueous 1 mol l^{-1} HCl; 10 mmol of aniline in 100 ml of aqueous 1 mol l^{-1} HCl. Reaction temperature of 35°C and reaction time of 1 day were employed. Yield was almost the same between in air (18%) and N_2 (16%), while number average molecular weight in air (3700) was higher than that in N_2 (750). Asturias *et al.*²³ showed polyaniline was oxidized in air in the course of reaction with $(\text{NH}_4)_2\text{S}_2\text{O}_8$. This suggests that the oxidation of aniline with FeCl_3 can possibly be promoted by O_2 in air and the synthesis in air is preferable to obtain high molecular weight.

Elemental composition of polyaniline synthesized with FeCl_3 coincided with that with $(\text{NH}_4)_2\text{S}_2\text{O}_8$, as shown in Table I. The difference was considered experimental error.

Solid state ^{13}C NMR spectrum of deprotonated polyaniline synthesized with FeCl_3 agreed with that with $(\text{NH}_4)_2\text{S}_2\text{O}_8$, as shown in Figure 9. Both spectra showed a spectrum of emeraldine base, which was described by Kaplan *et al.*²⁴ Peak assignment corresponds to numbering scheme given in structure 2.

Figure 8. Molecular weight distribution of polyaniline: (a) synthesized with 0 mol l^{-1} of HCl concentration; (b) 1 mol l^{-1} ; (c) 2 mol l^{-1} ; (d) 4 mol l^{-1} .

[2]

Table 1. Elemental composition of the polyanilines synthesized with FeCl_3 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$

	Oxidant	H/%	C/%	N/%	Total/%	N/C
Calculated		5.01	79.54	15.46	100.01	0.194
Observed	FeCl_3	5.26	79.41	15.33	100.00	0.193
Observed	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	5.41	79.26	15.33	100.00	0.193

Figure 9. Solid state ^{13}C NMR spectra of polyaniline measured with a CPMAS method: (a) synthesized with FeCl_3 ; (b) with $(\text{NH}_4)_2\text{S}_2\text{O}_8$. Tetramethylsilane was employed for standard. Assignments correspond to the numbering scheme of structure 2.

The C=N quinoid resonance (C-7) was observed at 157 ppm, which is typical for emeraldine and can not be observed in leucoemeraldine. From peak intensities, oxidation state of polyaniline synthesized with FeCl_3 was almost the same as that with $(\text{NH}_4)_2\text{S}_2\text{O}_8$.

The IR spectrum of polyaniline synthesized with FeCl_3 agreed with that with $(\text{NH}_4)_2\text{S}_2\text{O}_8$,

as shown in Figure 10. Both spectra showed that the polymers were emeraldine. IR spectra of polyaniline have been extensively studied.^{13,25-28} Bands at 3460 and 3390 cm^{-1} were assigned to the NH stretch of an aromatic amine; a band at 3020 cm^{-1} to an aromatic CH stretch; bands at 1590 and 1490 cm^{-1} to benzene and/or quinone ring deformation; a

Figure 10. FT-IR spectra of polyaniline: (a) synthesized with FeCl_3 ; (b) synthesized with $(\text{NH}_4)_2\text{S}_2\text{O}_8$.

band at 1290 cm^{-1} to the CN stretch of a secondary aromatic amine; a band at 830 cm^{-1} to an aromatic CH out-of-plane bending.

As a result of chemical analyses, the product is assumed emeraldine. It is concluded that from the view point of standard electrode

potential, emeraldine is synthesized with a milder oxidant, FeCl_3 , than $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and $\text{K}_2\text{Cr}_2\text{O}_7$, with which so far high molecular weight and yield were obtained. The dependency of yield and molecular weight on reaction conditions is consistent with the

competition reaction mechanism of growth and hydrolysis and the incorporation mechanism proposed for the electrochemical polymerization of aniline.

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