Chemical Preparation of Polyaniline and Its Derivatives by Using Cerium(IV) Sulfate. Novel Preparation of Polyxylidines

Naoki Toshima* and **Hu Yan**

Department of Applied Chemistry, Faculty of Engineering, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113

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Polyaniline and its derivatives were prepared by using the cerium(IV) sulfate as an oxidant instead of the conventional ammonium peroxodisulfate. The reaction conditions were optimized with emphasis on the conductivity and yield. The reaction of 3,5- and 2,3-dimethylaniline using cerium(IV) sulfate gave the corresponding polymers, respectively, although no polymeric products were obtained from these aniline derivatives using ammonium peroxodisulfate as an oxidant. The polyaniline and its derivatives were characteristic of the Emeraldine structure on the basis of the IR spectra. A partially belt-like morphology of the polyaniline, when prepared in an acidic medium, was observed by scanning electron microscopy. The polymerization mechanism by cerium(IV) ions is discussed on the basis of the change in the UV-vis spectra during the reaction.

Polyaniline exhibits an excellent environmental stability in its electroconducting form. In addition, the redox chemistry of polyaniline makes this polymer suitable for use as a positive electrode in secondary batteries.[1—3] Polyaniline can be prepared by either an electrochemical[4—8] or a chemical[9—18] method. The chemical method is of particular importance because it provides the most feasible route for the production of polyaniline on a large scale.[12] There have been many studies concerning the polymerization of aniline by chemical methods, especially by using ammonium peroxodisulfate as an oxidant.[13—16] However, the conventional chemical method, in which ammonium peroxodisulfate is used as an oxidant, does not give polymeric products in the polymerization of some aniline derivatives, for example, 3,5- and 2,3-dimethylanilines (xylidine) (cf. Scheme 1). In this case, the oxidation process probably leads to the formation of quinones.[16]

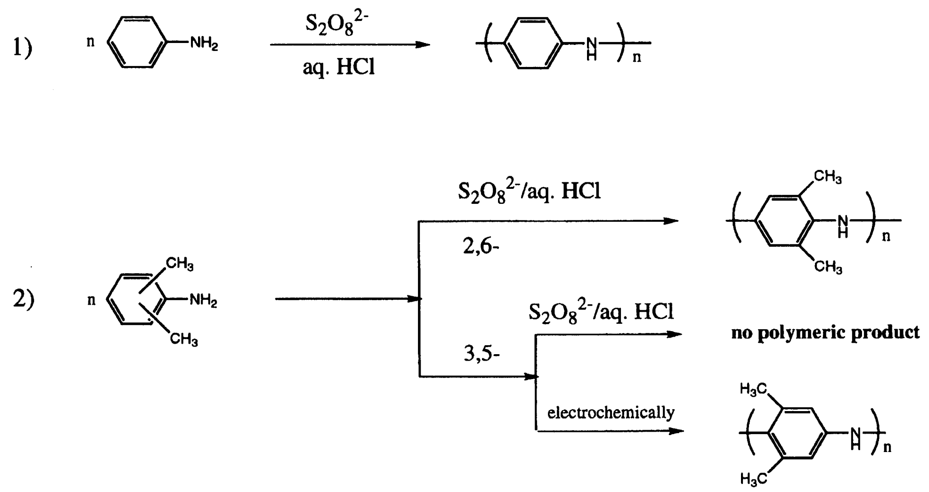
The cerium(IV) ion has a very high redox potential (E°(Ce(IV)/Ce(III))=1.74 V vs. NHE) among the usual metal ions.[19] In fact, cerium(IV) ions have been used for the oxidation of various organic compounds,[20] such as the oxidation of alcohol to aldehyde or ketone, aldehyde to carboxylic acid, etc. In addition, the cerium(IV) ion has been widely used as an initiator for vinyl radical polymerization[21—23] and graft copolymerization.[24] It can thus be expected that the use of cerium(IV) as an oxidant will give polyaniline from aniline in much higher yield than conventional oxidants, even under mild conditions. Furthermore, oxidation by cerium(IV) ions under mild conditions is expected to give the corresponding polymers from some hindered aniline derivatives, such as 3,5- and 2,3-dimethylanilines, although they can not give polymers by the conventional oxidant. Cerium(IV) salts have been used for the oxidation of aniline derivatives to the corresponding quinones.[25] However, there has been no report concerning the polymerization of aniline by using cerium(IV) ions as an oxidant.

Here, polymers of aniline and its derivatives were successfully prepared by using cerium(IV) sulfate as an oxidant instead of the conventional ammonium peroxodisulfate. The effects of the reaction conditions, such as the reaction temperature, reaction time, and the presence and concentration of acids, were investigated in order to optimize the reaction from the viewpoint of the electroconductivity and isolated yield of the produced polymer. The polymerization mechanism by cerium(IV) ions is discussed based on a comparison with that by copper(II) and peroxodisulfate ions.

Experimental

Materials. Aniline was distilled under reduced pressure prior to use. The other chemicals were used as received.

Preparation of Polyaniline and Its Derivatives. The chemical polymerizations of aniline were performed in both the presence and absence of protonic acids. Typically, a solution of aniline was added dropwise over a period of 15 min into a vigorously stirred aqueous solution of cerium(IV) sulfate kept at ca. 5 °C in an ice bath. After stirring for the designed time, the produced precipitates were separated by filtration, washed first with 1 mol dm^{-3} HCl, then with distilled water, and methanol, and finally with acetone in order to remove any inorganic materials and unreactive monomer, respectively; they were then dried under reduced pressure



Scheme 1. Preoxodisulfate $S_2O_8^{2-}$ can form polymer from 2,6-dimethylaniline, but it is not true for 3,5-dimethylaniline, although both polymerization can take place electrochemically.

at room temperature overnight.

The chemical polymerization of aniline derivatives was performed at 80 °C for 8 h. The other reaction conditions were the same as in the case of aniline.

Measurements. FT-IR studies were carried out with a Shimidzu FTIR-4000 spectrometer using a pressed KBr-pellet technique. The electroconductivity was measured for a pressed-pellet type sample of 10 mm in diameter and 1 mm in thickness with a conventional four-probe technique. Scanning electron micrographs of polyaniline, covered with a thin layer of sputtered gold, were measured at 25 kV and recorded on a Hitachi S-520 instrument. UV-vis studies were recorded with a Hitachi U-4000 spectrophotometer in a solution of *N*-methyl-2-pyrrolidone. Thermal analyses were carried out with a Shinku-Riko TGD-7000RH analyzer. Approximately 6 mg of the sample was heated at a rate of 10 $^\circ\mathrm{C\,min^{-1}}$ under a 120 $\mathrm{cm^3\,min^{-1}}$ flow of dry nitrogen.

Results and Discussion

Polymerization of Aniline. The polymerizations were performed by the oxidation of aniline with cerium(IV) sulfate $Ce(SO_4)_2$ under comparable conditions. The polymerization conditions were altered so as to be optimized with emphasis on the isolated yield and the electroconductivity. The results are given in Table 1. The polyaniline, prepared at the highest yield of 84% in a neutral medium at 5 °C and doped with a 1 $\mathrm{mol\,dm^{-3}}$ aqueous hydrochloric acid solution, exhibited a higher electroconductivity (1.3 $\mathrm{S\,cm^{-1}}$) than that prepared in an acidic medium. This result is quite different from the case of polymerization by conventional ammonium peroxodisulfate, since polymerization is usually performed in an acidic solution, and not so smooth in a neutral medium in the case of ammonium peroxodisulfate. Both polymers, prepared in an acidic medium and in a neutral one, have the same main chain according to the IR data. Details concerning the effect of the hydrochloric acid are discussed later.

The reaction temperature and time have rather big effects on the yield and the electroconductivity of the produced polyaniline in the present reaction. As for the reaction temperature, comparing the results in Runs 1—3 of Table 1, both the isolated yield and the electroconductivity of the polyaniline were highest at 5 °C among them. It could be considered that the polymerization process competes with the oxidation process of the produced polymer. The oxidation process can be accelerated by increasing the temperature. Over-oxidation could occur at high temperature, which could cause the polymer to degrade. Thus, the isolated yield and electroconductivity of the polyaniline become low at high temperature compared with the case of a polymer prepared at low temperature.

As for the reaction time, 8 h could be the optimum among Runs 1, 10, and 11 in Table 1 to obtain a polymer at the highest isolated yield and with the highest electroconductivity. This fact suggests that one of the propagation and oxidation processes does not yet complete to produce the Emeraldine[26] structure within a short reaction time, making the isolated yield and the electroconductivity low for a short reaction time. On the other hand, an over-oxidation process could occur during a long reaction time, making the produced polymer degrade, resulting in a low isolated yield and low electroconductivity.

The effect of hydrochloric acid was investigated with emphasis placed on the isolated yield and electroconductivity of the produced polyaniline. When the concentration of hydrochloric acid was varied, the polymer obtained in the absence of hydrochloric acid (Run 7) had the highest isolated yield and electroconductivity. It could be considered that the protons may accelerate the oxidation of aniline in the case of a negatively charged oxidant, such as peroxodisulfate $S_2O_8{}^{2-}$. In the present case, however, acceleration by hydrochloric acid was not observed, probably because cerium(IV) is a positively charged oxidant. A similar phenomenon

Table 1. Chemical Polymerization of Aniline by Using Cerium(IV) Sulfate as Oxidant

Run	Monomer/oxidant	Acid	Temp/	Time	Yield	σ
	mol/mol	mol dm^{-3}	°C	h	%	S cm^{-1}
1	1 : 2	1 M HCl	5	21	57	1.3×10^{-2}
2	1 : 2	1 M HCl	15	21	53	6.1×10^{-3}
3	1 : 2	1 M HCl	25	21	44	3.9×10^{-4}
4	1 : 1	1 M HCl	5	21	28	1.1×10^{-2}
5	2 : 1	1 M HCl	5	21	15	9.6×10^{-2}
6	1 : 2	0.5 M HCl	5	21	70	1.8×10^{-1}
7	1 : 2	None	5	21	78	8.8×10^{-1}
8	1 : 2	None	5	6	84	1.3
9	1 : 2	None	5	3	77	1.5
10	1 : 2	1 M HCl	5	8	73	2.0×10^{-1}
11	1 : 2	1 M HCl	5	5	51	2.8×10^{-3}

was observed in the polymerization of aniline catalyzed by copper(II) salts.[17] The detailed mechanism of the polymerization is discussed later.

Structure of the Polyaniline. The polyanilines prepared by the present method were characterized by FT-IR. The IR spectrum of the polymer which was produced at the highest yield and exhibited a high electroconductivity (Run 8) has peaks at 1580, 1490, 1310, 1250, 1150, 820, 600, and 510 cm^{-1}; the peak at 1490 cm^{-1} is attributable to C–N bonds of the benzenoid units, and the peak at 1580 cm^{-1} is attributable to C=N bonds of the quinonoid units. The IR spectrum of the polymer prepared by the present method is quite similar to that prepared by the conventional method using ammonium peroxodisulfate (peaks at 1575, 1490, 1300, 1243, 1145, 820, 600, and 510 cm^{-1}).[27]

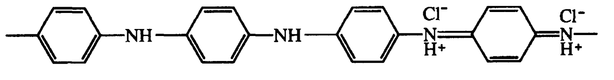
The UV-vis spectra of polyanilines prepared by peroxodisulfate $S_2O_8{}^{2-}$ and cerium(IV) ions were measured in *N*-methyl-2-pyrrolidone (NMP). Both spectra showed two absorption bands at 325 and 620 nm. The first absorption band at 325 nm is associated with a π–π^* transition of the conjugated ring systems.[28,29] The second band at 620 nm is assigned to be a benzenoid to a quinonoid excitonic transition.[30] The intensity of the second band at 620 nm in the spectrum of the polymer prepared by using cerium(IV) ions is rather weaker than that of the polymer prepared by using peroxodisulfate,[31] which indicates that the relative amount of the quinonoid diimine unit in the polyaniline prepared by using Ce(IV) ions is less than that prepared by using peroxodisulfate.

Thermogravimetric analyses (TGA) of the two samples indicated three stages of weight losses at around 100, 200, and 470 °C under nitrogen. The weight loss at around 100 °C has been assigned mainly to the loss of water.[32] The weight loss at around 200 °C is mainly due to low-molecular-weight chlorine compounds, such as hydrogen chloride, which is contained in the polymer as a dopant.[33] The weight loss at around 470 °C could be attributed to polymer decomposition. The curves of the two samples are essentially the same, which means that the polyaniline prepared by using cerium(IV) ions was doped by hydrogen chloride in essentially the same level as that prepared using peroxodisulfate.

The above results and the elemental analysis (Found: C, 57.4; H, 5.0; N, 10.8%. Calcd for $C_{24}H_{20}N_4(H_2O)_2Cl_2$: C, 61.1; H, 5.1; N, 11.9%) have suggested that the polyaniline prepared by using cerium(IV) sulfate as an oxidant has essentially the chloride-doped Emeraldine structure, as shown in Scheme 2.[34]

Polymerization of Aniline Derivatives. The polymerization of four dimethyl derivatives of aniline was examined by using the present method. The results are given in Table 2. It is noteworthy that cerium(IV) sulfate can cause the polymerization of 3,5- and 2,3-dimethylaniline (xylidine), resulting in polymeric products, while no polymeric products can be detected for these aniline derivatives when using the ammonium peroxodisulfate as the oxidant.[16]

The polymerization conditions were altered so as to be optimized with emphasis on the isolated yield of poly(3,5-dimethylaniline). The polymerizations of 3,5-dimethylaniline were performed by the oxidation of the monomer with cerium(IV) sulfate under comparable conditions. The results are shown in Table 3. The polymer, prepared at the highest yield of 44—47 % in a



Scheme 2. Structure of the Emeraldine salt.

Table 2. Chemical Oxidative Polymerization of Dimethylanilines by Using Cerium(IV) Sulfate[a)]

Monomer	Isolated yield/%	Color	Composition[b)]
3,5-	46	Brown	$C_{32.0}H_{32.8}N_{3.1}$
2,3-	70	Brown	$C_{32.0}H_{35.9}N_{3.0}$
2,6-	71	Dark-brown	$C_{32.0}H_{33.2}N_{2.4}$
2,5-	79	Grey	$C_{32.0}H_{23.4}N_{2.2}$

a) Monomer/oxidant = 1/1 mol/mol, in water at 80 °C for 8 h. b) The theoretical composition is $C_{32}H_{34}N_4$.

Table 3. Polymerization of 3,5-Dimethylaniline Using Cerium(IV) Sulfate as Oxidant in the Various Conditions

Run	Solvent	Temperature/°C	Time/h	Yield/%	σ/S cm^{-1}
1	Acetonitrile	20	4	12	—
2	Methanol	20	4	6	—
3	Ethanol	20	4	13	—
4	Acetonitrile/Water	20	4	21	6.7×10^{-5}
5	Acetonitrile/1 M HCl	20	4	0	—
6	Water	20	4	34	3.1×10^{-5}
7	Water	0	4	25	2.0×10^{-5}
8	Water	50	4	33	3.0×10^{-5}
9	Water	80	4	44	2.4×10^{-5}
10	Water	80	8	46	—
11	Water	80	18	47	—

neutral medium at 80 °C and doped with a 1 mol dm^{-3} aqueous solution of hydrochloric acid, does not exhibit high electroconductivity (2.4×10^{-5} S cm^{-1}).

The reaction temperature and reaction time have rather big effects on the reaction yield of the polymer. When the reaction temperature is varied, the highest isolated yield of the polymer is observed at 80 °C (cf. Runs 9, 10, and 11). It could be considered that the reaction temperature plays an important role in the polymerization process of inactive monomers, such as 3,5-dimethylaniline. Thus, the oxidation process can be accelerated by increasing the temperature. The IR and XPS data indicate that oxidation of the alkyl group of dimethylaniline did not occur, although the reaction proceeded at high temperature. When the reaction time was varied, the isolated yield of the polymer apparently did not change.

The effect of protonation was investigated with emphasis placed on the isolated yield of the produced polymer. When hydrochloric acid was added to the reaction mixtures, no polymeric product was obtained, as shown in Table 3 (Run 5). It could be considered that the protons may suppress the oxidation of monomers in the case of a positively charged oxidant, as in the present case (mentioned before).

The poly(3,5-dimethylaniline) obtained was characteristic of the Emeraldine structure on the basis of the IR results. The IR spectrum of the polymer, shown in Fig. 1(a), has a peak at 1470 cm^{-1} (C–N bonds) and another at 1600 cm^{-1} (C=N bonds). The spectrum is quite similar to that prepared by the electrochemical method in a mixed aqueous $LiClO_4$ and $HClO_4$ solution (cf. Fig. 1(b)).

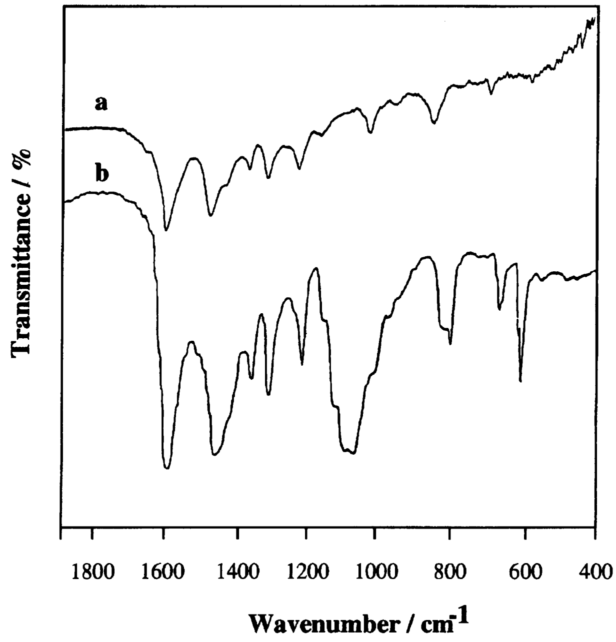


Fig. 1. FT-IR spectra of (a) the product obtained from 3,5-dimethylaniline by using cerium(IV) sulfate, and (b) poly(3,5-dimethylaniline) prepared by an electrochemical method in $LiClO_4/HClO_4$aq.

Mechanism of the Polymerization. In the UV-vis spectra of the reaction mixtures shown in Fig. 2, the maxima are observed at 320 and 527 nm. The peak at 527 nm increases, while the peak at 320 nm decreases, with increasing reaction time. It could be considered that the peak at 320 nm is due to the cerium(IV) complex of aniline, which forms at the beginning of polymerization, whereas the peak at 527 nm is due to the oligomer of aniline. In the case of the polymerization of aniline using $CuCl_2/O_2$ as an oxidant, similar changes were observed.[17] On the other hand, in the presence of hydrochloric acid, the absorbance maxima were observed at a long wavelength of 720 nm in the case of cerium(IV) sulfate, instead of 527 nm in the absence of hydrochloric acid. In the case of ammonium peroxodisulfate in the absence and presence of hydrochloric acid, the corresponding absorbance maxima were at 580 and 700 nm, respectively.

Figure 3 shows the time-dependent change in the absorbance at long wavelength of the UV-vis spectra in both the absence and presence of hydrochloric acid by using cerium(IV) sulfate and ammonium peroxodisulfate as an oxidant, respectively. In the case of cerium(IV) ion (Fig. 3c and d), the rate of polymerization appeared to decrease upon adding hydrochloric acid into

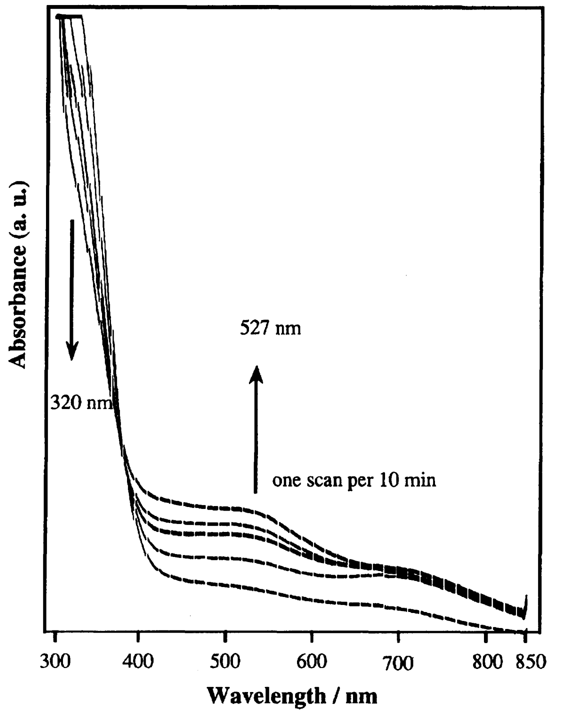


Fig. 2. In-situ UV-vis spectra of the aqueous mixtures of aniline and $Ce(SO_4)_2$ (mol/mol, 1/1) at room temperature. Change with every 10 min.

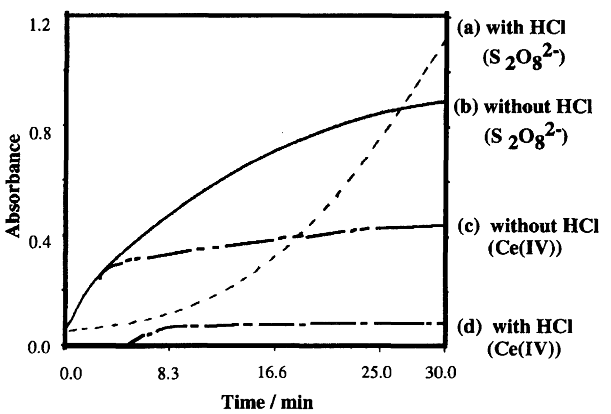


Fig. 3. Time-dependent absorbance change in the in-situ UV-vis spectra of the aqueous mixtures of aniline and $(NH_4)_2S_2O_8$ (mol/mol, 1/1) (a) at 700 nm in 1 mol dm^{-3} HCl and (b) at 580 nm in neutral medium, and of the aqueous mixture of aniline and $Ce(SO_4)_2$ (mol/mol, 1/1) (c) at 527 nm in neutral medium and (d) at 720 nm in 1 mol dm^{-3} HCl.

the reaction mixtures. This is quite different from the case of peroxodisulfate (Fig. 3a and b).

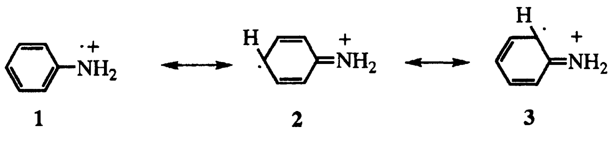
The results on the optimized reaction conditions have suggested that the polymerization of aniline proceeds through the cerium(IV) complex, as previously reported in the case of the copper(II) oxidant.[17] However, the formation of a complex between the cerium(IV) ion and the aniline protonated by hydrochloric acid is considered to be very difficult. Of course, the pH of the solution could influence the oxidation ability of cerium(IV) ions. However, the effect is usually small and a low pH could actually often increase the oxidation ability of metal ions.[35] Therefore, the fact that the presence of hydrochloric acid has depressed the polymerization of aniline by cerium(IV) ions could be attributed to a difficulty of complex formation due to an electrostatic repulsion.

On the other hand, in the case of the peroxodisulfate ion (Fig. 3a and b), the rate of the polymerization increases in the presence of hydrochloric acid. This is probably because protonation of the amino group makes it easy to form the intermediate complex with the negatively charged peroxodisulfate oxidant. In both cases, in the presence of hydrochloric acid, the reactions proceed after an induction period.

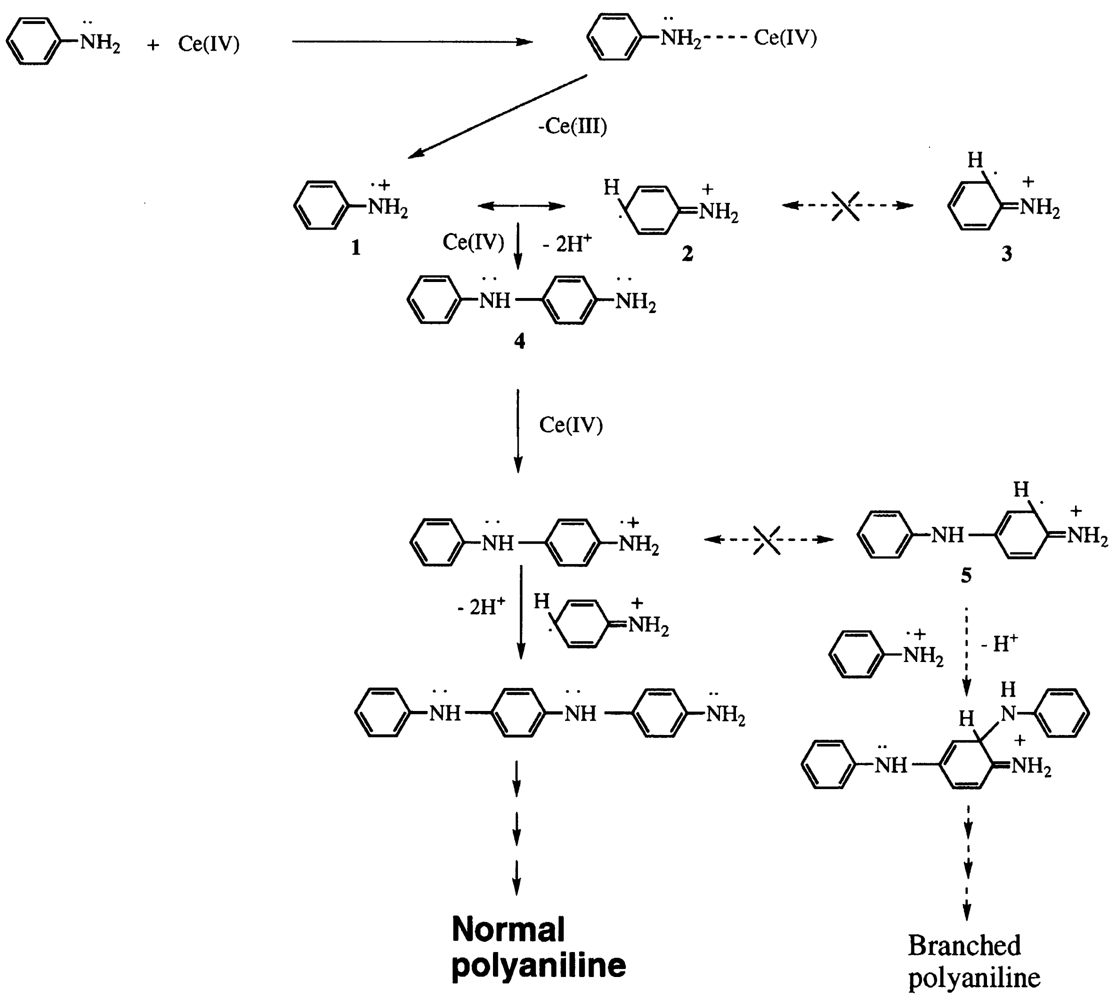
On the basis of the results of the UV-vis spectra, the cerium(IV) complex of aniline could be considered to be produced at the beginning of the polymerization. Then, a one-electron transfer occurs from the aniline to the cerium(IV) in the complex, resulting in the formation of a radical cation of aniline and cerium(III). The electron of the radical cation can delocalize. Thus, three canonical formulae can be written as in Scheme 3. In order to obtain normal linear polyaniline (and then a polyaniline with the Emeraldine structure), N-radical cation **1** and para radical cation **2** must be coupled, which should be followed by deprotonation, giving dimer **4**, as shown in Scheme 4.

The polymerization process after formation of the radical cation is considered to be quite similar to that suggested by E. M. Genies et al.[35] for the production of polyaniline by an electrochemical method. In contrast, the branched polyaniline was obtained in the catalytic polymerization of aniline by the $CuCl_2/O_2$ system.[17] For the formation of the branched polyaniline, ortho radical cations like **3** and **5** must contribute in the polymerization. Although an exact explanation is not yet clear, it might be suggested that copper ions could activate ortho radical cations, while cerium ions could activate para radical cations.

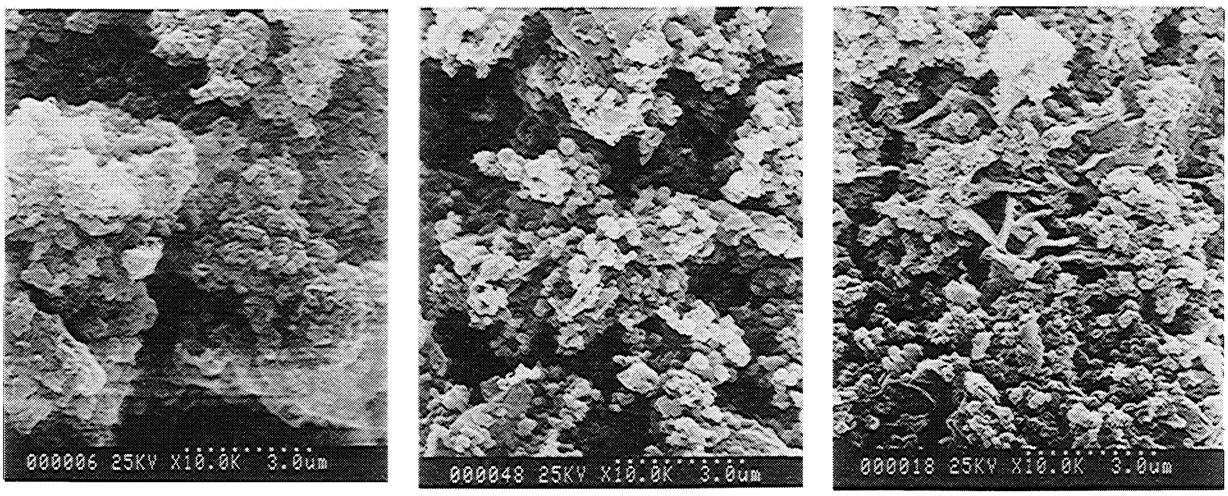
One of the important characteristics of the cerium(IV) ion for the polymerization of aniline derivatives is that cerium(IV) sulfate can produce the corresponding polymers from 3,5- and 2,3-dimethylaniline (xylidine), although ammonium peroxodisulfate, a conventional oxidant for the polymerization of aniline, can not produce the polymers.[16] It is generally considered that the two methyl substituents depress the reactivity of



Scheme 3. Canonical formulae of the radical cation of aniline.



Scheme 4. Suggested mechanism of the polymerization of the aniline by Ce(IV).



a **b** **c**

Fig. 4. Scanning electron micrographes of the polyanilines prepared by using (a) $S_2O_8^{2-}$ in 1 mol dm^{-3} HCl, (b) Ce(IV) in water, and (c) Ce(IV) in 1 mol dm^{-3} HCl solution, respectively.

the radicals due to a steric hindrance as well as an electron-releasing effect. Thus, ammonium peroxodisulfate as well as copper(II) chloride can not force the polymerization, while cerium(IV) sulfate can. Although the reason for this is not yet clear, the difference in the redox potential in copper and cerium (E°(Cu(II)/Cu(I))=0.554 V and E°(Ce(IV)/Ce(III))=1.74 V vs. NHE[19]) may give the answer. Cerium(III) ions, produced from cerium(IV) by the oxidation of aniline derivatives, might promote propagation by an interaction with the radical through the ligand.[36]

Morphology of the Polyaniline. The electrochemical method provides a fribric morphology in the polymerization of aniline,[37] while the conventional chemical method usually provides an amorphous morphology. However, some difference in the morphology was observed between the polyanilines by the present method and the conventional method. Thus, the polyaniline, obtained by using cerium(IV) sulfate in the acidic medium, provides a partially belt-like morphology in a scanning electron spectroscopic observation, as shown in Fig. 4. Ando et al. observed a similar fibric morphology of polyaniline prepared chemically in the presence of HBF_4.[38] The belt-like morphology could be crystalline like the fibric morphology. The relations between the morphology and the electroconductivity or the precipitating process are under investigation in our laboratory.

Conclusion

Polyaniline and its derivatives were prepared by using the cerium(IV) sulfate as an oxidant instead of the conventional ammonium peroxodisulfate. The reaction conditions were optimized with emphasis placed on the conductivity and yield. The reaction of 3,5- and 2,3-dimethylaniline by using cerium(IV) sulfate gave polymeric products, while no polymeric products were obtained by using the conventional ammonium peroxodisulfate as an oxidant. Although the reason is not yet clear, it might be because the cerium(III) ion, which has some electron-withdrawing property, can promote polymerization of the para radical cation of aniline by a weak interaction. The complex formation between cerium(IV) and aniline is quite probable at the beginning of the polymerization, which is the reason why the polymerization is depressed by the presence of hydrochloric acid.

The thus-produced polyaniline was characteristic of the Emeraldine structure on the basis of the IR spectra. The partially belt-like morphology of the polyaniline, when prepared in an acidic medium, was observed by scanning electron microscopy.

Thus, the present method can produce electroconducting, compact and partially belt-like polyaniline from aniline. The polymer has a sufficiently high electroconductivity (1.3 S cm^{-1}) to be used as a secondary battery. Furthermore, the polymer could have a higher volumetric charge density, which is an important parameter for application to a secondary battery,[34] since it has a more compact morphology than that produced by the conventional method.

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