

Aqueous polyaniline suspensions: chemical oxidative polymerization of dodecylbenzene-sulfonic acid aniline salt

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Chemical oxidative polymerization of dodecylbenzenesulfonic acid aniline salt in water using ammonium peroxydisulfate as oxidant was found to give an homogeneous polyaniline suspension. An aqueous transparent and green uniform suspension containing polyaniline complexed and doped with dodecylbenzenesulfonic acid was obtained to show a typical emeraldine salt spectrum. The polyaniline suspension was quite stable without any precipitation for several months and could be diluted with water. Polyaniline recovered from the reaction mixture with addition methanol was characterized. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Polyaniline has emerged as one of the most promising conducting polymers because of its stability and ease of preparation^{1–3}. There is a good deal of study of conducting polymers with the aim of discovering a new functional polymeric material^{4–7}. However, polyaniline processing has remained a difficult problem. Potential applications are still limited due to the inherent intractability, i.e. polyaniline decomposes without melting when heated and has very low solubility in the doped, conducting state even in highly polar solvents such as dimethyl formamide. Polyaniline is neither soluble nor fusible in organic solvents as well as water⁸. The introduction of alkyl substituents on the polymer backbone has considerably improved its solubility in the doped and undoped forms in common organic solvents and even in water^{9,10}. However, while the addition of side-groups has enhanced its solubility and processability, the electrical conductivity was reduced. The solubility of the emeraldine base form of polyaniline in NMP (N-methyl-2-pyrrolidone) enables the processing of films and fibres¹¹. Another way to obtain processable polyaniline is the preparation of polyaniline in colloidal form. Many attempts to produce colloidal polyaniline have been made by using polymeric surfactants^{12,13}. An approach was suggested consisting of graft copolymerization of aniline onto modified polymeric surfactants¹⁴. These systems significantly enhance the processability of the normally intractable polyaniline.

Cao *et al.* reported that polyaniline doped with dodecylbenzenesulfonic acid (DBSA) or camphor

sulfonic acid could be soluble in various organic solvents such as chloroform and xylene^{15,16}. They used this type of polyaniline for electroluminescent devices such as the hole injection layer of an electroluminescence cell component¹⁷. Angelopoulos *et al.* developed water-soluble electrically conducting polyaniline doped with functional acids such as polystyrene sulfonic acid¹⁸. The polymeric acid dopants can also be used as a template for the oxidative polymerization of aniline, which results in a water-soluble polyaniline.

We have reported that a morphology change and rate enhancement effect could be attained when polymerization of aniline was carried out in the presence of a polyelectrolyte or surfactant like sodium dodecyl sulfonate (SDS)¹⁹. An acceleration in the growth of polyaniline in the electropolymerization system in the presence of polyvinylsulfate or SDS was observed due to the high local concentration of aniline monomer in the reaction medium²⁰. We found that polymerization of the amphiphilic aniline monomer resulted in a soluble polyaniline suspension in water or organic solvents²¹. Furthermore, chemical polymerization of aniline in well organized system such as the micellar system may lead to not only an acceleration of polymerization rate but also an increase of molecular weight²².

In this report, oxidative polymerization of DBSA has led to a clear homogeneous polyaniline suspension in water. It has been necessary to investigate the optimum reaction conditions for the chemical synthesis of polyaniline aqueous suspension. We found that these optimized reaction conditions are suitable for the preparation of polyaniline suspension and that such systems significantly improve the processability of the normally intractable conducting polyaniline.

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EXPERIMENTAL

All reagents were used as received. The preparations were carried out in aqueous solution. The polymerization temperature was controlled by placing the reaction vessel in a regulating bath while monitoring the temperature with a thermometer that was inserted directly into the reaction mixture.

Dodecylbenzenesulfonic acid aniline salt (DBSA_n) was prepared by the reaction of dodecylbenzenesulfonic acid (DBSA) and aniline. Polymerization of DBSA_n was carried out by chemical oxidation of DBSA_n using ammonium persulfate (APS) as oxidant in an aqueous solution with different molar ratios of DBSA_n/oxidants. In all cases, a dark green coloured polyaniline suspension was obtained without any precipitation. When a small amount of methanol was added to the reaction mixture, polyaniline precipitated gradually.

The precipitated polyaniline was recovered from the polymerization mixture using excess methanol, filtered and then washed with distilled water until the washing liquid was completely colourless. In order to remove oligomers and other organic by-products the precipitate was washed with several portions of methanol and dried *in vacuo*.

For conductivity measurements, pellets of each sample of dry polyaniline were pressed, coated top and bottom with gold and placed between two electrodes. Conductivity measurements of the pellets were made at room temperature. The values of conductivities were calculated using the surface area and the thickness of each pellet and reproducible within $\pm 20\%$.

A spectrophotometer (Shimadzu UV-210A) was used to measure optical absorbances in the wavelength range 350–900 nm of an aqueous suspension of polyaniline. The polyaniline suspension was diluted 500 times with a purified water and the electronic absorption spectrum measured.

RESULTS AND DISCUSSION

Immediately after the addition of APS to DBSA_n solution, the slightly yellow tint of the reaction mixture became darker together with a slowly developing transparent green colouration. Polymerization proceeded as DBSA_n was oxidized to polyaniline emeraldine salt doped with DBSA. During the course of reaction no precipitation occurred in the polymerization mixture. A transparent dark green coloured suspension was obtained, which showed the presence of polyaniline emeraldine salt in the reaction mixture. When a small amount of methanol was added to the reaction mixture, polyaniline precipitated gradually from the reaction mixture.

Figure 1 shows the effect of varying the oxidant concentration on the yield and conductivity of polyaniline recovered from the polymerization mixture by adding an excess amount of methanol. The polymerization was carried out varying the APS concentration at constant DBSA_n concentration (5 mM) and 50°C for 0.5 h. The polymer yield increased linearly with APS concentration from 2 to 6 mM before decreasing sharply at 8 mM. Maximum conductivity of the polyaniline pellet was observed for the 6 mM sample, but conductivities above $10^{-1} \text{ S cm}^{-1}$ were obtained for all samples between 2 and 10 mM. Figure 1 also shows the effect of the monomer/oxidant molar ratio vs constant

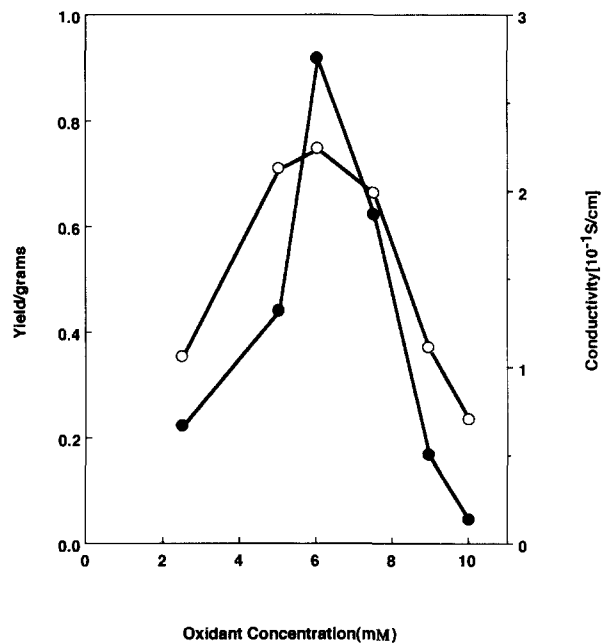


Figure 1 Effect of the oxidant concentration on the polymer yield and conductivity: \circ , polymer yield g^{-1} ; \bullet , conductivity ($10^{-1} \text{ S cm}^{-1}$)

DBSA_n concentration on the polymer yield and conductivity of polyaniline. Yield of polymerization and conductivity of polyaniline depend on the molar ratio of DBSA_n vs oxidant. Both conductivity and polymer yield increase with increasing oxidant vs monomer molar ratio of 1/1.2 and decrease with increasing ratio higher than 1/1.2 molar ratio. The compressed pellet conductivity of the recovered polyaniline also increased linearly with polymer yield up to 1.2.

The polymerization of aniline in HCl using APS as oxidant was previously investigated. It was shown that higher polymer yields were obtained by increasing the initial oxidant/monomer mole ratio up to 1.2. Assuming the persulfate anion was acting as a two-electron acceptor, the results suggest that approximately 2.3 electrons were removed from each aniline monomer unit. For values over 1.2 the polymer yield was reduced, presumably due to over-oxidation of polyaniline chains with concomitant formation of low-molecular weight by-products.

Figure 2 shows the effect of temperature on yield and conductivity of polyaniline recovered from the polymerization mixture. Polymerizations were carried out with an equimolar amount of DBSA_n and APS (5 mM) for 1 h at various temperatures. The yield and conductivity decreased proportionally with increasing temperature. In their early work, Cao *et al.* indicated that the viscosity of polyaniline is sensitive to the polymerization temperature. The viscosity of the polyaniline increased on decreasing the polymerization temperature. Side reaction such as hydrolysis occurred frequently at high temperature and byproducts having lower conductivity were increased in the polymerization mixture.

Figure 3 also shows the effect of polymerization time on the conductivity of polyaniline polymerized at various temperatures with an equimolar amount of DBSA_n and APS (5 mM). The conductivity of polyaniline polymerized for 1 h at lower temperature was higher than that of polyaniline polymerized within 0.5 h. At higher temperature the conductivity tendency

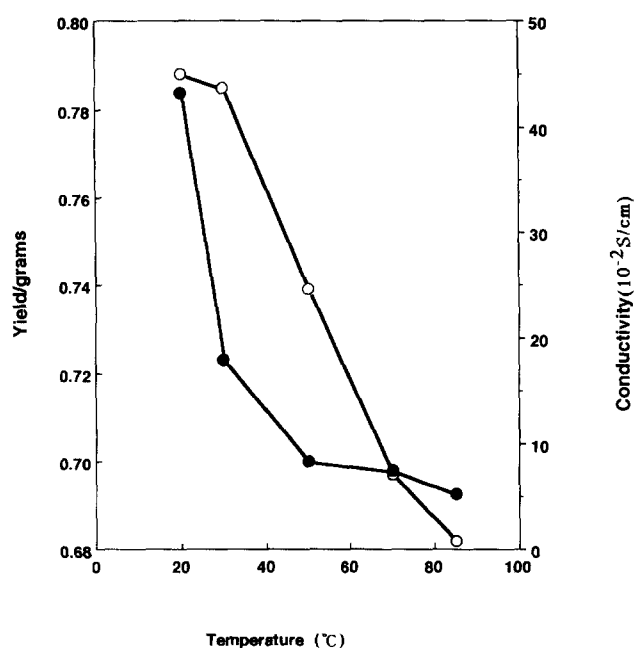


Figure 2 Effect of the polymerization temperature on the polymer yield and conductivity: ○, polymer yield g^{-1} ; ●, conductivity (10^{-1}S cm^{-1})

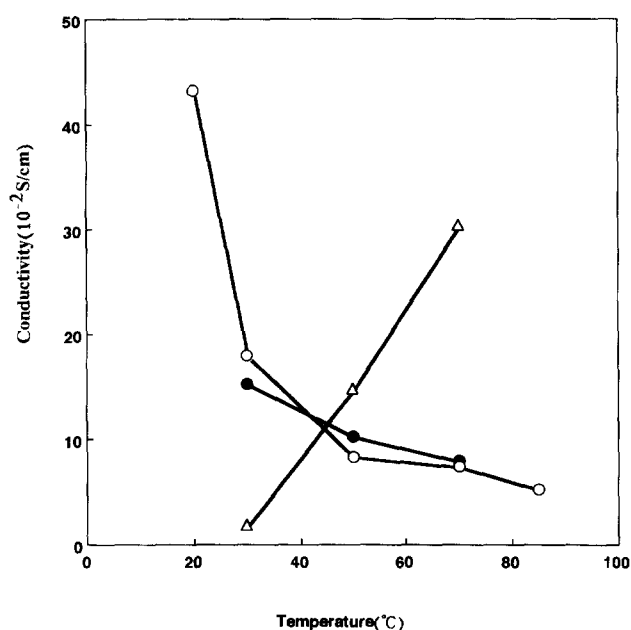


Figure 3 Effect of polymerization time on conductivity of polyaniline polymerized at various temperatures: Δ, 0.1 h; ○, 0.5 h; ●, 1 h

was reversed. This figure also shows that the conductivity was almost the same over periods of 0.5 h. The polymerization occurred relatively rapidly and was essentially completed in a short time. A short time after introduction of APS to the polymerization system, highly conducting polyaniline was produced in the polymerization mixture. Cao *et al.* reported that prolonged periods lead to slow hydrolysis, resulting in a decrease of the viscosity and are not necessary.

Figure 4 shows the effect of three different dopant anions and polymerization temperature on the polymer yield and conductivity under the same synthesis conditions. The DBSA anion could significantly affect the conductivity of polyaniline even at temperatures above

50°C. The conductivity was found to be consistently greater for the DBSA treated polyaniline. In general, polyaniline prepared at lower temperature shows good conductivity due to inhibition of side reaction such as hydrolysis. Furthermore, in HCl and PTS aqueous solution, polyaniline was precipitated from the reaction mixture proceeding with the course of reaction. However, for the DBSA system no precipitation was observed in the course of polymerization. After the polymerization reaction, a homogeneous and transparent aqueous suspension was obtained due to the doping of DBSA anion. Therefore, high quality polyaniline could be obtained resulting from the solubilization of polyaniline.

An aqueous polymerization mixture suspension could be diluted with water containing hydrochloric acid or sodium hydroxide to control environmental pH. It is well known that polyaniline film changes its colour with pH. This phenomenon also could be attained using aqueous polyaniline suspension. Therefore, we measured the electronic spectra of polyaniline directly with the aqueous polyaniline suspension (Figure 5). In the lower pH region, the electronic spectrum shows a maximum absorption at 800 nm due to the radical cation formed on the polyaniline backbone chain. The absorption maxima shifted toward a longer wavelength region from 800 to 860 nm (pH 7) in the acid protonated region. Other absorption bands observed at 420 and 330 nm did not shift with changing pH. At the higher basic pH region, the absorption spectrum was quite different from the acidic spectra. At pH 9, the absorption spectrum showed a shoulder at 410 nm and a maximum at 630 nm. At pH 11, each spectrum showed a maximum at 580 nm and the absorption maximum at 410 nm disappeared. These results are similar to our previous report²².

Figure 6 shows the relationship between the absorbance of an aqueous suspension of DBSA polymerization mixture measured at two different wavelengths and oxidant concentrations. During the course of polymerization, the aqueous reaction mixture suspension became a dark green colour with the introduction of

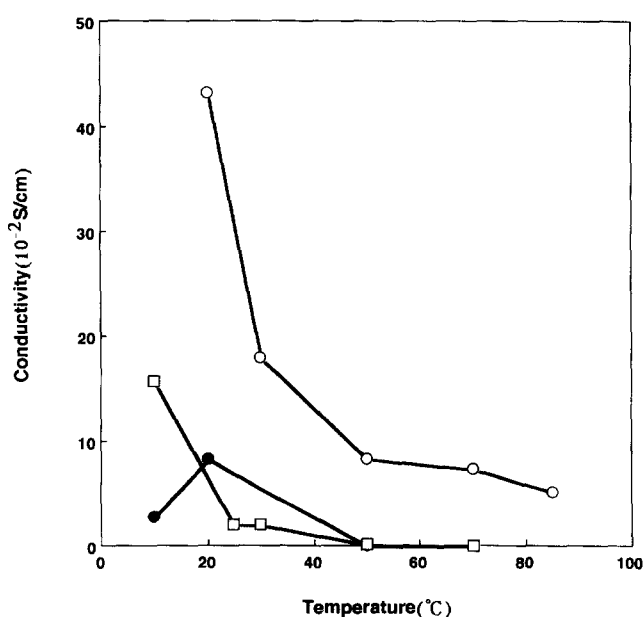


Figure 4 Effect of three different dopant anions and polymerization temperature on the polymer yield and conductivity: ○, DBSA; ●, HCl; □, PTS

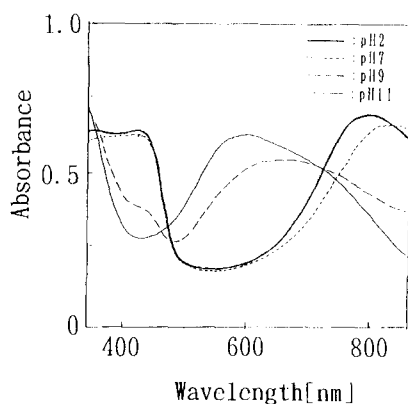


Figure 5 Absorption spectra of aqueous polyaniline suspension at various pHs: —, pH 2; ···, pH 7; - · -, pH 9; — — —, pH 11

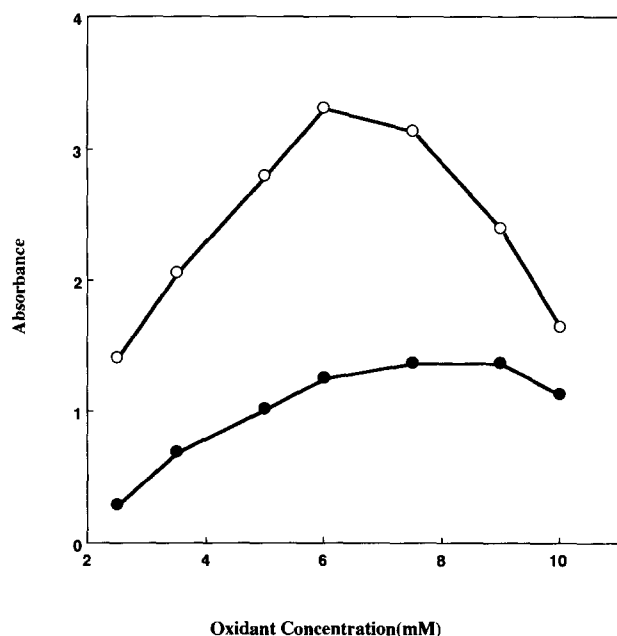


Figure 6 Relationship between the absorbance of aqueous polyaniline suspension measured at two different wavelengths and oxidant concentrations: ○, 800 nm; ●, 528 nm

APS. From the previous paper²³, the conducting form of the emeraldine salt has two characteristic absorption bands at 420 and 800 nm (polaron band). Furthermore, the electronic spectrum of fully oxidized pernigraniline shows maximum absorption values at 528 and 320 nm. Therefore, the electronic spectrum of the polymerization mixture gave us an information on the oxidation state of polyaniline.

These measurements were carried out using an aqueous suspension of the polymerization mixture after the reaction. The absorbance at 800 nm increases linearly with APS concentration from 2 to 6 mM before decreasing sharply at 8 mM. The maximum absorbance was observed for the polyaniline suspension polymerized at 6 mM APS concentration. On the other hand, absorbance at 528 nm gradually increased with increasing APS concentration, presumably due to the over-oxidation of the polyaniline emeraldine salt. These results show that polyaniline changed its oxidation state from the emeraldine salt to pernigraniline for

values over 6 mM oxidant concentration due to over-oxidation.

CONCLUSION

Chemical oxidative polymerization of DBSA using APS as an oxidant resulted in an homogeneous aqueous dark green suspension of polyaniline emeraldine salt. A homogeneous aqueous transparent dark green coloured suspension was obtained, which showed the presence of emeraldine salt in the reaction mixture. The obtained aqueous dark green coloured suspension containing polyaniline was quite stable without any precipitation for at least several months. The absorption peak characteristic of emeraldine salt was clearly seen at 420 and 800 nm. However, upon adding methanol or acetone miscible with water to the reaction solution, precipitation occurred to yield a powdery polyaniline solid. These results suggested that polyaniline was solubilized and stabilized in water by doping and complexing with DBSA.

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