A Study of Leucoemeraldine and the Effect of Redox Reactions on the Molecular Weight of Chemically Prepared Polyaniline

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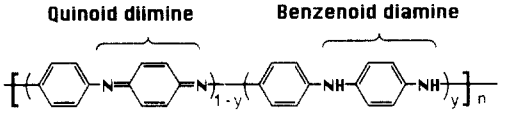
ABSTRACT: We present the first study of the chemical interconversion between leucoemeraldine and emeraldine bases of polyaniline in relation to the molecular weight and molecular weight distribution. Electronic absorption spectroscopy and gel-permeation chromatography were employed to monitor the changes in the oxidation state and molecular weight of the polyaniline, soluble in 1-methyl-2-pyrrolidinone, during the redox reactions. The molecular weight and molecular weight distribution of polyaniline were found to change drastically when the redox reactions were performed with the polymers in the solid phase while relatively little when the reactions were carried out with the polymers in the solution phase. The changes observed in the solid-phase reactions are attributed to the chemical cross-linking and/or branching by interchain reactions in the polymer particles, which are favored by the small interchain distances.

Introduction

Electronically conducting polymers have attracted considerable attention since the discovery that the conductivity of polyacetylene could reach the metallic region upon doping with oxidizing or reducing agents.[3] Among the known organic conducting polymers, polyaniline has proved particularly interesting for its good conductivity upon doping with nonoxidizing acids, excellent chemical stability, and rich electrochemistry.[4-6] Polyaniline can be prepared by either electrochemical or chemical oxidation of aniline.[4-7] Many derivatives of polyaniline were also synthesized by polymerizing ring- or nitrogen-substituted aniline monomers[8-12] and by copolymerization.[13] There has been much progress in improving the synthetic methodology and elucidating the mechanism of polymerization.[9,14] Numerous applications of polyaniline have been explored, such as photoimaging,[15] electrochromic displays,[16] specialty electrodes for electrocatalytic reactions,[17] lightweight batteries,[18] and semiconducting materials for electronic devices.[19,20]

Almost 100 years ago, there were intensive research efforts on the synthesis and characterization of polyaniline (known as "aniline black" then). These pioneering works by Willstätter, Dorogi, Green, and Woodhead established that the polymer exists in various oxidation states and that these oxidation states are interconvertible upon treating with an oxidant or a reducing agent.[21,22] A great deal more has been learned in the past 10 years about the structure of polyaniline with an array of modern experimental techniques. Currently, polyaniline in the base form is believed to consist of two main structural units, i.e., the benzenoid diamine and quinoid diimine, and can be represented schematically by the following formula.[5-7]



The oxidation state of polyaniline is determined by the y values. Pernigraniline is the completely oxidized form with $y = 0$, whereas leucoemeraldine is the fully reduced form ($y = 1$). Emeraldine contains an equal fraction of both reduced and oxidized forms ($y = 0.5$). Recently, pure leucoemeraldine and pernigraniline were synthesized and isolated successfully by MacDiarmid, Epstein, and coworkers.[5,23] Freshly prepared leucoemeraldine is an electric insulating white powder and is soluble in some organic solvents. The redox reactions of leucoemeraldine have also been studied to a certain extent.[24]

The physical and chemical properties of a polymeric material are known to depend strongly on its molecular weight and molecular weight distribution. However, relatively few reports have appeared in the literature about the molecular weight and its effects on the physicochemical properties of polyanilines.[8,25-27] We have found that the gel-permeation chromatographs of the emeraldine base (EB) of polyaniline synthesized both chemically[25] and electrochemically[27] have a bimodal elution pattern with 1-methyl-2-pyrrolidinone (NMP) as eluant. Depending on the synthesis conditions, the number-average molecular weight (M_n) of EB was typically in the orders of magnitude of 10^3–10^4 and 10^5–10^6 for the low and high molecular weight fractions, respectively, based on the calibration with monodisperse polystyrene standards. The high molecular weight fraction of the bimodal distribution accounts for ca. 30% of the whole elution peak area in NMP, while with tetrahydrofuran (THF) as eluant the high molecular weight fraction is less than 10% because NMP is a better solvent. The observation of the bimodal distribution is of great importance, which has led to the development of fractionation methods to afford high molecular weight and crystalline polyaniline.[28] Furthermore, we also observed that the molecular weight of the electrochemically polymerized polyaniline is altered irreversibly during the electrochemical redox process, which is believed to be caused by cross-linking of the polymer chains.[27]

In this article, we present a study of leucoemeraldine base (LB) and, for the first time, the relations of molecular weight and molecular weight distribution with the chemical redox conditions and the oxidation state of the chemically polymerized polyaniline. The interconversion between EB and LB was accomplished using chemical reduction/oxidation reagents with the polymer either in solid suspension or in NMP solution. The changes in the oxidation state and in the molecular weight during the reactions were continuously monitored with UV–vis–near-IR spectroscopy and with GPC, respectively.

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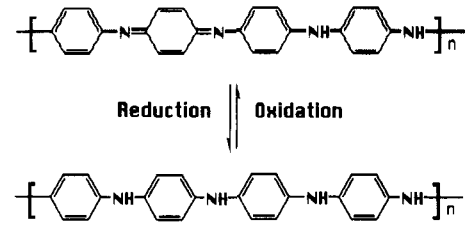
Experimental Section

Materials and Instrumentation. Aniline (99.5% Aldrich) was distilled twice under a reduced pressure. Reagent grade ammonium persulfate (99%, EM Science), hydrogen peroxide (30% by weight aqueous solution, EM Science), phenylhydrazine (Aldrich), hydrazine dihydrochloride (Kodak), sodium acetate (EM Science), and analytical grade lead dioxide (EM Science) were used as received. 1-Methyl-2-pyrrolidinone (NMP, Aldrich, HPLC grade) was used directly as solvent for spectroscopic studies and GPC eluant. ^{1}H NMR spectra were studied on an IBM Bruker WM250 spectrometer operating at 250 MHz with tetramethylsilane (TMS) as internal standard and DMSO-d_6 as solvent. Infrared spectra of the polymers were measured in KBr pellet form on a Perkin-Elmer Model 1600 FTIR spectrophotometer. Background absorbance due to air and KBr was subtracted from the spectra. UV–vis–near IR spectra were taken on a HP 8451 spectrophotometer. The λ_{max} values were generally reproducible to ±3 nm. The molecular weight measurements were performed on a Waters gel-permeation chromatograph Model IIA equipped with a Model 590 programmable solvent delivery module, a differential refractometer as detector, and an Ultrastyragel linear THF-packed column. The column was calibrated with acetone marker giving a tangent number approximately 13 000 plates per column. Approximately 0.1% (by weight) of the polymer solutions in NMP were prepared and were filtered through a 0.2-μm Teflon filter before the sample injection. Freshly prepared solutions were analyzed to exclude the possible aggregation effect. The temperature of both the GPC column and the detector was kept at 35 °C. Chromatographs were recorded with NMP as eluant at a flow rate of 1 mL/min. Number-average molecular weights (M_n) and weight-average molecular weights (M_w) were calculated from a calibration curve of six monodisperse polystyrene standards (Waters Associates) with molecular weights ranging from 1800 to 2 700 000.

Preparation of Emeraldine Base (EB). Emeraldine hydrochloride salt was prepared following the procedure employed by MacDiarmid et al.[7] For a typical example, aniline (5.0 g, 55 mmol) was dissolved in 400 mL of 1 M HCl aqueous solution followed by cooling to near 0 °C in an ice bath. Ammonium persulfate (3.20 g, 13.8 mmol) in 1 M HCl (100 mL) was introduced dropwise. After the addition was completed, the reaction mixture was stirred magnetically for 2 h at ca. 0 °C. The precipitate was filtered and washed exhaustively with 1 M HCl until the filtrate became colorless. Upon drying in vacuo for 40 h at 60 °C, a green powder of the emeraldine HCl salt was obtained in 7% yield and had a conductivity of ca. 10 S/cm. This salt was then dedoped by treating with excess 0.1 M NH_4OH for 4 h to afford the emeraldine base, which was nonconductive and partially soluble in organic solvents. Anal. Calcd for $[C_{12}H_9N_2]$: C, 79.54; H, 5.01; N, 15.46. Found: C, 80.31; H, 4.91; N, 15.67. IR (KBr pellet) in cm^{-1}: 3200–3400 (broad, N–H stretching); 3010, 2950 (aromatic C–H stretching); 1598 (quinoid C=N and C=C stretching); 1496 (aromatic ring stretching); 812 (aromatic C–H bending). ^{1}H NMR (DMSO-d_6) in ppm: 8.0–8.6 (very broad, NH); 7.0 (broad, all the ring protons). UV–vis–near IR (NMP solution) λ_{max} in nm (ϵ in M^{-1} cm^{-1}): 330 (9.5×10^6); 636 (7.7×10^6).

Preparation of Leucoemeraldine Base (LB). LB was prepared from the powder of EB by chemical reduction following the literature methods.[29,30] As a typical procedure, a finely ground powder of EB (0.5 g) was suspended and refluxed either in 99% phenylhydrazine (120 mL) or in an aqueous solution (150 mL) of hydrazine dihydrochloride (10.0 g) and sodium acetate (8.20 g) for 24 h under nitrogen. The refluxing temperatures were about 120 or 105 °C, respectively. The reaction mixture was filtered and washed exhaustively with methanol under a nitrogen atmosphere. Upon drying under dynamic vacuum at 80 °C for 20 h, a gray powder of leucoemeraldine base was obtained in 68 and 95% yields with phenylhydrazine and hydrazine, respectively. The reduction by phenylhydrazine was apparently more complete than that with hydrazine. The related results presented in the text were obtained from the LB samples reduced by phenylhydrazine, unless otherwise specified. Anal. Calcd for $[C_{12}H_{10}N_2]$: C, 79.10; H, 5.53; N, 15.37. Found for the LB prepared with phenylhdrazine: C, 78.91; H, 5.43; N, 15.05. IR (KBr pellet) in cm^{-1}: 3400 (N–H stretching); 3010, 2950 (aromatic C–H stretching); 1065 (quinoid C=N and C=C stretching); 1500 (aromatic ring stretching); 812 (aromatic C–H bending). ^{1}H NMR (DMSO-d_6) in ppm: 7.4 (broad, 1 H, NH); 6.8 (broad, 4 H, the ring protons). UV–vis–near IR (NMP solution) λ_{max} in nm (ϵ in M^{-1} cm^{-1}): 342 (1.7×10^7); 630 (2.0×10^6).

Scheme 1



Oxidation of LB Solution with Molecular Oxygen. As a general procedure, 3.0 mg of LB was dissolved in 3 mL of NMP with stirring at room temperature. The fresh solution was filtered through a Teflon filter unit (0.2 μm) with a syringe to a test tube fitted with a glass gas inlet and outlet. The solution was subsequently purged with dry oxygen at room temperature. At different time intervals, 10 μL of the solution was taken and injected into the GPC, while another 10 μL was diluted with 3.0 mL of NMP solvent for the UV–vis–near IR spectral measurement. For comparison, the same procedure was used to oxidize and characterize the emeraldine base.

Oxidation of LB Solution with H_2O_2. Leucoemeraldine base (0.6 mg) was dissolved in NMP (3 mL) with stirring at room temperature. The solution was filtered through a 0.2-μm Teflon filter to a quartz cuvette (Helma) of 1-cm path length. Aqueous H_2O_2 (30%, 0.1 mL) was syringed into the cuvette with nitrogen bubbling. The electronic absorption spectrum was recorded immediately after the nitrogen flow was stopped and the solution became still.

Oxidation of LB Solution with PbO_2. A fine powder of PbO_2 (1.0 g) was charged into a saturated solution of LB (ca. 100 mg) in NMP. The heterogeneous mixture was stirred magnetically at 80 °C for 24 h. Upon cooling to room temperature, the mixture was filtered on a Büchner funnel three times. The filtrate was collected and further filtered through a 0.2-μm Teflon filter unit under the protection of nitrogen before the GPC measurement.

Oxidation of LB Powder with H_2O_2. A fine powder (100 mg) of LB was suspended in 30 mL of an aqueous solution of hydrogen peroxide at the concentrations of 30, 20, 10, 1.0, and 0.1%. A few drops of HCl (1.0 M) were added as catalyst to the reaction mixture via syringe until the pH reached 3.5. After 15 min of stirring at room temperature, the polymer was collected on a Büchner funnel and washed with three portions of 100 mL of 0.1 M NH_4OH. The polymer was then dried under dynamic vacuum and dissolved in NMP for the spectral and GPC measurements as described earlier. For comparison, EB powder was also subjected to the same treatment.

Results and Discussion

The emeraldine base (EB) of polyaniline was reduced toward the leucoemeraldine base (LB) with phenylhydrazine and hydrazine[29,30] as depicted in Scheme 1. The structure of the resultant LB was characterized by elemental analysis, IR, UV–vis–near IR, and ^{1}H NMR spectroscopy. The results obtained for LB are compared with those for EB.

Both LB and EB gave apparently satisfactory elemental analysis. The ^{1}H NMR spectrum of EB in DMSO-d_6 shows a broad signal around 7.0 ppm, which is assigned to the aromatic protons. The NH proton signal is very broad in the range of ca. 8.0–8.6.[13,31] The ^{1}H NMR spectrum of LB in DMSO-d_6 exhibits two broad, but well-separated peaks at 6.8 and 7.4 ppm for the benzenoid and NH protons, respectively. The ratio of the integrated areas under these two signals is approximately 4. The assignment of NH protons was further confirmed by D_2O exchange reactions.

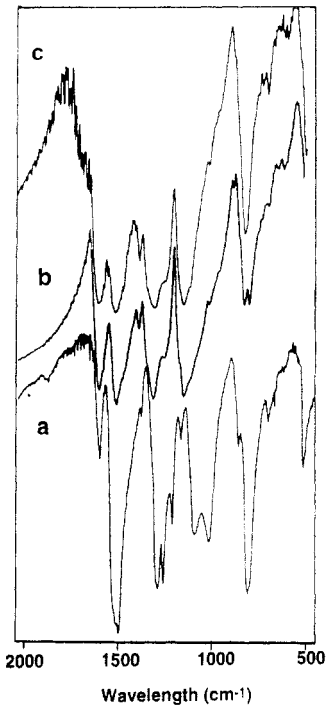


Figure 1. FTIR spectra of (a) leucoemeraldine base (LB) prepared by reduction of emeraldine base (EB) with phenylhydrazine, (b) the pristine EB, and (c) LB after oxidation with a 30% aqueous solution of H_2O_2 for 15 min.

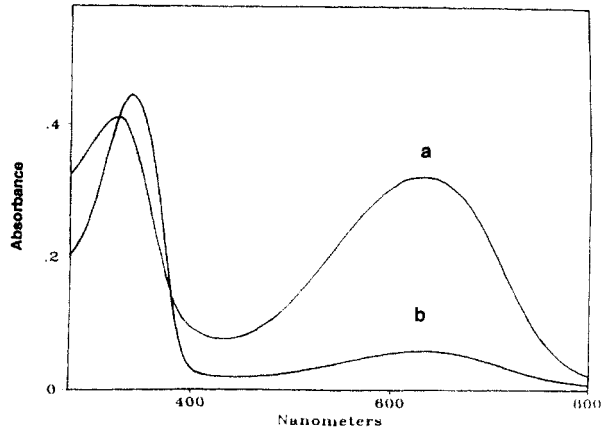


Figure 2. UV–vis spectra recorded in NMP solution of (a) emeraldine base and (b) leucoemeraldine base prepared by reduction of emeraldine base with phenylhydrazine.

In comparison with EB, the upfield shifts in both the aromatic and the NH proton signals of LB can be attributed to the stronger electron-donating nature of the amine group than that of the imine.

The FTIR spectra of polyaniline base after being subjected to various redox processes are compared in Figure 1. In general, the characteristic band at 1598 cm^{-1} arises mainly from both C=N and C=C stretching of the quinoid diimine unit, while the band near 1500 cm^{-1} is attributed to the C–C aromatic ring stretching of the benzenoid diamine unit.[30,32] The intensity ratio of these two absorption peaks is indicative of the extent of oxidation. For example, this ratio is ca. 80% for EB (Figure 1b) and decreases by fourfold to ca. 20% for LB (Figure 1a). When the LB powder was treated with a 30% aqueous solution of hydrogen peroxide, the peak at 1598 cm^{-1} regained its intensity and the spectrum (Figure 1c) appeared nearly identical to that of EB (Figure 1b). Figure 2 shows the electronic absorption spectra of EB and LB in NMP solution. Both spectra show two broad absorption bands with λ_{max} of EB at 330 and 636 nm and of LB at 342 and 630 nm. The first absorption band (Band I) at 330 and 342 nm (ca. 3.8 eV) is associated with a π–π^* transition of the conjugated ring systems.[30,33,34] The hypsochromic shift from LB to EB in this band reflects the difference in the extent of π-conjugation.[29,32] The second band (Band II) at ca. 630 nm (2.0 eV) has been assigned to a benzenoid to quinoid excitonic transition.[33] Band II plays an important role in switching polyaniline from an electric insulator to a conductor upon doping.[33,34] Furthermore, the intensity ratio of Band I to Band II (I_1/I_2) indicates the relative amount of quinoid diimine unit in polyaniline (i.e., the oxidation state of polyaniline).[30,35] This ratio was found to be ca. 16 ± 2 for the LB solution and 1.7 ± 0.4 for the EB solution.

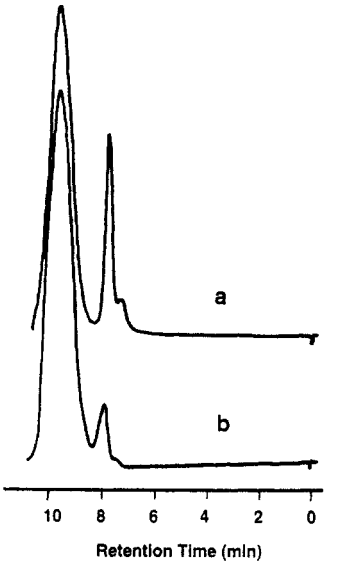


Figure 3. GPC curves of (a) EB and (b) LB prepared by reduction of EB with phenylhydrazine, recorded in NMP solution.

All the above results indicate that EB has been significantly reduced toward the formation of LB. The IR and UV spectral data suggest that there might be some residual quinoid diimine units in the resultant LB based on the appearance of the absorption bands at 1598 cm^{-1} and 630 nm. However, the amount of the diimine units must be quite small because they escaped detection by elemental analysis and NMR spectroscopy. Since the main objective of this work is to study the influence of the *relative* changes in the oxidation state on the molecular weight of polyaniline, the residual diimine units will not affect our results.

The molecular weight and molecular weight distribution of LB and EB were studied using gel-permeation chromatography (GPC) in NMP solution. The representative GPC curves are illustrated in Figure 3. The elution pattern of EB (Figure 3a) appears as two well-separated main fractions with number-average molecular weights of ca. 7000 and 580 000, respectively, based on the polystyrene calibration. The percentage peak area of the high molecular weight fraction is about 28 ± 3%. The GPC of LB (Figure 3b) also shows two fractions with M_n of 6000 and 240 000. However, the percentage of high molecular weight fraction is decreased significantly to 7 ± 2%. There are two possible explanations for the drastic decrease in both the molecular weight and the percentage fraction of the high molecular weight peak. First, the difference in the GPC curves between EB and LB could result from the probably higher hydrodynamic volume of the quinoid diimine units than that for the benzenoid diamine units. This possibility has been investigated and excluded in our earlier work on electrochemical redox reactions of poly-

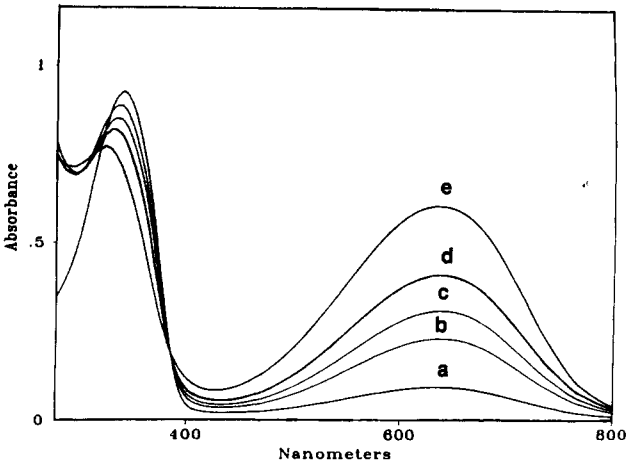


Figure 4. Representative UV–visible spectra for leucoemeraldine base in NMP after oxidation with molecular oxygen for various reaction periods: (a), 0, (b) 0.75, (c) 2, (d) 3, and (e) 15 h.

aniline[27] and will be discussed further in later sections. Second, an extensive degradation of the polyaniline chains took place during the reduction process. It was reported[36] that in the reaction of secondary and tertiary aromatic amines with hydrazine there is a considerable amount of carbon–nitrogen bond cleavage. Such a cleavage, if occurring in the reduction of EB, would lead to the decrease in the molecular weight of the polymer. To gain further knowledge about the relations of molecular weight and molecular weight distribution with the reaction conditions, we have investigated the reoxidation of LB to EB with a series of oxidants and the accompanying changes in the chromatographs, as discussed in the following sections.

Oxidation of LB in NMP Solution. LB dissolved in NMP was oxidized by bubbling oxygen gas through the solution at room temperature. The solution gradually turned dark blue upon oxidation, which was monitored by UV–vis–near IR spectroscopy. Figure 4 shows that Band II grows in the electronic absorption spectra as the oxidation proceeds. After continuous bubbling of oxygen through the solution for 15 h, the intensity of Band II was increased by a factor of 5 while λ_{max} remained approximately unchanged. Band I exhibits a gradual hypsochromic shift from 342 toward 330 nm. These observations indicate a progressive oxidation of LB, i.e., the conversion of the benzenoid amine units to the quinoid diimine units in the polymer. The intensity of Band I was not affected as much though slightly decreased. This is consistent with the results of theoretical calculations,[37] which suggests that the oxidation should have relatively little effect on the intensity of the π–π^* band. Therefore, changes in the intensity ratio of I_1/I_2 are mainly governed by the population of quinoid diimine units and are indicative of the relative oxidation state of polyaniline. Figure 5 shows the relationship between I_1/I_2 and the time of oxygen treatment for three different samples. Before the oxidation, the I_1/I_2 values were 16 and 6 for the LB samples prepared with phenylhydrazine and with hydrazine as reducing agents, respectively, and 1.7 for the pristine EB. As the oxidation begins, the I_1/I_2 values for the LB samples decrease drastically. The decrease then slows down and eventually levels off. The I_1/I_2 values for EB remains essentially unchanged during the entire period (Figure 5). After 20 h of oxygen treatment, all three samples have a constant I_1/I_2 value of 1.7 ± 0.4. These results indicate that the LB samples have been oxidized to the emeraldine oxidation state and that the molecular oxygen may not be strong enough to oxidize the emeraldine to a higher oxidation state, e.g., pernigraniline.

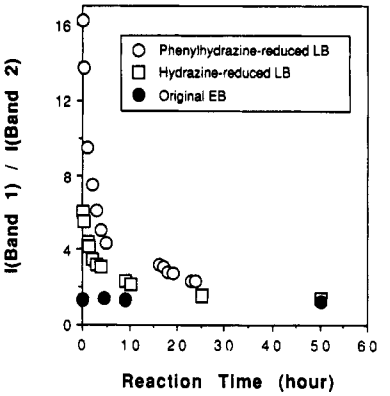


Figure 5. Change in the oxidation state as represented by the intensity ratio of UV–vis absorption Band I to Band II (i.e., I_1/I_2) as a function of reaction time in the oxygen treatment of (○) LB prepared from reduction of EB with phenylhydrazine, (□) LB prepared from reduction of EB with hy drazine, and (●) the pristine EB in NMP solution.

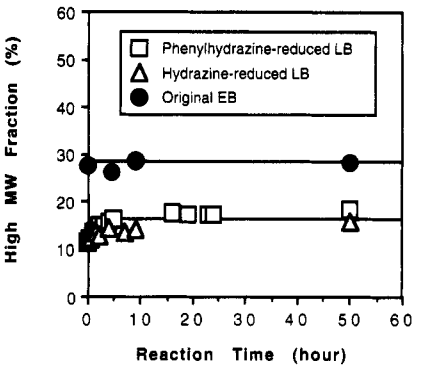


Figure 6. Plots of the high molecular weight fraction against time of oxygen treatment of (□) LB prepared from reduction of EB with phenylhydrazine, (△) LB prepared from reduction of EB with hydrazine, and (●) the pristine EB in NMP solution.

The molecular weights of all the samples were monitored simultaneously with GPC measurements during the oxygen treatment. There is no significant change in the GPC bimodal elution pattern. As demonstrated in Figure 6, the fraction of the high molecular weight peak shows an increase initially and then remains essentially constant during the rest period of the oxygen treatment for all the LB samples either reduced by phenylhydrazine or by hydrazine. The oxygen treatment has no effect on the GPC of the EB sample throughout the entire period (Figure 6). The lack of a strong dependence of the GPC elution pattern on the oxidation state is consistent with our earlier observations on the electrochemically prepared polyaniline.[27]

Addition of a small amount of aqueous hydrogen peroxide to the LB–NMP solution does not result in precipitation, which makes it possible to monitor the spectroscopic change during the oxidation of LB in the solution phase. Upon the addition of hydrogen peroxide to the LB–NMP solution, the intensity of Band II is increased immediately. This increase continues with the reaction time but slows down after about 60 min. Band I shows a slight decrease in intensity and a hypsochromic shift. As shown in Figure 7, the I_1/I_2 value decreases drastically in the beginning and reaches a constant value of ca. 2 after 120 min. Comparing with 50 h for the system of oxidation by molecular oxygen to reach a constant I_1/I_2 value, the overall rate of oxidation by hydrogen peroxide is much higher, probably because it is a homogeneous solution reaction. The oxidation state of the product should be close to that of EB because of their similar I_1/I_2 values.

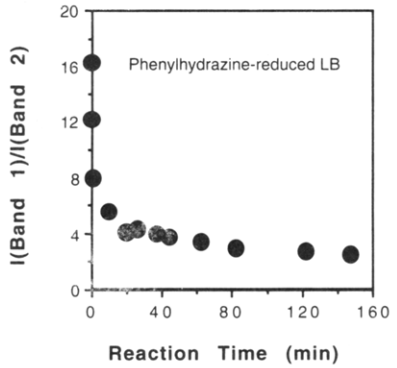


Figure 7. Change in the oxidation state as represented by the intensity ratio of UV–vis absorption Band I to Band II (i.e., I_2/I_2) as a function of time during the oxidation of LB in NMP solution by 30% H_2O_2.

Oxidation of LB and EB in Solid Suspension. Because of the low solubility of polyaniline, most of its chemical and electrochemical redox reactions have been studied in a heterogeneous system with the polymer in the solid form (e.g., powder or film) as reactant. Therefore, we investigated the oxidation of LB as a solid suspension in an oxidant solution. The results from reaction of a finely ground powder of LB with aqueous hydrogen peroxide solution at various concentrations (0.1–30%) we summarized in Table 1. The electronic absorption spectral and GPC measurements were taken upon the oxidation products in NMP solution. As the concentration of the oxidant increases, Band I appears to shift gradually from 342 nm for LB to 330 nm for EB, and the λ_{max} of Band II remains approximately the same at 639 ± 3 nm. Again, the I_1/I_2 value drops rapidly and reaches 2.1 at 30% H_2O_2 concentration, which is close to that for EB (Figure 8a). All the spectral data are similar to those obtained from the solution oxidation of LB. However, in sharp contrast, the molecular weight and molecular weight distribution exhibit remarkable differences from those of the solution oxidation. As shown in Figure 8b, the high molecular weight fraction is increased significantly from 7% for LB to 23 and 63% for the products oxidized with 10 and 30% aqueous hydrogen peroxide, respectively. It is important to note that the high molecular weight fraction of these oxidation products is greater than that of the pristine EB, whereas their oxidation states are lower than or about same as that of the EB. This is again consistent with our suggestion[27] that the bimodal GPC elution pattern should not be directly dependent on the oxidation state of polyaniline. We propose that the changes in molecular weight distribution during the oxidation of the LB in solid suspension might originate from cross-linking and/or branching reactions between the polymer chains.

There are several possible mechanisms for chemical cross-linking reactions. First, the oxidation of LB would lead to formation of semiquinone cation radicals along the polymer chains, which may undergo an interchain radical coupling reaction resulting in the cross-links.[38,39] Second, an acid-catalyzed nucleophilic attack on the quinoid diimine ring, which is generated from the oxidation of the benzenoid diamine unit in LB, by primary or secondary aromatic amine groups, followed by oxidation, would lead to formation of azophenine. Further ring fusion reactions of azophenine could result in phenazine compounds[39,40] that lead to branched and cross-linked polyaniline. The second scenario is illustrated in Scheme 2 with the reactions between two primary amine groups in the polyaniline chain ends and a quinoid diimine unit as an example.

There are numerous secondary amine groups and probably a primary amine end group in a LB polymer chain. All these groups could react with the quinoid diimine units in the neighboring polymer chains during the oxidation to afford branched and cross-linked products. In particular, the starting material LB may have a large fraction (i.e., ca. 93%) of polymer chains with relatively low molecular weights and, therefore, a great number of less sterically hindered NH_2 end groups that are available to react with the quinoid ring sites. Table 1 also includes the number-average molecular weight (M_n) and the polydispersity (M_w/M_n) of the oxidation products calculated for both the low and high molecular weight fractions.[16] Upon oxidation, the M_n value for the high molecular weight fraction increases from 300 000 to 560 000 at the hydrogen peroxide concentrations of 0.1 and 30%, respectively. This increase relative to the pristine LB is illustrated in Figure 9a. Thus, the higher H_2O_2 concentration results in more quinoid diimine units, which in turn provide more cross-linking sites and lead to higher molecular weights. Furthermore, the polydispersity is also increased from 1.5 to 3.9 (Figure 10a). On the other hand, the M_n (Figure 9b) and polydispersity (Figure 10b) of the low molecular weight fraction vary in a relatively less extent. All these data are consistent with the proposed cross-linking and branching reactions.

The interchain separation of EB in the solid state has been estimated to be 3.5 Å.[20] This may help in explaining the difference between the solution and solid-phase oxidation of LB. In the solid state, the adjacent polymer chains are close enough for the interchain branching or cross-linking reactions to occur, while in the solution oxidation the polymer chains might be too far from each other to effect a significant interchain reaction. As a control experiment, we treated EB in suspension in 30% H_2O_2 for 15 min. The M_n value and percentage peak area for the high molecular weight fraction were found to increase to 650 000 and 54%, respectively. The same reaction in NMP solution had much less effect on the molecular weight and GPC elution pattern. We have also employed powdered lead oxide (PbO_2) in excess to oxidize LB in NMP solution at 80 °C.[29,30] The results are given in Table 1 (entry 8). The λ_{max} of Band I and I_1/I_2 value for the oxidation product reveal that its oxidation state is similar to, or somewhat higher than, those of the emeraldine. The molecular weight and percentage of the high molecular weight fraction show little change from those of the pristine material. At least the extent of cross-linking or branching by PbO_2 oxidation in solution is less than that by concentrated H_2O_2 oxidation in the solid phase. These results further demonstrate that as long as the polymer chains are separated in the solution phase, the probability of cross-linking and branching reactions is significantly reduced.

It is well known that the overoxidation of polyaniline is always accompanied by decomposition of the polymer chains.[41] For example, polyaniline decomposes completely in concentrated dichromate and permanganate solutions.[42] To evaluate the effect of decomposition on the molecular weight, both LB and EB powders were treated with concentrated hydrogen peroxide (30%) for a prolonged reaction time of 24 h. After the oxidation, the GPC curves of the polymers still exhibit a bimodal elution pattern. However, there are appreciable changes in the molecular weight and the percentage fraction of the high molecular weight peak. For the high molecular weight peak of the oxidized LB, the percentage fraction was found to be increased to 82% while the M_n decreased to 330 000 with

Table 1. UV-Vis Absorption Band, Number-Average Molecular Weight (M_n), and Polydispersity (M_w/M_n) of Polyaniline upon Various Redox Treatments

entry	polymer and redox conditions[a]	λ_{max1} (nm)	λ_{max2} (nm)	I_1/I_2	high MW fraction (%)[b]	M_n (high)[b]	M_w/M_n (high)[b]	M_n (low)[b]	M_w/M_n (low)[b]
1	leucoemeraldine base (LB)	342	630	16.2	7	240 000	1.4	6000	2.4
2	LB–0.1% H_2O_2 (aq)[c]	342	636	6.9	7	300 000	1.5	8000	2.2
3	LB–1% H_2O_2 (aq)	342	641	6.7	9	330 000	1.5	9200	2.3
4	LB–10% H_2O_2 (aq)	340	640	4.8	23	380 000	2.0	9200	2.2
5	LB–20% H_2O_2 (aq)	338	636	2.3	35	430 000	3.2	8700	2.2
6	LB–30% H_2O_2 (aq)	334	638	2.1	63	560 000	3.9	8800	1.8
7	emeraldine base (EB)	330	636	1.7	28	580 000	2.7	7000	2.8
8	LB–PbO_2	336	622	1.6	7	300 000	1.3	9400	2.0
9	LB–30% H_2O_2 (aq), 24 h	328	632	1.3	82	330 000	2.2	8100	4.4
10	EB–30% H_2O_2 (aq), 24 h	328	622	1.3	64	770 000	3.4	6300	2.0
11	LB–30% H_2O_2 (aq), 34 h, then $PhNHNH_2$	340	632	5.1	59	260 000	2.2	5000	1.7

[a] Entry 1, the original leucoemeraldine base; entries 2–6, the LB samples after oxidation in suspension by various concentrations of H_2O_2 aqueous solution for 15 min at room temperature; entry 7 is the original emeraldine base; entry 8, LB after oxidation in NMP solution with powdered PbO_2; entries 9 and 10, LB after overoxidation in suspension with 30% H_2O_2 aqueous solution for 24 h; entry 11, the LB sample after reduction of the sample described in entry 9 with phenylhydrazine. [b] Molecular weight and polydispersity were obtained from GPC measurements in NMP solution with polystyrene calibration. The molecular weights are calculated separately on the high and low molecular weight fractions in the bimodal GPC elution pattern.

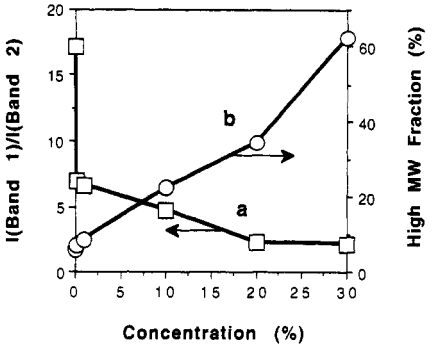


Figure 8. Relations of (a) the oxidation state as represented by the intensity ratio of UV–vis absorption Band I to Band II (i.e., I_1/I_2) and (b) the high molecular weight fraction with concentration of H_2O_2 (percent by weight) in the oxidation of LB in powder form suspended in aqueous H_2O_2 solution for 15 min.

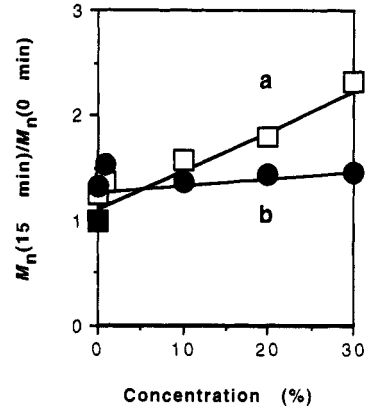
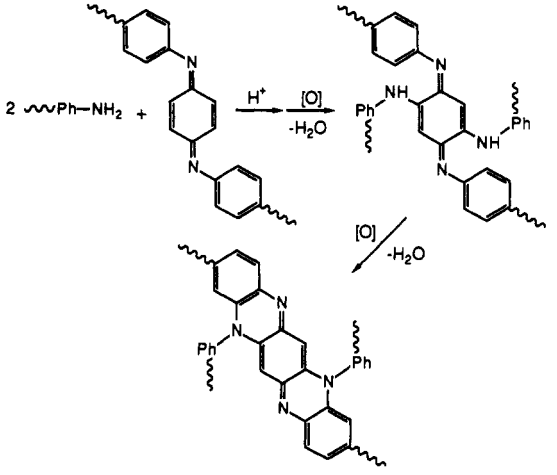


Figure 9. Change in the ratio of the number-average molecular weight (M_n) of the product from oxidation of LB in suspension in aqueous H_2O_2 solution for 15 min to that of the original LB before the oxidation as a function of the concentration of H_2O_2 for (a) the high molecular weight fraction and (b) the low molecular weight fraction of the polymers.

Scheme 2



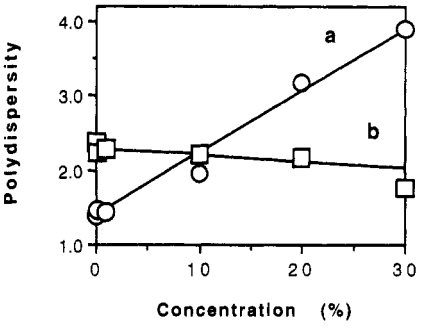


Figure 10. Change in the polydispersity (M_w/M_n) of the product from oxidation of LB in suspension in aqueous H_2O_2 solution as a function of the concentration of H_2O_2 for (a) the high molecular weight fraction and (b) the low molecular weight fraction of the polymer.

a polydispersity of 2.2 (Table 1, entry 9) as compared with those of the LB oxidized by 30% H_2O_2 for 15 min (Table 1, entry 6). This observation indicates that the decomposition because of overoxidation leads to a decrease in the molecular weight while the cross-linking and branching yield a greater percentage of the high molecular weight fraction. Of the oxidized EB, both M_n and the percentage fraction of the high molecular weight peak are increased to 770 000 and 66%, respectively (Table 1, entry 10) as compared with those of the pristine EB (entry 7). In this case, the decrease in the molecular weight owing to overoxidation might be compensated by the molecular weight increase owing to the cross-linking and branching. Although the molecular weight and molecular weight distribution are significantly affected by the overoxidation, the oxidation state of polyaniline remains approximately at the emeraldine level. This is evidenced by the facts that the λ_{max} of Band I of both overoxidized LB and EB is about 328 nm with the I_1/I_2 value of 1.3.

When the overoxidized LB and EB were subjected to the reduction process by refluxing in phenylhydrazine, the products were blue-gray in reflection. The GPC curves of these second-time reduced samples also displayed a

bimodal elution pattern. However, the percentage of the high molecular weight fraction remained high, i.e., 59 and 64% for the products from overoxidized LB and EB, respectively, compared to 7 and 28% for the original LB and EB. This lack of chemical reversibility could be again attributed to the cross-linking and branching structure in the polymer acquired from the prior oxidation process.

Conclusions

Leucoemeraldine base was prepared by chemical reduction of the emeraldine base of polyaniline and was characterized by elemental analysis, IR, ^{1}H NMR, and UV–vis–near-IR spectroscopy. Both LB and EB were subjected to various chemical redox reactions with molecular oxygen, hydrogen peroxide, lead dioxide, hydrazine, and phenylhydrazine as oxidizing or reducing agents. The oxidation state of the reaction products was monitored by electronic absorption spectroscopy, and the molecular weight and molecular weight distribution were measured by GPC in NMP solution. A bimodal GPC elution pattern was observed for all of the polyaniline samples. We have found that the molecular weight and molecular weight distribution of polyaniline show relatively little change when the redox reactions are carried out with the polymers in the solution phase. In sharp contrast, there are significant changes in both parameters when the redox reactions are performed with the polymers in the solid state. As a powdered LB was oxidized to EB by aqueous hydrogen peroxide, the molecular weight and percentage of the high molecular weight fraction increased with the concentration of the oxidant. We attribute these changes to the chemical cross-linking and/or branching by interchain reactions in the polymer particles, where the interchain distance is small to facilitate the reactions. The increase in the molecular weight during the oxidation of polyaniline in the solid state is apparently in competition with the decomposition of the polymer because of overoxidation. The overoxidized polyaniline could not be reduced to LB of the original molecular weight and molecular weight distribution because of the irreversibility of the cross-linking and branching reactions.

This work represents the first study of the relations of molecular weight and molecular weight distribution with chemical redox reaction and oxidation state of polyaniline. However, it should be cautioned that the GPC results were only obtained from the soluble fraction of the polymers, which may or may not be applicable to the polyaniline fraction insoluble in NMP. Currently, we are exploring the synthesis of completely soluble oligomers and derivatives of polyaniline in an effort to develop a thorough understanding of the rich redox chemistry of polyaniline and its relations to the molecular weight and molecular weight distribution.

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