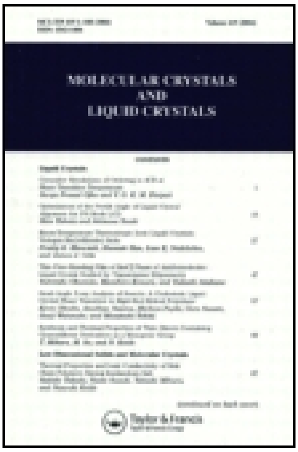

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Polyaniline: Solutions, Films and Oxidation State

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Polyaniline: Solutions, Films and Oxidation State

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The emeraldine oxidation state of polyaniline in its base form, "emeraldine base" can be solution-processed to yield large flexible films which can be doped to the metallic conducting regime ($\sigma \sim 1-5$ S/cm). The approximate solubility of emeraldine base at room temperature in 80% aqueous acetic acid, 60% and 88% aqueous formic acid, dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and N-methylpyrrolidinone (NMP) have been determined. Both emeraldine base and emeraldine hydrochloride can be sublimed onto a variety of substrates to produce high quality, ~2000 Å thick films which are similar but not identical to emeraldine base. Emeraldine base, which is slowly oxidized by air, can be reconverted to the emeraldine oxidation state by treatment with dilute aqueous acids.

"Polyaniline," synthesized either by the chemical or electrochemical oxidative polymerization of aniline, has recently aroused considerable

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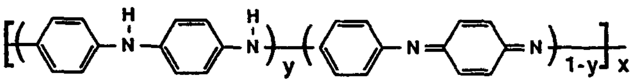
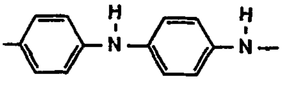
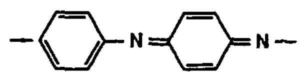
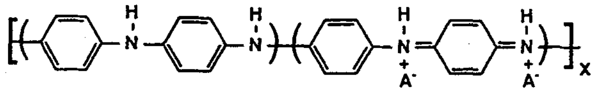
interest.[1-5] The base form of the polymer in the emeraldine oxidation state ($y = 0.5$)



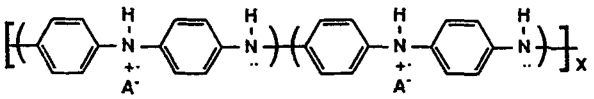
which contains equal numbers of alternating reduced,

 and oxidized, 

repeat units can be protonated by dilute aqueous acids such as HCl[1-5] to produce the corresponding salt (A = anion)



which we believe exists as the polysemiquinone radical cation[5-7].



The polymer exhibits conductivities of ~1–5 S/cm when approximately half of its nitrogen atoms are protonated as shown above. The dependence of conductivity on the extent of protonation has been described elsewhere.[1,6,7] In the following discussion, forms of polyaniline in the emeraldine oxidation state will, for convenience, be referred to simply as "emeraldine."

In order for conducting polymers to be technologically useful, it is important that they, in some way, be processable. We have previously described in detail the casting of free-standing films of emeraldine acetate ($\sigma \sim 0.5$–2 S/cm) from solutions of emeraldine base in 80% aqueous acetic acid.[4] These films may be deprotonated with dilute aqueous ammonium hydroxide to produce relatively flexible, free-standing, lustrous, coppery-colored films of emeraldine base ($\sigma \sim 10^{-10}$ S/cm), which can in turn be converted to free-standing, lustrous, dark blue films of emeraldine hydrochloride ($\sigma \sim 1$–5 S/cm). These films have proven to be superior for certain chemical and physical studies[4,5] to powders of the corresponding forms of the polymer.

The present investigation was carried out in order to: (i) study the nature of solutions of emeraldine base in selected solvents, (ii) use the solutions for casting films of the polymer, (iii) make films of the polymer by sublimation processes and (iv) study the conversion of higher oxidation states of polyaniline ($y < 0.5$) to the emeraldine oxidation state ($y = 0.5$).

EXPERIMENTAL

A. Synthesis of the emeraldine base form of polyaniline

Emeraldine hydrochloride powder was synthesized from aniline and $(NH_4)_2S_2O_8$ and converted to analytically pure emeraldine base using the detailed method we have described previously.[6]

B. Solutions of emeraldine base in selected solvents

The approximate solubility of emeraldine base in 80% aqueous acetic acid, 60% and 88% aqueous formic acid, dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) were obtained using variations of the general method below.

Approximately 0.4 g of finely powdered emeraldine base was added to 100 ml of the solvent to give an intensely-colored solution/suspension which was stirred magnetically at room temperature for ~15 minutes and then centrifuged. The liquid phase was carefully removed by a Pasteur pipette and the residue was washed with an additional 10 ml portion of solvent which became only faintly colored indicating that essentially all the material soluble under the above conditions had been in the solution removed by the Pasteur pipette. The precipitate was washed several times with water and several times with diethyl ether. It is insoluble in both these liquids, the wash solutions being colorless. It was subsequently dried under dynamic vacuum for ~48 hours and weighed. The difference between the weight of the emeraldine base initially used and the residue gives the weight of emeraldine base which had dissolved. It should be stressed that the value thus obtained is a *minimum* measure of solubility. It is not known whether the insoluble material is a higher molecular weight form of the polymer or a cross-linked form of the polymer which is insoluble in the solvent employed. However, in view of the fact that the elemental analysis of the emeraldine base used was consistent with its postulated composition, the insoluble material must have a composition identical to, or very close to that of the emeraldine base. It should also be noted that no claim is made concerning the nature of the polymer in the liquid phase *i.e.* whether it is present completely in "true" solution or whether it is present in whole or in part as colloidal particles; however, on passage through a 2000 Å micropore filter only a small amount of material remains on the filter.

In the case of the 80% acetic acid, the blue color in the initial intensely-colored blue-green solution/suspension faded within ~15 minutes at room temperature to give an intense green color with a faint yellow tint; however, little fading of the blue color occurred within 6 hours at ~0°C.

When 88% formic acid was employed, all the emeraldine base dissolved under the above conditions. Additional small weighed quantities of emeraldine base were added to the solvent, which was stirred magnetically for ~15 minutes after each addition. When a total of 1.8 g of polymer had been added, no particles could be observed on the walls of the flask containing the stirred solution. However, an additional increment of 0.2 g of emeraldine base resulted in the appearance of undissolved particles of solid on the walls of the flask. A similar procedure was used to obtain the approximate maximum solubility of emeraldine base in 80% formic acid.

The intense initial blue color observed in both types of acid solution faded very much more rapidly to the intense green color in the case of the formic acid solutions than in the case of the 80% acetic acid solution. The intense dark blue solution/suspension in the DMSO and DMF solutions did not change color during handling.

The weights of emeraldine base dissolved under the above experimental conditions are (grams/100 ml of solvent): 80% acetic acid, ~0.32; 60% aqueous formic acid ~0.8; 88% aqueous formic acid ~1.8; DMSO, ~0.32; DMF, ~0.24.

C. Casting of films of polyaniline from NMP solutions

Finely-ground emeraldine base (~1 g) was stirred magnetically in 250 ml of NMP (b.p. 202°C) at room temperature for ~8 hours after which time the intense blue solution was filtered through a Buchner funnel (Whatman #2 filter paper). No observable insoluble material remained on the filter. This solution could be used to cast thin films but usually a more concentrated solution is more desirable. This may be obtained by partial evaporation of the NMP solvent (Buchi Rotavapor, Model R 110) under dynamic vacuum at ~40°C. The NMP is removed at a rate of ~1.5 ml/min. Solutions in which no particulate material could be observed containing ~1 g emeraldine base in 25 ml of NMP can be readily obtained by this method.

Films cast from very thick solutions tend to be brittle while films made from very dilute solutions are very thin and may have pinholes. A solution containing ~1 g of emeraldine base in ~70 ml of NMP is generally satisfactory for casting films.

To cast films from solution, a Pasteur pipette is used to distribute an even layer of liquid over a piece of glass. The glass must be clean and level to obtain an even coating. The thickness of the film can be controlled by the concentration of the solution and by the quantity of the solution applied to the glass. For example, a small piece of glass (7.5 cm × 2.5 cm) may be completely coated by 1 ml of the solution but surface tension effects may allow the application of up to 3 ml of solution, resulting in a film three times as thick.

The coated glass can be dried in an oven in air between 60–70°C for ~4 hours or in a desiccator under dynamic vacuum at room temperature for ~8 hours. The drying time varies with the concentration of the solution as well as with the amount of solution applied.

When the film appears to be visually dry, it can easily be removed from the glass substrate by immersion in water for ~5 minutes after which time the film will begin to lift off from the glass. Occasionally, it is necessary to use a razor blade to initially separate a portion of the film from the edge of the substrate. The film may then be washed with five 70 ml-portions of distilled water to remove traces of NMP which is soluble in water. It is then placed between two pieces of glossy weighing paper (Fisher Scientific Co.) and a sheet of glass is placed on top to keep the film flat as it dries either in air (~16 hours) or under dynamic vacuum in a vacuum desiccator (~20 mins.). This will remove most of the water, the remaining amounts being removed by heating the film to ~85°C on the vacuum line under dynamic vacuum for ~3 hours. Similar results may be obtained by using methanol instead of water.

When films are prepared by evaporation on NMP in air at 60–70°C, the side of the film exposed to the air has a distinct dark purple-blue tint while that adjacent to the glass has a bronze-like tint. This suggests that some oxidation of the emeraldine oxidation state (y = 0.5 in the general formula of polyaniline) had occurred to give a form of polyaniline where $y < 0.5$.

The infrared spectrum of such a film showed no trace of NMP. The principal absorptions are: 3657(vw), 3389(m), 3275(w), 3028(m), 2540(w), 2382(vw). 2332(vw), 2112(vw), 2006(vw), 1888(w), 1749(vw), 1595(vs), 1501(vs), 1381(m), 1308(s), 1217(m), 1167(s), 1105(m), 1011(w), 984(vw), 957(w), 851(w), 831(s), 746(w), 716(vw), 700(vw), 635(vw), 586(vw) cm^{-1}. It was essentially identical to both that of the emeraldine base used in preparing the NMP solutions and to that of emeraldine base reported elsewhere[4,8] except for a difference in the relative intensities of the peaks at 1598 and 1500 cm^{-1} which have been reported as being influenced by the oxidation state.[8] The intensities of these peaks suggested the films were somewhat more oxidized than the polymer base powder from which they were prepared.

Free-standing, lustrous, flexible films up to 12 cm × 12 cm have been obtained by the above method. These are shiny on both sides and are usually 0.01–0.04 mm thick. They contained no pinholes or tears. Upon creasing these films firmly between two fingernails, they return to their original shape without breaking. The mechanical properties of the films suggest that at least a portion of the polymer must be present as a relatively high molecular weight component. When shaken the films "rattle" in a manner similar to aluminum foil.

D. Chemical modification of free-standing films of polyaniline

The films ($\sigma \sim 10^{-10}$ S/cm) described in the preceding section can be doped (protonated) to the metallic conducting regime by immersion in 1M aqueous HCl for ~24 hours. The color changes from intense purple-blue to intense blue instantly. The film is then placed between the sheets of weighing paper (no washing) and is dried first in the vacuum desiccator and then at ~85°C as described previously. Four-probe conductivities of the flexible, lustrous, intense dark blue films in the range 1–5 S/cm are commonly obtained. These values are identical to those obtained for compressed pellets of the chemically synthesized emeraldine hydrochloride powder.[1,6]

The films may be readily undoped by treatment with 0.1M aqueous ammonium hydroxide for ~24 hours. Upon immersion in the base, the color changes instantly to a highly reflective, lustrous, copper color characteristic of the pure emeraldine oxidation state in the base form. The principal absorptions in the infrared spectrum of this material are: 3391 (m), 3028(m), 2538(vw), 2480(vw), 2384(vw), 1888(w), 1751(vw), 1595(vs), 1508(vs), 1379(m), 1308(s), 1248(vw), 1167(s), 1011(w), 957(w), 935(vw), 831(s), 744(vw), 708(vw), 660(vw), 642(vw) cm^{-1}. It can be seen that there is no significant difference between this spectrum and that of the polymer where "y"' < 0.5 discussed earlier. The emeraldine base film may be reconverted to the doped metallic emeraldine hydrochloride film by treatment with 1M HCl.

The mechanical properties of both the emeraldine hydrochloride and of the pure emeraldine base films are qualitatively identical to those of the films described in the previous section.

E. Production of films of a form of polyaniline by sublimation

Emeraldine base as well as emeraldine hydrochloride powders were sublimed in a vacuum evaporator (Ladd Research Industries, Inc.

Model 40000-425) at a pressure of ~5 × 10^{-6} torr with a sample temperature of ~400°C and a substrate temperature of ~40–50°C. A variety of substrates such as platinum, glass, quartz, Teflon, etc. were used. High quality transparent (2000–2500 Å thick) films which were pinhole-free and exhibited a relatively featureless, somewhat nodular morphology by scanning electron microscopy were obtained by this process.

Four gold strips were evaporated onto the surface of the films deposited on glass substrates (5.0 cm × 2.5 cm × 0.1 cm) in order to obtain 4-probe conductivities. Essentially the same conductivity was obtained for materials sublimed from emeraldine base (1.7 × 10^{-8} S/cm) and those sublimed from emeraldine hydrochloride (7.4 × 10^{-7} S/cm).

Treatment of the film/electrode assemblies (obtained by evaporation of emeraldine base) with gaseous HCl or ~0.1M aqueous HCl converted them to a clear pale green color by transmitted light, characteristic of protonated emeraldine hydrochloride. The film treated with 0.1M HCl had a conductivity of 1.3 × 10^{-5} S/cm; while that treated with gaseous HCl exhibited a conductivity of 3.5 × 10^{-4} S/cm. When the original brown films were exposed to air for several months they developed a deep blue color by transmitted light characteristic of the emeraldine base form of polyaniline.

The visible/UV spectra of films sublimed from emeraldine base or emeraldine hydrochloride onto quartz substrates were almost identical to each other and very similar to the spectrum of a solution of emeraldine base in DMF.[8-10] The sublimed films, emeraldine base, and emeraldine salts all have strong absorptions at ~4 eV.[8-10] The films sublimed from emeraldine base also had a moderately strong absorption at ~2.2 eV whereas the films sublimed from emeraldine hydrochloride had a weaker absorption at ~2.2 eV. These ~2.2 eV absorptions may be compared with the strong 2 eV peak of emeraldine base and the absence of such a peak in emeraldine hydrochloride.[5,8,9] These observations showed, not unexpectedly, that most of the HCl present in emeraldine hydrochloride had been dissociated during its sublimation and its conversion to a material very similar to, but not identical with, emeraldine base. The infrared spectra of the sublimed films were, however, essentially identical to that of solid emeraldine base. This is interpreted to indicate existence of the same polyaniline backbone structure in the sublimed material as in the parent polymer.

Films sublimed onto tin oxide-conducting glass substrate from both emeraldine base and emeraldine hydrochloride were electrochemically active as shown by their cyclic voltammograms which were recorded in 1M aqueous HCl. The color changes were very similar to those observed with emeraldine base under identical experimental conditions,[3] changing from pale yellow at −0.2V vs. SCE through green to deep blue-purple at +0.8V vs. SCE. The cyclic voltammograms were also similar to that of emeraldine base except that an oxidation and reduction peak ($E_{1/2}$ = 0.51V) occurred between the two sets of peaks characteristic of parent polyaniline. This peak is frequently observed in slightly decomposed emeraldine base after extensive cycling between −0.2V to +0.8V.

DISCUSSION

The present study demonstrates that the emeraldine base form of polyaniline is a solution-processable polymer from which large, flexible films can be cast. These can subsequently be doped to the metallic conducting regime. It also shows for the first time, to the best of our knowledge, that a conducting polymer can be sublimed to produce high quality films.

The approximate solubilities of emeraldine base in 80% aqueous acetic acid, 60% and 88% aqueous formic acid, DMSO, DMF and NMP have been determined under selected experimental conditions. The best solvent for producing high quality free-standing films of emeraldine base is undoubtedly NMP. This is presumably related to the much higher solubility of emeraldine base in this solvent. The flexibility and general mechanical properties of the emeraldine base and emeraldine hydrochloride films strongly suggest that at least a portion of the polymer must be present as a relatively high molecular weight component qualitatively consistent with the reported molecular weight of 80,000 for the emeraldine base.[11] The mechanical properties of both the non-doped and doped films are greatly superior to those of films cast from 80% acetic acid which we have described previously.[4] They are also much superior to the electrochemically synthesized films on tin oxide conducting glass, which could be removed from the glass only by treatment with 3M aqueous HCl.[3,9]

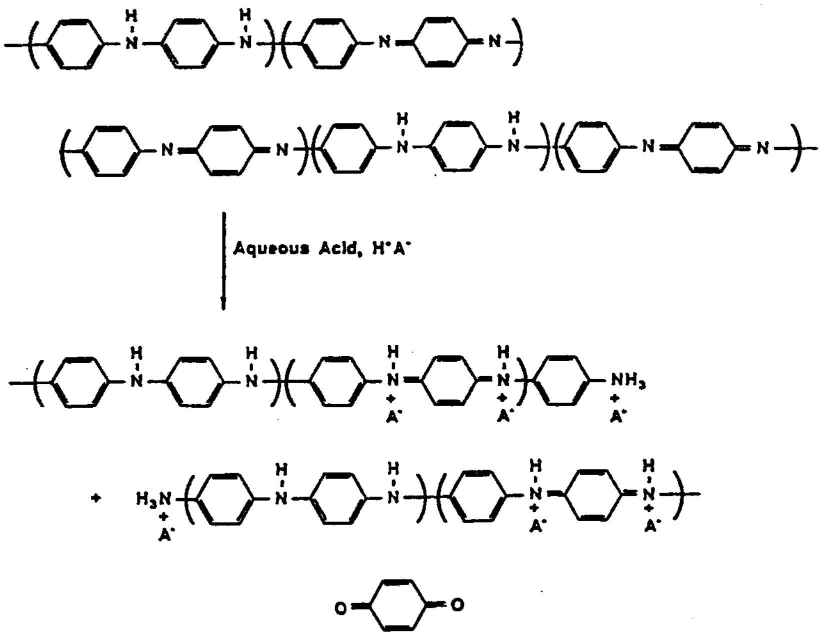
Our preliminary studies have shown that both emeraldine base and emeraldine hydrochloride may be sublimed to form films of a material whose visible/UV and infrared spectra and electrochemical behavior are very similar to, but not identical with, those of emeraldine base. The films so produced can be doped by HCl, either gaseous or in aqueous solution with a concommitant increase in conductivity of up to four orders of magnitude. The sublimation mechanism is not yet understood but we believe that lower molecular weight species are probably involved and that the original brown film is in a more reduced state than emeraldine base *i.e.* $y > 0.5$. When the properties of these films are more clearly defined and understood, it appears possible that they may have potential application in electronic devices since they can be deposited by vapor phase deposition techniques commonly used in device fabrication.

It has been known for almost 80 years[12] that emeraldine base, particularly when moist (with water) is oxidized by air to give polyanilines having a value of $y < 0.5$ in the general polyaniline formula and that aqueous acid converts the more highly oxidized polymer back to the emeraldine oxidation state.[12] These conclusions are consistent with our observation that a sample of emeraldine base which had been dissolved in *e.g.* 80% aqueous acetic acid gave an initially dark blue-green solution which changed to dark green in ~15 minutes at room temperature. This sample of emeraldine base had been exposed to air while wet with aqueous ammonium hydroxide during the deprotonation step of its synthesis. However, a different sample of emeraldine base, whose synthesis by deprotonation of emeraldine hydrochloride had been performed entirely in the absence of air, dissolved in the acetic acid to give an *immediate* green color. The blue color observed initially in the acetic acid solution of the first sample of polyaniline appears to be representative of a more highly oxidized form of the polymer which slowly decomposes in the acid solution.[12]

These observations are also consistent with the fact that the emeraldine base film obtained from NMP solution by evaporation of the solvent at 60–70°C in air had a purple tint, especially on the side exposed to the air, suggestive of some oxidation of the film during this process. However, as we had noted, treatment of this film with aqueous hydrochloric acid followed by aqueous ammonium hydroxide resulted in the formation of a lustrous copper-colored film characteristic of emeraldine base. In this respect, it is interesting to note that the film of emeraldine acetate obtained from aqueous acetic acid solutions and then rapidly converted to emeraldine base with aqueous ammonium hydroxide also yielded lustrous copper-colored films of emeraldine base. The acetic acid solution presumably converted any more highly oxidized form of polyaniline to the emeraldine oxidation state prior to deposition of the emeraldine acetate film.

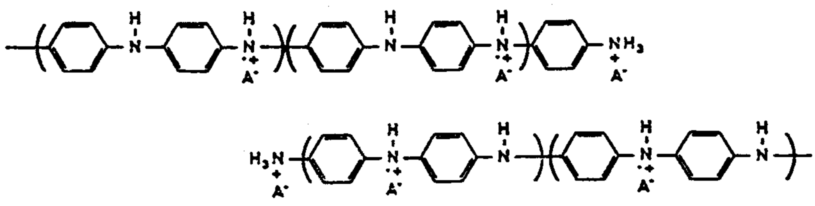
We believe that the very convenient and apparently fortuitous conversion of higher oxidation states of polyaniline to the emeraldine oxidation state by aqueous acid may be depicted for simplicity by the reaction given in scheme I.

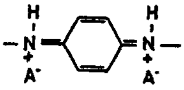
Scheme I:

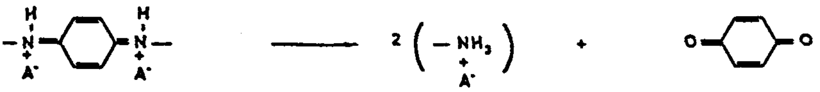


By way of an example, two oxidized repeat units are placed adjacent to each other in the reactant polymer in scheme I to represent an excess of the oxidized repeat units over and above that required by the emeraldine oxidation state which contains equal numbers of oxidized and reduced repeat units. However, we believe[5–7,10] that the emeraldine segments shown in the product species in the above equation do not exist in the spinless bipolaronic form depicted but rather in the polaronic form given in scheme II.

Scheme II:

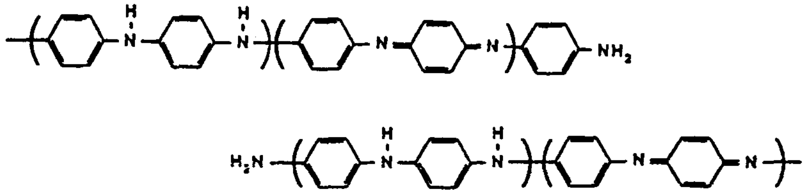


As can be seen, the resonance between the oxidized and reduced repeat units permitted in the protonated emeraldine oxidation state (*i.e.* the polysemiquinone radical cation), derived from equal numbers of oxidized and reduced repeat units, eliminates the presence of the  groups which are known to hydrolyze readily in aqueous acid[13] viz.,



The adjacent oxidized repeat units which must be present when $y < 0.5$ reduce the possibility of this resonance in the vicinity of these groups and hence hydrolysis occurs until excess oxidized repeat units have been removed and the emeraldine oxidation state has been reattained. This process will reduce the chain length of a given polymer molecule, with the introduction of the chain terminating groups depicted in the equation above. Treatment of the shortened chain segments shown above with aqueous ammonium hydroxide results in deprotonation with formation of the copper-colored emeraldine base film shown in scheme III.

Scheme III:



The apparent stability of the emeraldine oxidation state to hydrolysis by aqueous acid is strong chemical evidence in favor of the polaronic form rather than the bipolaronic form as the predominant species in protonated emeraldine base when doped to the metallic conducting regime. It should be stressed that because of the inherent limitations of hydrogen analyses, elemental analyses are of no use in determining the value of "*y*" in the general polyaniline formula since different compositions vary by only the number of hydrogen atoms present, which alters the relative weight percentages of the different elements to only a very small extent.

CONCLUSIONS

The observation that the emeraldine oxidation state of polyaniline in its base form is soluble in several aqueous and non-aqueous solvents permits it to be solution-processed to produce large, flexible, free-standing films of the emeraldine base polymer which can be protonated (doped) to give flexible films having conductivities of ~1–5 S/cm. Both emeraldine base and emeraldine hydrochloride can be sublimed to give high quality films having very similar, but not identical properties to those of emeraldine base. In order to obtain films in the emeraldine oxidation state they should be treated with dilute aqueous acid to remove any excess oxidized repeat units by hydrolysis.

Acknowledgments

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