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A.G. MacDiarmid and A.J. Epstein

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"POLYANILINE: SYNTHESIS, CHEMISTRY AND PROCESSING"

by

A.G. MacDiarmid and A.J. Epstein

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University of Pennsylvania
Department of Chemistry
Philadelphia, PA 19104-6323

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Polyanilines: Synthesis, Chemistry and Processing

by

Alan G. MacDiarmid
Department of Chemistry
University of Pennsylvania
Philadelphia, PA 19104-6323 USA

and

Arthur J. Epstein
Department of Physics
The Ohio State University
Columbus, OH 43210-1106 USA

SUMMARY: The polyanilines and their derivatives are a large class of mixed oxidation state polymers which can be synthesized by the oxidative polymerization of the appropriate monomeric aniline. Certain oxidation states of the polymer can be "doped" to the metallic conducting regime either by aqueous protonic acids or by partial oxidation. The synthesis and key chemical reactions of certain forms of the polymer will be discussed. The elucidation of the intrinsic properties of the doped polymer by stretch-orientation which results in significant increases in conductivity, crystallinity and tensile strength will be described.

1. INTRODUCTION

An organic polymer that possesses the electrical, electronic, magnetic and optical properties of a metal while retaining the mechanical properties, processibility, etc. commonly associated with a conventional polymer, is termed an "Intrinsically Conducting

Polymer," (ICP) more commonly known as a "Synthetic Metal." Its properties are intrinsic to a "doped" form of the polymer. This class of polymer is completely different from "conducting polymers" which are merely a physical mixture of a non-conductive polymer with a conducting material such as a metal or carbon powder distributed throughout the material.

The polyanilines constitute a large class of conducting polymers which are formed by the chemical or electrochemical oxidative polymerization of aniline or its derivatives.¹⁾ Some forms of the polymer can be "doped" either chemically or electrochemically with a concomitant increase in electronic conductivity of ≈ 10 orders of magnitude to produce powders, films or fibers having conductivities in the metallic conducting regime.

The scientific and technological interest in the polyanilines stems from the richness of their chemistry and their physics due to the many ways by which their chemistry, electrochemistry, electronic, magnetic and optical properties can be fine-tuned by the facile synthesis of a large variety of ring- and N-substituted derivatives. Their ready processibility adds yet another dimension to methods by which their intrinsic properties can be both explored and exploited.

The polyanilines are probably the most rapidly growing class of conducting polymers as can be seen from the number of papers and patents (1237) published during the last five years,²⁾ viz., 1986 (108); 1987 (221); 1988 (236); 1989 (383); 1990 to June 3, 1991 (289). These figures are due in large part to the very considerable industrial interest in the polyanilines as evidenced by, for example, the following announcements: 1987 - manufacture and sale of rechargeable polyaniline batteries (Bridgestone Corp., Japan and Sieko Corp., Japan); February 28, 1990 - announcement of a joint venture by Lockheed Corp. (USA) and Hexcel Corp. (USA) to manufacture polyaniline and its blends; April 10, 1991 - announcement by Neste Oy (Finland) of start-up of pilot plant production of polyaniline and polythiophene derivatives to support application development of conducting polymers; April 22, 1991 - announcement of a joint venture by Uniax Corp. (USA) and Neste Corp. (Finland) for research and development of polythiophenes and polyanilines; May 6, 1991 -

announcement of a joint venture by Allied-Signal Corp. (USA), AmeriChem (USA) and Zipperling-Kessler and Co. (Germany) to manufacture large quantities of polyaniline and polyaniline blends with polyvinylchloride, Nylons, etc. for use in e.g., EMI shielding. These materials are now commercially available in large quantities.

2. THE CONCEPT OF DOPING

Until the discovery of the novel protonic acid doping of polyaniline during which the number of electrons associated with the polymer chain remains unchanged,¹⁾ the doping of all conducting polymers had previously been accomplished by the partial removal (oxidation) or addition (reduction) of electrons from or to the π system of the polymer backbone.³⁻⁵⁾ In order to appreciate the unusual protonic acid doping phenomena in polyanilines, it is desirable to first examine what is understood by the term "doping" as applied to a conducting polymer.

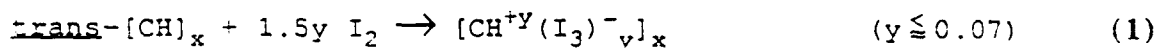
The concept of doping is the unique, central, underlying and unifying theme which distinguishes conducting polymers from all other types of polymers.^{3,6,7)} During the doping process, an organic polymer, either an insulator or semiconductor having a small conductivity, typically in the range 10^{-10} to 10^{-5} S/cm, is converted to a polymer which is in the "metallic" conducting regime (≈ 1 to $\approx 10^4$ S/cm). The controlled addition of known, usually small ($\leq 10\%$) and non-stoichiometric quantities of chemical species results in dramatic changes in the electronic, electrical, magnetic, optical and structural properties of the polymer. Doping is reversible to produce the original polymer with little or no degradation of the polymer backbone. Both doping and undoping processes, involving dopant counter ions which stabilize the doped state, may be carried chemically or electrochemically.³⁾ Transitory doping by methods which introduce no dopant ions are also known.⁸⁾ By controllably adjusting the doping level, a conductivity anywhere between that of the undoped (insulating or semi-conducting) and that of the fully doped (highly conducting) form of the polymer may be easily obtained. Conducting blends of a (doped) conducting polymer with a conventional polymer (insulator), whose conductivity can be adjusted by varying the relative proportions of each polymer, can be

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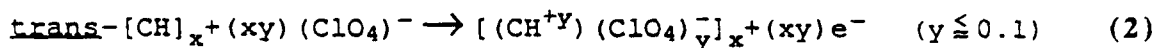
made.^{9,10)} This permits the optimization of the best properties of each type of polymer.

In the "doped" state, the backbone of a conducting polymer consists of a delocalized π system. In the undoped state, the polymer may have a conjugated backbone such as in trans-(CH)_x, which is retained in a modified form after doping, or it may have a non-conjugated backbone, as in polyaniline (leucoemeraldine base form), which becomes conjugated only after p-doping, or it may have a non-conjugated structure as in the emeraldine base form of polyaniline which becomes conjugated only after protonic acid doping.

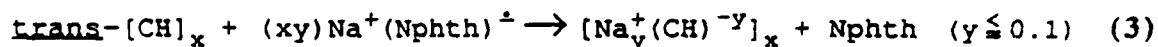
P-doping, i.e. partial oxidation of the π and/or σ backbone of an organic polymer, was first discovered by treating trans-polyacetylene with an oxidizing agent such as iodine, viz.,^{6,7)}



This process was accompanied by an increase in conductivity from $\approx 10^{-5}$ S/cm to $\approx 10^3$ S/cm. If the polymer is stretch-oriented 5 to 6 fold before doping, conductivities parallel to the direction of stretching up to $\approx 10^5$ S/cm can be obtained.³⁾ P-doping can also be accomplished by electrochemical anodic oxidation by immersing a trans-(CH)_x film in, for example, a solution of LiClO₄ dissolved in propylene carbonate and attaching it to the positive terminal of a d.c. power source, the negative terminal being attached to an electrode also immersed in the solution, viz.,¹¹⁾

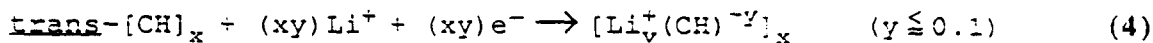


N-doping, i.e. partial reduction of the backbone π system of an organic polymer, was also discovered using trans-(CH)_x by treating it with a reducing agent such as liquid sodium amalgam or preferably sodium naphthalide, viz.,^{6,7)}



N-doping can also be carried out by electrochemical cathodic reduction¹²⁾ by immersing a trans-(CH)_x film in, for example, a

solution of LiClO_4 dissolved in tetrahydrofuran and attaching it to the negative terminal of a d.c. power source, the positive terminal being attached to an electrode also immersed in the solution, viz.,



3. THE POLYANILINES

The polyanilines refer to a class of polymers which can be considered as being derived from a polymer, the base form of which has the generalized composition: $\left[\left(\text{C}_6\text{H}_4\text{-NH-C}_6\text{H}_4\text{-NH} \right)_y \left(\text{C}_6\text{H}_4\text{-N}=\text{C}_6\text{H}_4\text{-N} \right)_{1-y} \right]_x$ and which consists of alternating reduced, $\text{C}_6\text{H}_4\text{-NH-C}_6\text{H}_4\text{-NH}$ and oxidized, $\text{C}_6\text{H}_4\text{-N}=\text{C}_6\text{H}_4\text{-N}$ repeat units.^{1,13,14} The average oxidation state, $(1-y)$ can be varied continuously from zero to give the completely reduced polymer, $\left[\text{C}_6\text{H}_4\text{-NH-C}_6\text{H}_4\text{-NH} \right]_x$ to 0.5 to give the "half-oxidized" polymer, $\left[\left(\text{C}_6\text{H}_4\text{-NH-C}_6\text{H}_4\text{-NH} \right) \left(\text{C}_6\text{H}_4\text{-N}=\text{C}_6\text{H}_4\text{-N} \right) \right]_x$, to one to give the completely oxidized polymer, $\left[\text{C}_6\text{H}_4\text{-N}=\text{C}_6\text{H}_4\text{-N} \right]_x$. The terms "leucoemeraldine", "emeraldine" and "pernigraniline" refer to the different oxidation states of the polymer where $(1-y) = 0, 0.5$ and 1 , respectively, either in the base form, e.g. emeraldine base or in the protonated salt form, e.g. emeraldine hydrochloride.^{1,13,14} In principle, the imine nitrogen atoms can be protonated in whole or in part to give the corresponding salts, the degree of protonation of the polymeric base depending on its oxidation state and on the pH of the aqueous acid. Complete protonation of the imine nitrogen atoms in emeraldine base by, e.g. aqueous HCl , results in the formation of a delocalized polysemi-quinone radical cation as discussed in Section 8^{1,14,15} and is accompanied by an increase in conductivity of $\approx 10^{10}$.

4. SYNTHESIS OF POLYANILINE

(Emeraldine and Pernigraniline Oxidation States)

The partly protonated emeraldine hydrochloride salt can be synthesized easily as a partly crystalline black-green precipitate by the oxidative polymerization of aniline, $(\text{C}_6\text{H}_5)\text{NH}_2$, in aqueous acid media by a variety of oxidizing agents, the most commonly used

being ammonium peroxydisulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, in aqueous HCl.^{1,13-15)} It can also be synthesized from aniline electrochemically in aqueous HCl. It can be deprotonated by aqueous ammonium hydroxide to give an essentially amorphous black-blue emeraldine base powder with a coppery, metallic glint having an oxidation state as determined by volumetric TiCl_3 titration corresponding approximately to that of the ideal emeraldine oxidation state.¹⁶⁾ The ^{13}C ¹⁷⁾ and ^{15}N NMR ¹⁸⁾ spectra of emeraldine base are consistent with its being composed principally of alternating oxidized and reduced repeat units.

We have found recently,¹⁹⁻²¹⁾ using a potential profiling technique whereby the potential of the system in which the aniline is undergoing polymerization is constantly monitored, that polyaniline in the pernigraniline oxidation state is actually the first formed product in the common method of synthesizing the emeraldine oxidation state by the oxidative polymerization of aniline as described above.²¹⁾

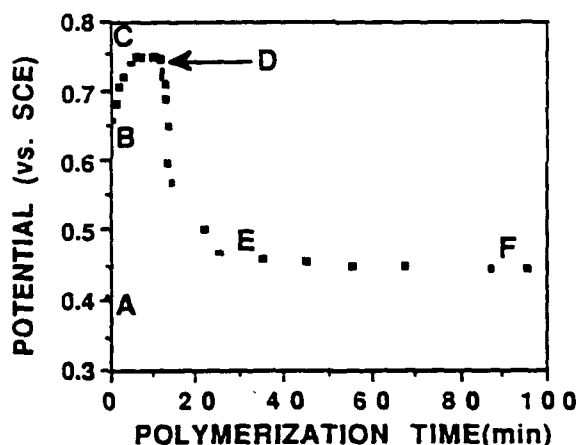
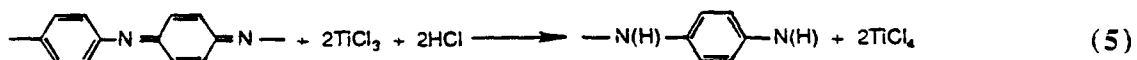


Figure 1 - Potential-Time Profile of a Conventional Chemical Oxidative Polymerization of Aniline Using Ammonium Peroxydisulfate in Aqueous 1.0M HCl ²¹⁾ (Pt electrode; SCE ref).

When the synthesis is carried out at $\approx 0^\circ\text{C}$ using excess aniline, the initial oxidation potential of the reaction system increases from $\approx 0.40\text{V}$ (vs. SCE) (Figure 1, point A) to $\approx 0.66\text{V}$ (point B) immediately after adding the $(\text{NH}_4)_2\text{S}_2\text{O}_8$, to $\approx 0.75\text{V}$ (point C) within ≈ 2 minutes at which value it stays essentially constant before it begins to fall rapidly after ≈ 10 minutes (point D), reaching $\approx 0.47\text{V}$ at point E, and $\approx 0.44\text{V}$ at point F, a value characteristic of the

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emeraldine oxidation state.²²⁾ If the reaction mixture at point D is poured into cold ($\approx 5^\circ\text{C}$) aqueous NaOH solution, analytically pure pernigraniline base powder (Calc., for $\text{C}_6\text{H}_4\text{N}$; C, 79.98; H, 4.48; N, 15.54%. Found, C, 79.35; H, 4.31; N, 15.41; Total, 99.07%) is obtained. Elemental analyses are not sufficiently accurate to determine the oxidation state since the composition of the tetrameric units of emeraldine and pernigraniline bases differ by only two hydrogen atoms. Volumetric determination of the oxidation state by TiCl_3 ^{16,23,24)} based on the reaction,



was therefore employed. The polymer was found to be in the completely oxidized state. The value of $(1-y)$ in the generalized formula of polyaniline base given above being 0.96 ± 0.02 . Its electronic and infrared spectra were identical to those of pure pernigraniline base powder synthesized using $m\text{-Cl}(\text{C}_6\text{H}_4)\text{C}(\text{O})\text{OOH}/\text{N}(\text{C}_2\text{H}_5)_3$ as described in Section 6.²⁵⁾

If the reaction mixture was poured into aqueous NH_4OH at point F, a precipitate of analytically pure emeraldine base was obtained. The weight of polymer increased substantially on proceeding from point D to point E and then remained relatively constant. If the pure pernigraniline base, formed at point D was isolated and then treated with an excess of a mixture of aniline and HCl , analytically pure emeraldine base was produced after deprotonation.

Initial polymerization of aniline is slow but oligomers, once formed, react very much more rapidly with aniline to produce the polymer. Since the oxidation potential (1.05V vs. SCE) of the $(\text{NH}_4)_2\text{S}_2\text{O}_8/1\text{M HCl}$ is sufficiently high to oxidize any polymer in the emeraldine oxidation state ($\approx 0.43\text{V}$)²²⁾ to the pernigraniline oxidation state ($\approx 0.83\text{V}$),²⁵⁾ it is clear why the polymer in the pernigraniline oxidation state is first formed. At point D it has been shown that essentially all the $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is consumed. The polymer in the pernigraniline oxidation state (of unknown protonation level) is a sufficiently strong oxidizing agent to oxidatively polymerize the excess aniline to the emeraldine

1



It is clear that the pernigraniline oxidation state has a sufficiently large oxidation potential ($\approx 0.83\text{V}$ vs. SCE) to oxidatively polymerize aniline since it is known that oxidation of aniline commences at a potential of $\approx 0.7\text{V}$.²⁶⁾

The emeraldine hydrochloride is thus formed in two different ways: (i) as the product of the reduction of the pernigraniline oxidation state, and (ii) as the product of the oxidative polymerization of aniline by the pernigraniline oxidation state. The molecular weight of the product after conversion to emeraldine base by deprotonation was determined in a ≈ 0.5 wt.% LiCl solution in NMP by gel permeation chromatography (GPC) using narrow polystyrene standards. The monomodal symmetrical peak obtained gave values of $(\bar{M}_w) = 64,452$, $^{21)} (\bar{M}_n) = 25,283$, and $(\bar{M}_w/\bar{M}_n) = 2.55$. Treatment of the polymer with additional $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (to oxidize the material to the pernigraniline oxidation state) and additional aniline resulted in an increase in molecular weight of the product. Repetition of this procedure using the newly formed emeraldine hydrochloride resulted in a further increase in molecular weight. After three such cycles a maximum $(\bar{M}_w)$ value of 89,633 $((\bar{M}_w/\bar{M}_n) = 2.46)$ was obtained which fell to a value of 84,172 $((\bar{M}_w/\bar{M}_n) = 2.54)$ after six such cycles.²⁷⁾ This suggests that some of the newly-added aniline adds to the previously existing polyaniline by some type of living polymerization process to increase its molecular weight while the greater portion produces polyaniline from new nucleation sites which is therefore of lower molecular weight. The effect of formation of new nucleation sites finally predominates over addition to previously existing polymer chains.

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The above reaction can be used in a novel process to produce block co-polymers of aniline. For example, if, instead of adding additional aniline in cycle 1, o-toluidine, $\text{CH}_3(\text{C}_6\text{H}_4)\text{NH}_2$ is added, the resulting polyaniline hydrochloride (emeraldine oxidation state) is consistent with solubility, elemental analysis and spectroscopic studies as being a block co-polymer containing $\approx 10\%$ of polytoluidine and $\approx 90\%$ polyaniline.²⁸⁾

It is interesting to note that the molecular weight of the polyaniline may be increased substantially by reducing the number of nucleation sites during the polymerization of aniline.²⁷⁾ This is accomplished by having relatively insoluble solid anilinium hydrochloride, $\text{C}_6\text{H}_5\text{NH}_2\cdot\text{HCl}$, present in the reaction vessel. The concentration of free aniline in solution is thus very small but is constantly automatically replenished as it is consumed by virtue of the fact that more of the anilinium hydrochloride dissolves as needed. This is accomplished simply by cooling the reaction vessel to ≈ -20 to -30°C . Lithium chloride is added to stop the contents from freezing. As the temperature is lowered to $\approx -9^\circ\text{C}$ the anilinium hydrochloride precipitates. Molecular weights up to $\bar{M}_n=127,000$, $\bar{M}_w=440,000$ and $\bar{M}_w/\bar{M}_n\approx 3.5$ can readily be obtained by this method. It can be seen that these values are substantially greater than those obtained by the conventional synthetic method described above.

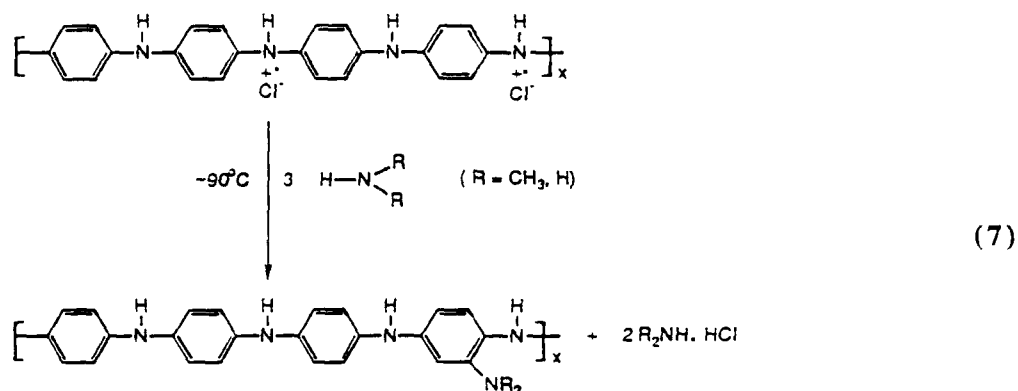
Light scattering studies performed on leucoemeraldine base obtained by reduction of emeraldine base with hydrazine show that $\bar{M}_w$ values (GPC) are approximately twice those obtained from light scattering studies. Hence, the $\bar{M}_w$ values obtained by GPC studies on polyaniline should be divided by two to obtain more accurate values.²⁹⁾

5. SELECTED REACTIONS OF THE EMERALDINE OXIDATION STATE

A. Reaction of Emeraldine Hydrochloride with Gaseous Ammonia and Dimethyl Amine.

As noted in the previous section, the emeraldine oxidation state of polyaniline formed by the oxidative polymerization of aniline with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is obtained as the (protonated) emeraldine hydrochloride salt. This is then deprotonated to the emeraldine base by

ammonium hydroxide. It is interesting to note that water is essential for this reaction. For example, if emeraldine hydrochloride is treated with dry gaseous NH_3 or gaseous $(\text{CH}_3)_2\text{NH}$, reductive ring amination occurs to give ring substituted polyaniline in the (completely reduced) leucoemeraldine oxidation state, viz.,³⁰⁾

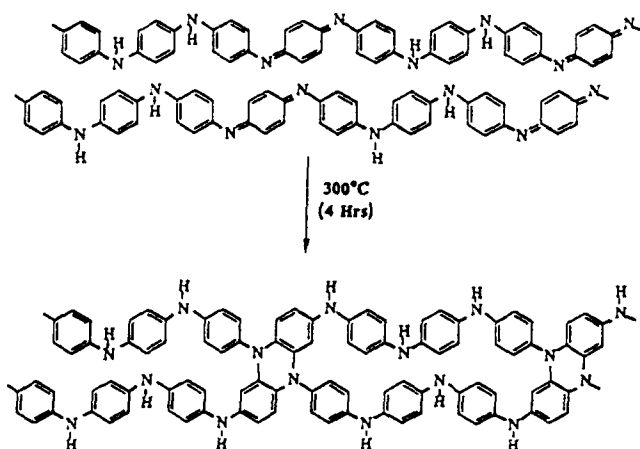


The nature of the products are consistent with their vis/uv and I/R spectra, cyclic voltamograms and elemental analyses: For NH_3 : Calc. for $\text{C}_{24}\text{H}_{21}\text{N}_5$: C, 75.98; H, 5.54; N, 18.46%. Found: C, 75.27; H, 5.61; N, 17.87%; Total 98.75%. For $(\text{CH}_3)_2\text{NH}$: Calc. for $\text{C}_{26}\text{H}_{25}\text{N}_5$: C, 77.22; H, 5.46; N, 17.32%;. Found: C, 76.91; H, 5.61; N, 17.07% Total 99.96%. This type of reaction opens up an interesting new class of polyanilines which undergo protonation at two completely different sites - at $-\text{N}^+=$ and at $-\text{NR}_2$. Use of diamines such as phenylene-diamine results in controlled cross-linking of polymer chains by conjugated groups leading to the formation of 2D/3D polyanilines.

B. Thermal Cross-Linking of Emeraldine Base

When emeraldine base is heated in in vacuo an internal rearrangement occurs to produce a cross-linked polymer in the reduced (leucoemeraldine) oxidation state.³¹⁾ T.G.A. and D.S.C. studies show a strong exotherm at $\approx 300^\circ\text{C}$ with no accompanying weight loss. This is consistent with elemental analyses which show no change in composition during this process. This arrangement reaction occurs with powders, free-standing films or fibers of the polymer. Vis/uv, I/R, cyclic voltamograms and TiCl_3 titration studies are consistent with reductive cross-linking of the type

involving phenazine-like cross-links.³²⁾ The resulting 2D/3D polymer is still electrochemically active and preliminary studies indicate that it undergoes oxidative doping to give a polymer having a conductivity in the 10^{-2} S/cm range.



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6. SYNTHESIS AND CHEMISTRY OF PERNIGRANILINE BASE

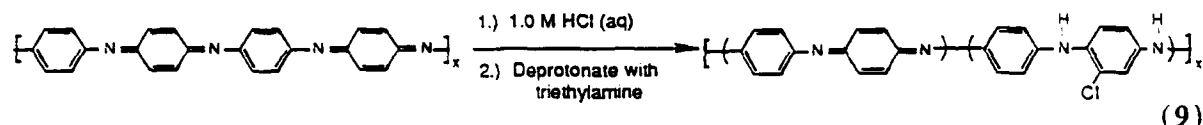
A. Synthesis

Oxidation of emeraldine base powder with an acetic acid solution of m-chloroperbenzoic acid followed by deprotonation with triethylamine results in analytically pure pernigraniline base²⁵⁾ (Calc. for C_6H_4N : C, 79.98; H, 4.48; N, 15.54%. Found: C, 79.98; H, 4.87; N, 15.63; Total 100.38%). The polymer was found to be in the completely oxidized state, within experimental error, the value of $(1-y)$ in the generalized formula of polyaniline base being 0.97 ± 0.02 . It is critically important to note that the cyclic voltammogram of the polymer contained no "central" peak; impure samples may contain a large central peak. The above procedure can be used to synthesize pernigraniline base in the form of a free-flowing powder or as large (10cm x 10cm), lustrous, bronze-colored, free-standing films.

B. Reaction of Pernigraniline Base with Aqueous HCl

In view of the predicted³³⁾ presence of two different types of solitons in the pernigraniline oxidation state, attempts were made to protonate pernigraniline base under similar conditions to those used for the protonation of emeraldine base as described in Section

8. We find that treatment of pernigraniline base with aqueous 1M HCl (54 hours) results in a completely different type of reaction; instead, it is reduced to the emeraldine oxidation state (as shown by vis/uv and I/R spectroscopic studies) with concomitant ring chlorination, viz.,³⁴⁾



consistent with its elemental analysis; Calc. $\text{C}_{24}\text{H}_{18}\text{N}_4\text{Cl}$: C, 72.45; H, 4.57; N, 14.07; Cl, 8.91%. Found: C, 73.44; H, 4.63; N, 13.57; Cl, 8.60; Total, 100.21%. Its conductivity before deprotonation (compressed pellet) was $\approx 0.1 \text{ S/cm}$. It appears that protonation of --N= atoms first occurs as in the protonation of emeraldine base but that this is then immediately followed by a rearrangement reaction to give the ring-substituted product.

It can now be seen that the pernigraniline oxidation state initially formed in the oxidative polymerization of aniline with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as described in Section 4, can undergo further reaction not only with aniline but also with HCl in a competing reaction. Hence, if sufficient aniline is not used in the standard synthesis of the emeraldine oxidation state from aniline, then the pernigraniline oxidation state initially formed as described in Section 4 may undergo, at least in part, further reaction with the HCl present in the reaction mixture to give some ring chlorination. This helps to explain several reports in the literature^{35,36)} that emeraldine base sometimes contains small but significant quantities of C-Cl bonds when synthesized by standard procedures and/or that oxidative decomposition of emeraldine hydrochloride can lead to the formation of such bonds. It may also be related to the extensive ring bromination which results when emeraldine base is protonated by aqueous HBr.³⁷⁾

C. N-Doping of Pernigraniline Base

Since pernigraniline base does not undergo protonic acid doping, an attempt was made to ascertain if it would undergo reductive n-type doping of its π system analogous to the n-doping of $(\text{CH})_x$.

Treatment of pernigraniline base film or powder with 0.1M sodium naphthalide (tetrahydrofuran solution) resulted in the formation of orange-red transparent films or dark red powders respectively, with concomitant disappearance of the strong absorption at 530nm characteristic of pernigraniline base and its replacement by a new strong band at 440nm.³⁸⁾ A variety of studies showed that the composition of the film was $\text{Na}^+ \left[\text{—C}_6\text{H}_4\text{—N}=\text{C}_6\text{H}_4\text{—N}=\text{C}_6\text{H}_4\text{—N}=\text{C}_6\text{H}_4\text{—N—} \right]_x^-$. This n-doping was accompanied by more than an eight order of magnitude increase in conductivity to approximately 10^{-1} S/cm. Magnetic studies showed ≈ 1 spin per four ring-N units.

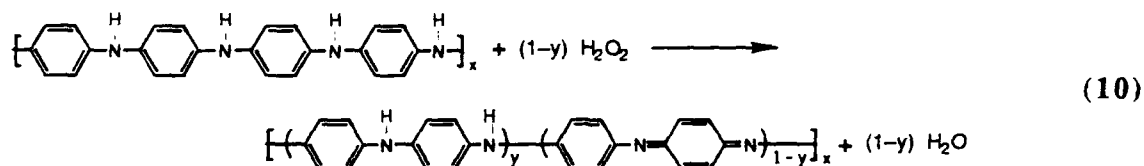
Partial exposure of the n-doped polymer to air resulted in the disappearance of the strong band at 440nm and the appearance of a new strong broad band at 1161nm. A material previously described as n-doped pernigraniline³⁹⁾ had a similar spectrum. This was, therefore, partly decomposed material. Complete undoping of the n-doped polymer showed that no irreversible degradation of the polymer backbone had occurred during the doping/undoping process. A full theoretical analysis of the vis/uv spectrum of this n-doped polymer remains to be undertaken; however, it seems not unlikely that n-doping has resulted in a new type of Peierls gap which has shifted from 535nm in pernigraniline base to 440nm in n-doped pernigraniline.⁴⁰⁾

7. ALLOWED OXIDATION STATES OF POLYANILINE

As can be seen from the generalized formula of polyaniline base, $\left[\text{—C}_6\text{H}_4\text{—N}^{\text{H}}\text{—C}_6\text{H}_4\text{—N}^{\text{H}}\text{—} \right]_y \left(\text{—C}_6\text{H}_4\text{—N}=\text{C}_6\text{H}_4\text{—N}=\text{C}_6\text{H}_4\text{—N}=\text{C}_6\text{H}_4\text{—N—} \right)_{1-y}$, the polymer could, in principle, exist in a continuum of oxidation states ranging from the completely reduced material in the leucoemeraldine oxidation state, $(1-y)=0$ to the completely oxidized material in the pernigraniline oxidation state, $(1-y)=1$. However, we have shown previously from isosbestic vis/uv spectroscopic studies²¹⁾ that at least in N-methyl-2-pyrrolidinone (NMP) solution in the range $(1-y)=0$ to $(1-y)=0.5$ (emeraldine oxidation state) only two chromophores are present, characteristic of $(1-y)=0$ and $(1-y)=0.5$ species and that all intermediate oxidation states consist, at the molecular level, only of mixtures of the chromophores characteristic of these two states.³⁰⁾

Since most of the properties of polyaniline of interest are concerned with the solid state, we have carried out a series of studies in the solid state which show that the same phenomenon is true in the $(1-y)=0$ to $(1-y)=0.5$ oxidation state range and that a similar phenomenon is found in the $(1-y)=0.5$ to $(1-y)=1$ oxidation state range where all intermediate oxidation states in these two ranges consist, at the molecular level, only of mixtures of the chromophores characteristic of the two states defining the beginning and end of each range.

A thin film of leucoemeraldine base was spun on a glass plate and was oxidized in increments by exposure to H_2O_2 vapor for ≈ 15 minutes, viz.,



Vis/uv spectra were recorded after each exposure and for convenience are shown as two sets: Figure 2 showing the spectra for average oxidation states between $(1-y)=0$ and $(1-y)=0.5$, and, Figure 3 showing the spectra for average oxidation states between $(1-y)=0.5$ and $(1-y)=1$.

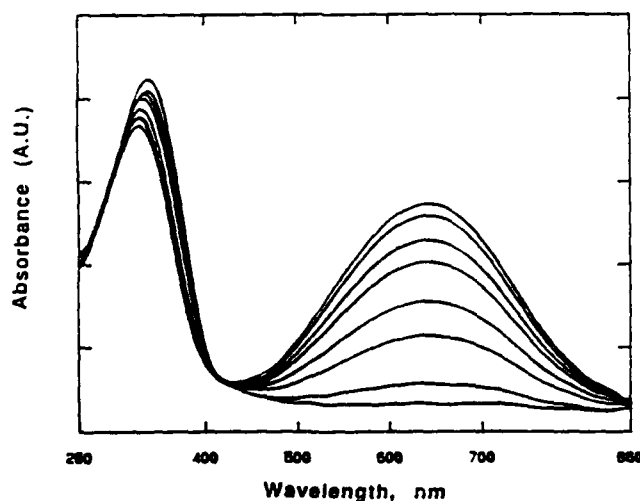


Figure 2 - Vis/uv Spectra of Films of Polyaniline Bases in Average Oxidation States Intermediate Between That of Leucoemeraldine, $(1-y)=0$ and Emeraldine, $(1-y)=0.5$.

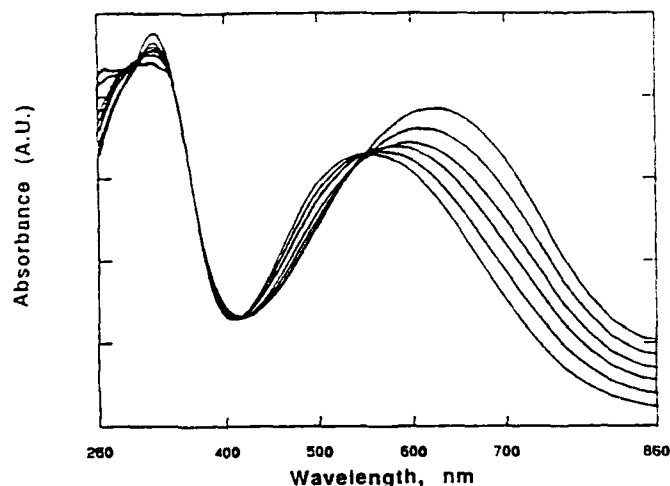


Figure 3 - Vis/uv Spectra of Films of Polyaniline Bases in Average Oxidation States Intermediate Between That of Emeraldine, $(1-y)=0.5$ and Pernigraniline, $(1-y)=1.0$.

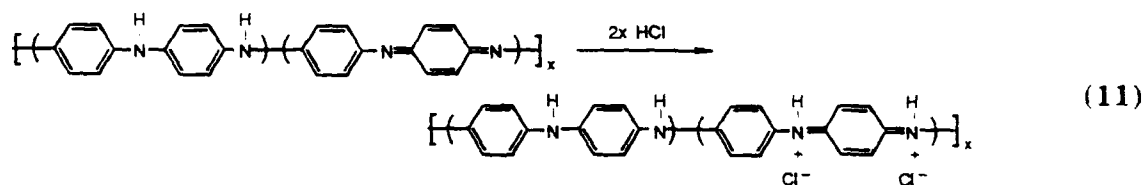
In each figure the isosbestic points show that the reduced form is oxidized in one step, without passing through any observable intermediate form, to the more highly oxidized form. Within each set, increasing oxidation merely increases the absorbance intensity, i.e. increases the amount of the oxidized species; no new intermediate species with its own unique chromophore is produced.

As might be expected, the chromophore associated with the emeraldine base oxidation state, $(1-y)=0.5$, is certainly no greater than eight ring-N units since the octomer and polymer in the emeraldine oxidation state have identical vis/uv spectra.⁴¹⁾ These results should prove to be of considerable use in interpreting and analyzing many of the properties of polyanilines in average oxidation states intermediate between any two of the three discrete oxidation states.

8. DOPING OF POLYANILINE

Polyaniline holds a special position amongst conducting polymers in that its most highly conducting doped form can be reached by two completely different processes - protonic acid doping and oxidative doping. Protonic acid doping of emeraldine base with, for example 1M aqueous HCl results in complete protonation of the imine nitrogen

atoms to give the fully protonated emeraldine hydrochloride salt:^{13,14)}



As shown in Figure 4, protonation is accompanied by a 9 to 10 order of magnitude increase in conductivity (to 1-5 S/cm; 4 probe; compressed powder pellet) reaching a maximum in $\approx 1\text{M}$ aqueous HCl.

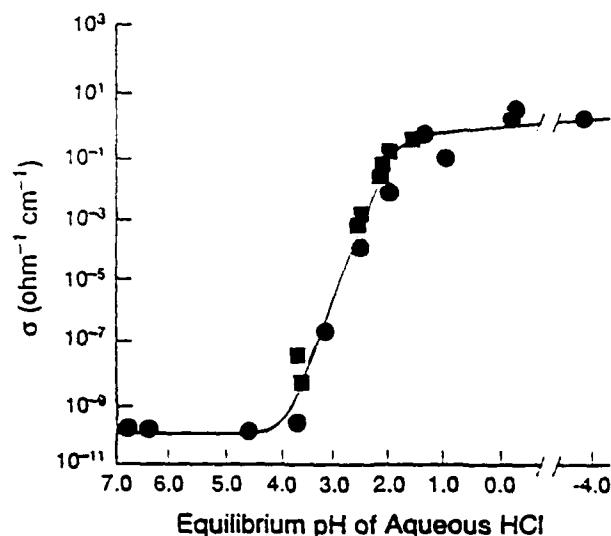


Figure 4 - Conductivity of emeraldine base as a function of pH of HCl dopant solution as it undergoes protonic acid doping (● and ■ represent two independent series of experiments).^{13,14)}

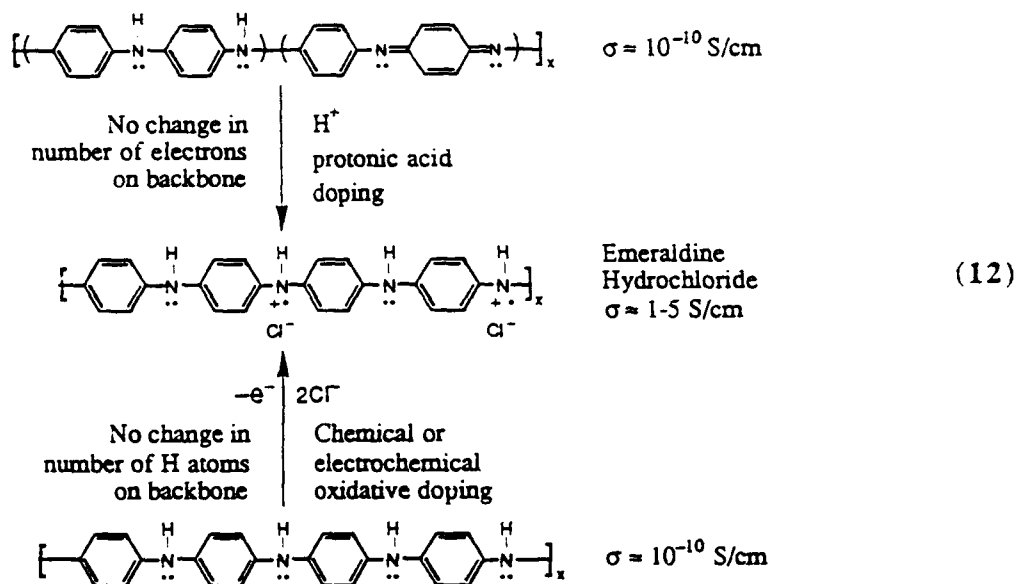
If this fully protonated emeraldine base should have the above dication, i.e. bipolaron constitution as shown in Equation 11, it would be diamagnetic. However, extensive magnetic studies¹⁾ have shown that it is strongly paramagnetic and that its Pauli (temperature-independent) magnetic susceptibility increases linearly with the extent of protonation. These observations and other earlier studies^{42,43)} show that the protonated polymer is actually a polysemiquinone radical cation, one resonance form consisting of two separated polarons: $\left[\text{C}_6\text{H}_4\text{-NH-C}_6\text{H}_4\text{-NH}^+\text{C}_6\text{H}_4\text{-NH}^+ \right]_x$, resulting from an

"internal" redox reaction whereby the oxidation states of all the

rings become equivalent and the oxidation states of all the nitrogen atoms become equivalent.

It can be seen from the alternative resonance form where the charge and spin would be placed on the other set of nitrogen atoms that the overall structure is expected to have extensive spin and charge delocalization. This results in a half-filled polaron conduction band.

The same doped polymer can also be obtained by oxidation of leucoemeraldine base with Cl_2 ¹⁾ as shown schematically below:



(9) RELATIONSHIP BETWEEN MOLECULAR WEIGHT AND CONDUCTIVITY

As-synthesized¹⁵⁾ emeraldine base in NMP solution containing 0.5 wt.% LiCl was passed through a preparative G.P.C. column and six separate fractions were collected, the lowest molecular weight fraction ($\bar{M}_{\text{peak}} < 5000$) being discarded, since in a separate study it was shown that it contained oxygen-containing impurities.⁴⁴⁾ Each of the six fractions (Table 1) was shown to be pure emeraldine base by elemental analysis, infrared and electronic spectral studies and by cyclic voltammetry.²¹⁾

It can be seen from Figure 5 that the conductivity of the doped polymer rises monotonically with molecular weight up to a value of

$\approx 150,000$ ($\approx 1,600$ ring-nitrogen repeat units) after which it changes relatively little. The reason for the change in dependency of conductivity on molecular weight is not clearly apparent; however, it is not caused by a change in the degree of crystallinity, since all fractions exhibited approximately the same crystallinity by x-ray diffraction studies.

Table 1. Characterization of Fractions of Emeraldine Base From Preparative G.P.C. Studies (a, b)

Fraction	$\bar{M}_{\text{peak}}$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Conductivity (b) (S/cm)
1	15000	12000	22000	1.8	1.2
2	29000	22000	42000	1.9	2.4
3	58000	40000	73000	1.8	7.9
4	96000	78000	125000	1.6	13.1
5	174000	148000	211000	1.4	17.0
6	320000	264000	380000	1.4	14.9

(a) Polystyrene standard; (b) Compressed pellet (4-probe) after doping with 1M aq. HCl for 48 hours.

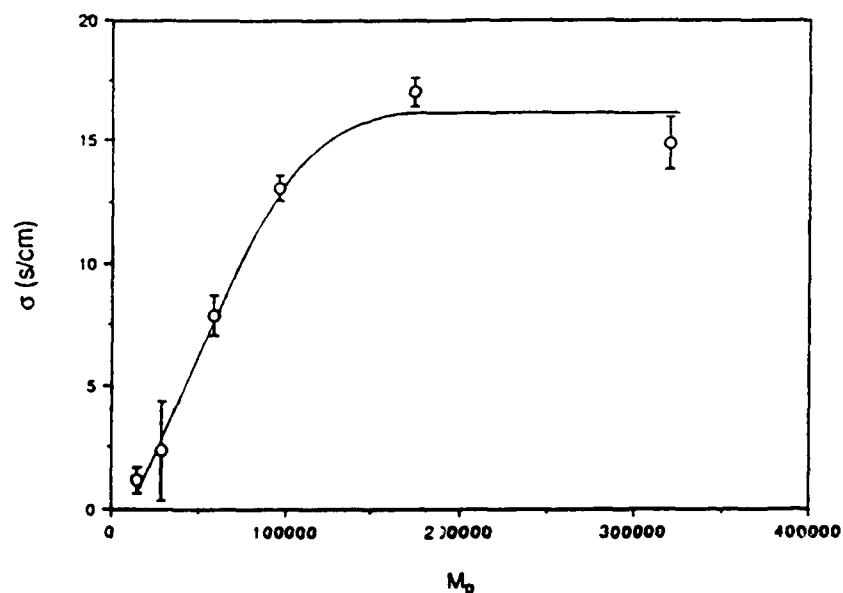


Figure 5 - Dependency of Conductivity (σ) of Doped Polyaniline (Emeraldine Oxidation State) on Molecular Weight.²¹⁾

(10) RELATIONSHIP BETWEEN DEGREE OF STRETCH ORIENTATION,
CRYSTALLINITY, CONDUCTIVITY AND TENSILE STRENGTH OF POLYANILINE

"As-synthesized" emeraldine base is very soluble in NMP.⁴⁵⁾ However, the term "soluble" must be used with caution since it is not clear how much of the polymer in, for example, a viscous $\approx 20\%$ by weight "solution" is in "true" solution.^{21,45,46)} It has been known for some time that emeraldine base is readily solution-processible^{45,46)} and that it may be cast as free-standing, flexible, coppery-colored films from its solutions in NMP. These films can be doped with $\approx 1M$ aqueous HCl to give the corresponding flexible, lustrous, purple-blue films ($\sigma \approx 1-4$ S/cm) of emeraldine hydrochloride⁴⁵⁾ which are partly crystalline. However, as shown below, the intrinsic properties of a conducting polymer can only be approached through processing.

(A) Aligned Films

Uniaxially oriented, partly crystalline emeraldine base films are obtained by simultaneous heat treatment and mechanical stretching of films formed from "as-synthesized" emeraldine base containing ≈ 15 wt.% NMP plasticizer.^{1,21)} Samples are observed to elongate by up to four times their original length when stretched above the glass transition temperature ($\geq 110^\circ C$)^{1,21)} by simply attaching a weight to the film. The resulting films have an anisotropic X-ray diffraction and optical response, with a misorientation of only a few degrees.¹⁾

Lustrous, copper-colored ribbons of uniaxially oriented emeraldine base film up to 1.2 meters (4 feet) in length and 2.5 cm in width (thickness $\approx 20\mu m$) of various draw ratios can be readily fabricated by stretch-orienting emeraldine base films previously cast from NMP solution at $\approx 140^\circ C$ between two metal rollers rotating at different speeds.^{21,31)}

As can be seen from Figure 6 the apparent degree of crystallinity is greatly increased by processing of this type. The solubility of the polymer is greatly dependent on its degree of crystallinity. The unstretched film ($l/l_0=1$) is, for example, $\approx 90\%$ re-soluble in NMP whereas the highly crystalline film ($l/l_0=4$) is insoluble in NMP.

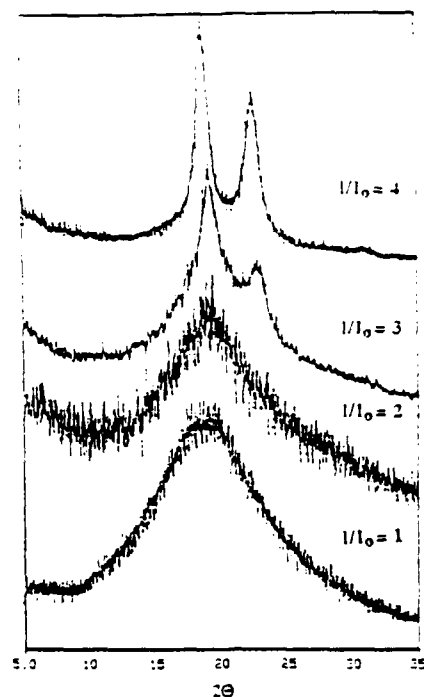


Figure 6 - X-Ray Diffraction Spectra of Ribbons of Emeraldine Base of Increasing Draw Ratio, (l/l_0 ; l = final length; l_0 = original length before stretching.)^{21,31)}

The conductivity of the HCl-doped uniaxially oriented ribbons increases on stretching ($l/l_0=1$, $\sigma \approx 5$ S/cm; $l/l_0=4$, $\sigma \approx 80$ S/cm). It should be noted that their conductivity is greatly dependent on their method of drying; conductivities of ≈ 300 S/cm can be obtained for films which have not been dried to any great extent.^{21,31)}

Table 2. Tensile Strength (MPa)^a of Emeraldine Base Ribbons as a Function of Draw Ratio (l/l_0)²¹⁾

	<u>Uniaxial Orientation:</u>				<u>Biaxial Orientation</u> ^b :
	$l/l_0=1$	$l/l_0=2$	$l/l_0=3$	$l/l_0=4$	$l/l_0=2$
Tensile Strength(Av.)	54.4	53.2	75.9	124.1	122.4
(Best)	59.9	62.1	82.8	144.8	131.6

(a) gauge length = 3 inches (7.6 cm); (b) $l/l_0 = 2$ in both directions

The tensile strength of the ribbons increases significantly with an increase in draw ratio (and crystallinity) as shown in Table 2.²¹⁾ As expected, biaxially oriented films exhibit significantly greater tensile strength than uniaxially oriented film for the same draw ratio ($l/l_0=2$).

The above observations show that polyaniline can be processed by methods used for commercial polymers. Even at this very early stage, its tensile strength approaches the lower tensile strength range of commercial polymers such as Nylon 6. Unstretched Nylon 6 has tensile strengths ranging from 69 to 81 MPa.⁴⁷⁾

(B) Aligned Fibers

Fibers ($\approx 30-70$ mm) of emeraldine base can be formed by drawing a $\approx 20\%$ by weight "solution" of emeraldine base in NMP in a water/NMP solution.²¹⁾ If desired, the emeraldine base "solution" in NMP may also be drawn in aqueous HCl which results in direct formation of the doped fiber. Fibers can also be spun from NMP solution.

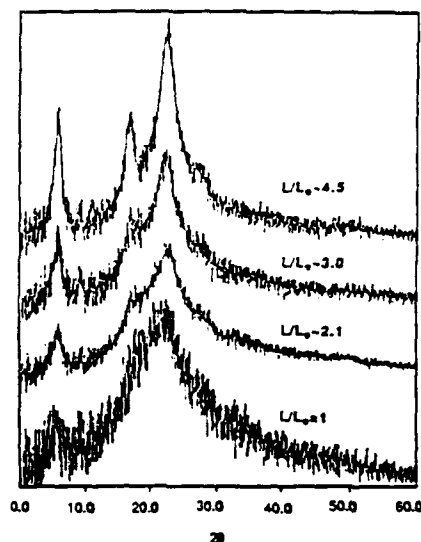


Figure 7 - Change in X-ray Diffraction Spectra of Stretch-Oriented Fibers of Emeraldine Base Drawn in Aqueous/NMP to Selected Values After Doping in 1M HCl, (l_0 = original length, l = final length).²¹⁾

The drawn fibers (containing NMP as plasticizer) can be thermally stretch-oriented at $\approx 140^\circ\text{C}$ up to 4.5 times their original length in

a similar manner to emeraldine base films.²¹⁾ X-ray diffraction studies show directional enhancement of the Debye-Scherrer rings. The change in X-ray diffraction spectra of stretch-oriented fibers after doping in 1M HCl are shown in Figure 7. A monotonic increase in apparent crystallinity with draw ratio is observed, as shown in Figure 8.²¹⁾ Doping with 1M aqueous HCl results in a significant increase in the conductivity parallel to the direction of stretching ($\sigma \approx 40-170$ S/cm) as compared to the conductivity of the polymer powder from which the fibers are prepared ($\sigma \approx 1-5$ S/cm).²¹⁾

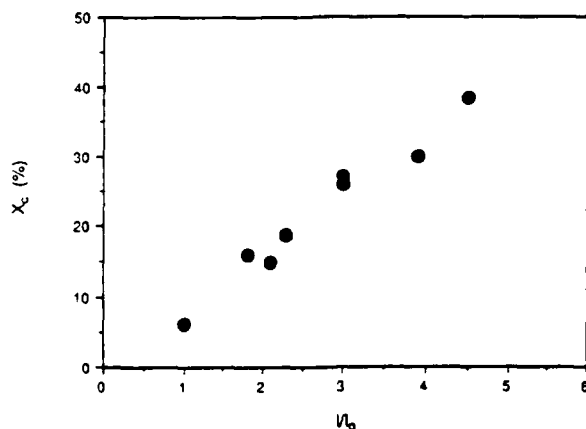


Figure 8 - Crystallinity vs. Draw Ratio (l/l_0) for Emeraldine.HCl Fibers [X_c = fractional integrated radial intensity (sum of 010, 012, 200 crystal peaks)].²¹⁾

As can be seen from Figure 9, the conductivity of the HCl-doped drawn fibers increases monotonically with draw ratio, (l/l_0).²¹⁾

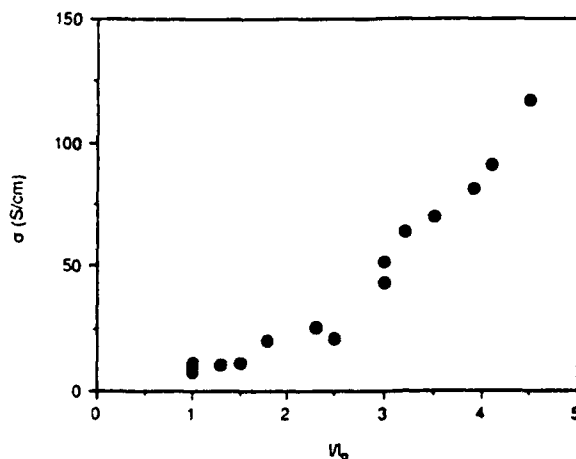


Figure 9 - Conductivity vs. Draw Ratio (l/l_0) for Emeraldine.HCl Fibers.²¹⁾

It should be stressed that the above data were obtained using "as-synthesized" emeraldine base containing low molecular weight polymer and low molecular weight impurities.²¹⁾ Since l/l_0 in general will increase with increasing molecular weight if the polymer chains are not entangled, it is apparent that use of higher molecular weight polymer should result in greater l/l_0 ratios and hence in even higher conductivities. From Figures 8 and 9 it is apparent that the conductivity of the fibers also increases monotonically with increase in apparent crystallinity. The increase in crystallinity is due to the formation of new crystallites, not to the growth of previously existing crystallites.^{31,48)}

Preliminary studies show that emeraldine base fibers both before and after doping with 1M aqueous HCl exhibit promising mechanical properties.²¹⁾ Values for 7.6cm gauge length emeraldine base fibers stretch-oriented ($l/l_0 \approx 3-4$) at $\approx 140^\circ\text{C}$ are (tensile strength, MPa; initial modulus, GPa): 318(Av.); 366(Best) and 8.1(Av.); 8.6(Best). After doping, corresponding values are: 150(Av.); 176(Best) and 4.6(Av.); 5.0(Best). X-ray diffraction studies show some reduction in crystallinity after doping, consistent with the reduction in tensile strength. As expected, the tensile strength of the oriented emeraldine base fibers are greater than those of oriented films. As can be seen on comparing the above tensile strengths with those of, for example, fibers of Nylon 6 (200-905 MPa)⁴⁹⁾ the mechanical properties of polyaniline fibers, considering the early stage of development, are most encouraging.

11. CONCLUSIONS

The parent, unsubstituted polyanilines hold a special place in the whole conducting polymer field in that in the non-doped form they exist in three completely different oxidation states. Furthermore, one of these forms, i.e. that involving a "mixed" oxidation state, is protonically acid doped to the metallic regime by a process involving no change in the number of electrons on the polymer chain; the completely reduced form on the other hand is oxidatively doped, either chemically or electrochemically, by conventional redox doping found in other conducting polymers. These properties, together with the ready processibility of polyaniline

2-

into oriented films and fibers, offer a richness of chemistry and physics unparalleled in many other polymers of this type.

The potentially very extensive derivative chemistry of the polyanilines, which has of yet been virtually unexplored will undoubtedly permit controlled fine-tuning of electronic, electrical, magnetic, spectroscopic and mechanical properties and will lead to an appreciation of the relationship of these properties to the nature of the chemical substituent. An understanding of the fundamental science of polyaniline, now that pure materials of known chemical composition and oxidation state are reproducibly attainable, is slowly beginning to unfold, thus permitting in-depth exploration and exploitation of a class of polymers not only of fundamental scientific interest but also of real potential technological importance.

12. ACKNOWLEDGEMENTS

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