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The synthesis and p- and n-doping of polyacetylene, $(CH)_x$, the prototype conducting polymer or "synthetic metal" is described together with a qualitative description of its band structure and changes in band structure on doping to yield positive and negative solitons. Other conducting polymers are briefly discussed. The polyanilines, a large class of versatile conducting polymers involving a novel non-redox doping process, considered as being of significant commercial technological importance are discussed in particular with reference to their ease of processing. Present and future technological uses of conducting polymers are noted.

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"THE POLYANILINES: A NOVEL CLASS OF CONDUCTING POLYMERS"

by

A.G. MacDiarmid

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"THE POLYANILINES: A NOVEL CLASS OF CONDUCTING POLYMERS"

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ABSTRACT

The concept of doping is shown to be the unique, central, underlying and unifying theme which distinguishes conducting polymers from all other types of polymers. The polyanilines and their ring– and nitrogen– substituted derivatives constitute a large class of conducting polymers of variable oxidation state which are unusual in that, depending on the oxidation state, the most highly conducting form can be synthesized by both protonic acid doping and by oxidative doping. The number of electrons associated with the polymer backbone undergoes no change during the former process, whereas the latter process results in a decrease in the number of electrons associated with the polymer backbone. The isolation of intermediate forms of polyaniline produced during its conventional synthesis by oxidative polymerization of aniline is described. It is shown that polyaniline is readily solution–processible and that mechanical alignment of free–standing films and fibers results in significant increases in conductivity, crystallinity and tensile strength whereby the intrinsic properties of both the doped and undoped forms of the polymer begin to become apparent.

(A) 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 and are formed by the chemical or electrochemical oxidative polymerization of aniline or its ring– or N–substituted derivatives (MacDiarmid and Epstein 1989). They can be prepared in three different oxidation states; 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 (STN Computer File 1991), 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 Oy (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 pilot plant quantities.

* **Editor:** Since the material from the asterisk on to the end of the preceeding paragraph deals with more commercially–oriented than scientifically–oriented material, I would prefer that this be placed in some way, if it can be done, in the reference section of this paper. Can you advise? Many thanks! **Author.**

(B) THE CONCEPT OF DOPING

Prior to the discovery of the novel protonic acid doping of polyaniline during which the number of electrons associated with the polymer chain remain unchanged (MacDiarmid and Epstein 1989), the doping of all conducting polymers had previously been accomplished by redox doping. This involves the partial addition (reduction) or removal (oxidation) of electrons to or from the π system of the polymer backbone (Kanatzidis 1990; MacDiarmid and Heeger 1979/80; Skotheim 1986). 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.

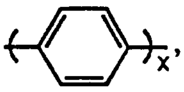
The concept of doping is the unique, central, underlying and unifying theme which distinguishes conducting polymers from all other types of polymers (Kanatzidis 1990; Chiang et al. 1977, 1978). During the doping process, an organic polymer, either an insulator or semi–conductor having a small conductivity, 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 ≈10^4 S/cm). The controlled addition of known, usually small (≤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 (Kanatzidis 1990). Transitory doping by methods which introduce no dopant ions are also known (Ziemelis et al. 1991). 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 made (Kulkarni et al. 1991; Shacklette et al. 1991). This permits the optimization of the best properties of each type of polymer.

Since the initial discovery in 1977, that polyacetylene $(CH)_x$, now commonly known as the prototype conducting polymer, could be p– or n–doped, either chemically or electrochemically to the metallic state (Chiang et al. 1977, 1978; MacInnes et al. 1981; Nigrey et al. 1979), the development of the field of conducting polymers has continued to accelerate at an unexpectedly rapid rate and a variety of other conducting polymers and their derivatives have been discovered (Kanatzidis 1990; Skotheim 1986). This rapid growth rate has been stimulated by the field's fundamental synthetic novelty and importance to a cross–disciplinary section of investigators – chemists, electrochemists, experimental and theoretical physicists and electronic and electrical engineers.

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 a non–conjugated structure as in the emeraldine base form of polyaniline which becomes conjugated only after protonic acid doping.

(1) Redox Doping Involving Dopant Ions

All conducting polymers (and most of their derivatives), e.g. polyparaphenylene,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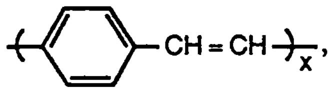
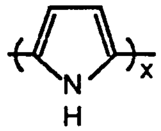

, polypyrrole,

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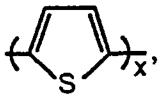
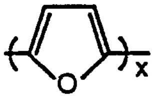
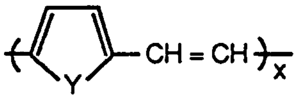
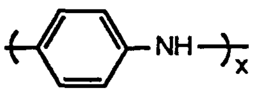
polythiophene,

, polyfuran,

, and poly(heteroaromatic vinylenes)


(where Y = NH, NR, S and O), polyaniline,

, etc.

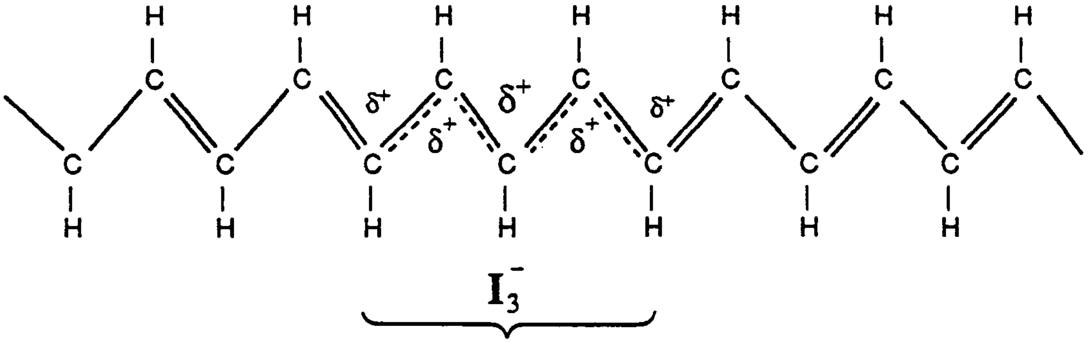
undergo either p– and/or n– redox doping by chemical and/or electrochemical processes during which the number of electrons associated with the polymer backbone changes (Kanatzidis 1990; Skotheim 1986). Selected examples of the different types of doping are presented below.

Chemical and Electrochemical P–Doping: P–doping, i.e. partial oxidation of the π backbone of an organic polymer, was first discovered by treating trans–polyacetylene with an oxidizing agent such as iodine, (Chiang et al. 1977, 1978), viz:

$$\text{trans–}[CH]_x + 1.5y\, I_2 \longrightarrow [CH^{+y}(I_3)^-{}_y]_x \qquad (y \leqq 0.07) \qquad (1)$$

This process was accompanied by an increase in conductivity from ≈10^{-5} S/cm to ≈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 ≈10^{5} S/cm can be obtained (Kanatzidis 1990; Skotheim 1986).

Approximately 85% of the positive charge is delocalized over ≈15CH units (depicted below, for simplicity over only 5 units) to give a positive "soliton," viz.,



P–doping can also be accomplished by electrochemical anodic oxidation by immersing a <u>trans</u>–(CH)$_x$ film in, e.g. a solution of LiClO$_4$ 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, (Nigrey <u>et al.</u> 1979), viz.

$$\underline{\text{trans}}\text{–}[\mathrm{CH}]_x + (xy)(\mathrm{ClO_4})^- \longrightarrow [(\mathrm{CH}^{+y})(\mathrm{ClO_4})_y^-]_x + (xy)e^- \qquad (y \leqq 0.1) \qquad (2)$$

<u>Chemical and Electrochemical N–Doping</u>: N–doping, i.e. partial reduction of the backbone π system of an organic polymer, was also discovered using <u>trans</u>–(CH)$_x$ by treating it with a reducing agent such as liquid sodium amalgam or preferably sodium naphthalide, (Chiang <u>et al.</u> 1977, 1978), viz.

$$\underline{\text{trans}}\text{–}[\mathrm{CH}]_x + (xy)\mathrm{Na}^+(\mathrm{Nphth})^- \longrightarrow [\mathrm{Na}_y^+(\mathrm{CH})^{-y}]_x + \mathrm{Nphth} \qquad (y \leqq 0.1) \qquad (3)$$

The antibonding π^* system is partially populated by this process which is accompanied by an increase in conductivity of $\approx 10^3$ S/cm.

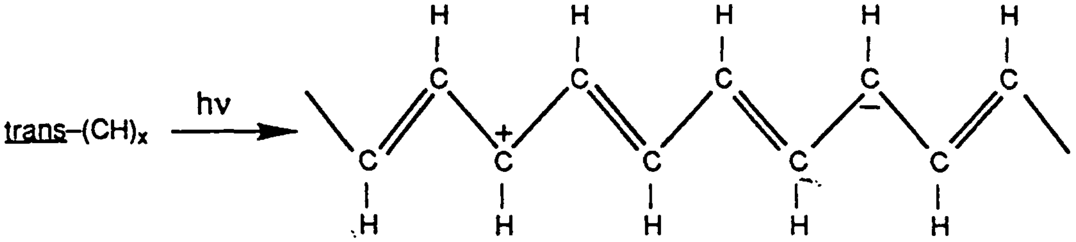
N–doping can also be carried out by electrochemical cathodic reduction (MacInnes <u>et al.</u> 1981) by immersing a <u>trans</u>–$(CH)_x$ film in, e.g. a solution of $LiClO_4$ dissolved in tetrahydrofuran and attaching it to the negative terminal of a d.c. power source, the positive terminal being attached to an electrode also immersed in the solution, viz.,

$$\underline{\text{trans}}\text{–}[CH]_x + (xy)Li^+ + (xy)e^- \longrightarrow [Li_y^+(CH)^{-y}]_x \qquad (y \leqq 0.1) \qquad (4)$$

In all the chemical and electrochemical p– and n–doping processes discovered for $(CH)_x$ and for the analogous processes in other conducting polymers, counter "dopant" ions are introduced which stabilize the charge on the polymer backbone. In each case, spectroscopic signatures, e.g. those of solitons, polarons, bipolarons, etc. are obtained characteristic of the given charged polymer. However, the doping phenomena concept extends considerably beyond that given above to "doping" processes where no counter dopant ion is involved, i.e. to doping processes in which transitory "doped" species are produced, which have similar spectroscopic signatures to polymers containing dopant ions. Such type of doping can provide information not obtainable by chemical or electrochemical doping. Examples of such types of redox doping which can be termed "photo–doping" and "charge–injection doping" are given below.

(2) Redox Doping Involving No Dopant Ions

<u>Photo–Doping</u>: When <u>trans</u>–$(CH)_x$, for example, is exposed to radiation of energy greater than its band gap electrons are promoted across the gap and the polymer undergoes "photo–doping." Under appropriate experimental conditions, spectroscopic signatures characteristic of, for example, solitons can be observed, (Heeger <u>et al.</u> 1988), viz.



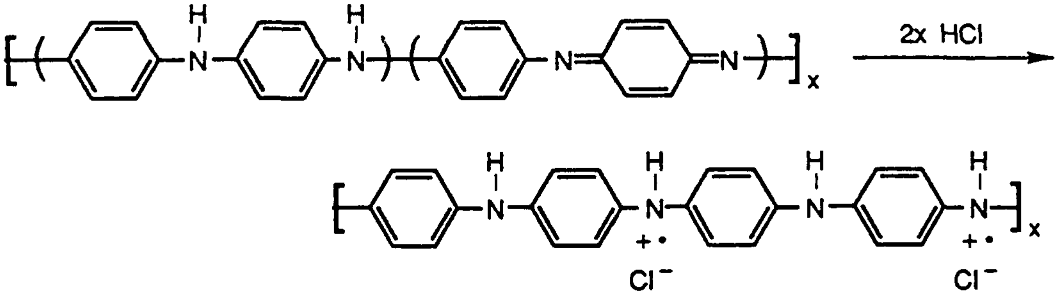
(5)

The positive and negative solitons are here illustrated diagrammatically for simplicity as residing only on one CH unit; they are actually delocalized over ≈15 CH units as mentioned previously. They disappear rapidly due to recombination of electrons and holes when irradiation is discontinued. If a potential is applied during irradiation, then the electrons and holes separate and photoconductivity is observed.

Charge–Injection Doping: Charge–injection doping is most conveniently carried out using a Metal Insulator Semiconductor (MIS) configuration involving a metal and a conducting polymer separated by a thin layer of a high dielectric strength insulator. Application of an appropriate potential across the structure can give rise, for example, to a surface charge layer, the "accumulation" layer which has been extensively investigated for conducting polymers (Burroughes et al. 1988, 1990; Ziemelis et al. 1991). The resulting charges in the polymer, e.g. $(CH)_x$ or poly(3–hexyl thienylene), are present without any associated dopant ion so that the spectroscopic properties of the charged species so formed can be examined in the absence of dopant ion. Using this approach, spectroscopic studies of $(CH)_x$ show the signatures characteristic of solitons and the mid–gap absorption band observed in the chemically and electrochemically doped polymer. However, coulombic interaction between charge on the chain and dopant ion is a very strong interaction and one that can totally alter the energetics of the system. Studies of this type strongly suggest that the formation and role of bipolarons in chemically and/or electrochemically doped polymers should be carefully re–examined since they may be stable only in the presence of the dopant counter ion (Burroughes et al. 1988, 1990; Ziemelis et al. 1991).

(3) Non–Redox Doping

This type of doping differs from redox doping described above in that the number of electrons associated with the polymer backbone does not change during the doping process. The emeraldine base form of polyaniline was the first example of the doping of an organic polymer to a highly conducting regime by a process of this type. This was accomplished by treating emeraldine base with aqueous protonic acids and is accompanied by a nine to ten order of magnitude increase in conductivity (up to ≈10^2 S/cm) to produce the protonated emeraldine base, (Chiang and MacDiarmid 1986; MacDiarmid and Epstein 1989, 1990b; MacDiarmid et al. 1987a) viz.,

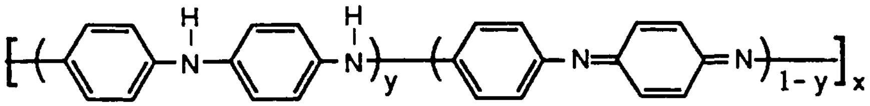
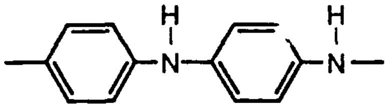
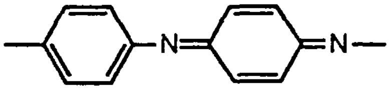
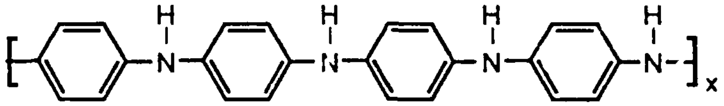
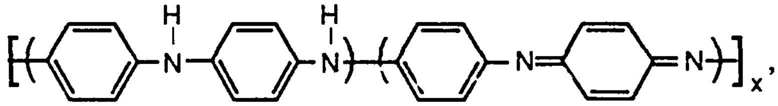
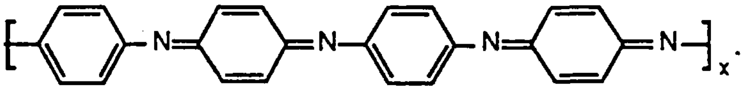


(6)

This phenomena will be discussed in greater detail in Section C3. Protonic acid doping has subsequently been extended to systems such as poly(heteroaromatic vinylenes) (Han and Elsenbaumer 1989).

(C) 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:

 and which consists of alternating reduced, , and oxidized,  repeat units (Chiang and MacDiarmid 1986; MacDiarmid and Epstein 1989; MacDiarmid et al. 1987a). The average oxidation state, (1–y) can be varied continuously from zero to give the completely reduced polymer, , to 0.5 to give the "half–oxidized" polymer, , to one to give the completely oxidized polymer, .

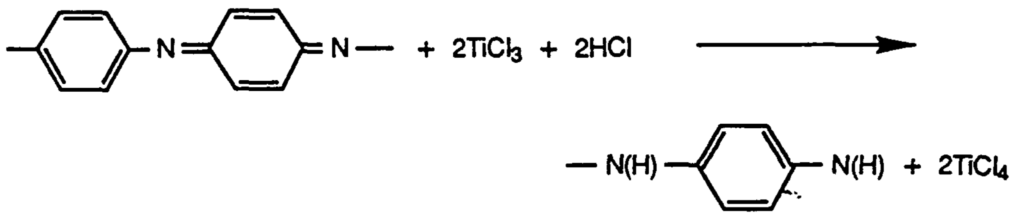
The terms "leucoemeraldine", "emeraldine" and "pernigraniline" refer to the different oxidation states of the polymer where (1–y) = 0, 0.5 and 1, respectively, either in the base form, e.g. emeraldine base or in the protonated salt form, e.g. emeraldine hydrochloride (Chiang and MacDiarmid 1986; MacDiarmid and Epstein 1989; MacDiarmid et al. 1987a). 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 delocalized poly–semiquinone radical cation as discussed in Section C3 (MacDiarmid and Epstein 1989; MacDiarmid et al. 1987a,b) and is accompanied by an increase in conductivity of $\approx 10^{10}$.

(1) Synthesis

The partly protonated emeraldine hydrochloride salt can be synthesized easily as a partly crystalline black–green precipitate by the oxidative polymerization of aniline, $(C_6H_5)NH_2$, in aqueous acid media by a variety of oxidizing agents, the most commonly used being ammonium peroxydisulfate, $(NH_4)_2S_2O_8$, in aqueous HCl (Chiang and MacDiarmid 1986; MacDiarmid and Epstein 1989; MacDiarmid et al. 1987a,b). 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 average oxidation state as determined by volumetric $TiCl_3$ titration corresponding approximately to that of the ideal emeraldine oxidation state (Asturias et al. 1989). The ^{13}C (Kaplan et al. 1989) and ^{15}N NMR (Richter et al. 1989) spectra of emeraldine base are consistent with its being composed principally of alternating oxidized and reduced repeat units.

We have found recently (MacDiarmid and Epstein 1990a,b; Manohar et al. 1989), 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.

When the synthesis is carried out at ≈0°C using excess aniline, the initial oxidation potential of the reaction system increases from ≈0.40V (vs. SCE) (FIGURE 1, point A) to ≈0.66V (point B) immediately after adding the $(NH_4)_2S_2O_8$, to ≈0.75V (point C) within ≈2 minutes at which value it stays essentially constant before it begins to fall rapidly after ≈10 minutes (point D), reaching ≈0.47V at point E, and ≈0.44V at point F, a value characteristic of the emeraldine oxidation state (Huang et al. 1987). If the reaction mixture at point D is poured into cold (≈5°C) aqueous NaOH solution, analytically pure pernigraniline base powder (Calc., for C_6H_4N; 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 $TiCl_3$ (Asurtias et al. 1989; Green and Woodhead 1910, 1912) based on the reaction,

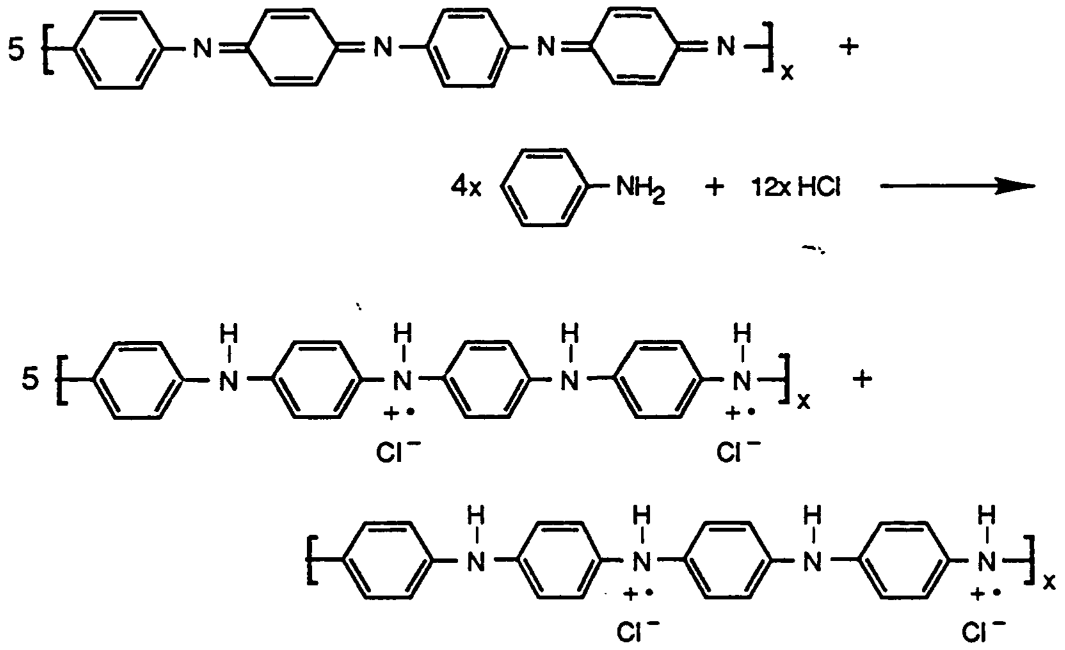


(7)

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*–$Cl(C_6H_4)C(O)OOH/\ N(C_2H_5)_3$ (Sun <u>et al.</u> 1990).

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 $(NH_4)_2S_2O_8$/1M HCl is sufficiently high to oxidize any polymer in the emeraldine oxidation state (≈0.43V) (Huang <u>et al.</u> 1987) to the pernigraniline oxidation state (≈0.83V), (Sun <u>et al.</u> 1990) 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 $(NH_4)_2S_2O_8$ 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 oxidation state while it is itself reduced to the emeraldine oxidation state, viz.,



(8)

It is clear that the pernigraniline oxidation state has a sufficiently large oxidation potential (≈0.83V vs. SCE) to oxidatively polymerize aniline since it is known that oxidation of aniline commences at a potential of ≈0.7V (Huang et al. 1986).

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 ($\overline{M}_w$) =64,452, ($\overline{M}_n$) =25,283, and ($\overline{M}_w/\overline{M}_n$) =2.55 (MacDiarmid and Epstein 1990b). Treatment of the polymer with additional $(NH_4)_2S_2O_8$ (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 ($\overline{M}_w$) value of 89,633 (($\overline{M}_w/\overline{M}_n$) =2.46) was obtained which fell to a value of 84,172 (($\overline{M}_w/\overline{M}_n$) =2.54) after six such cycles (Manohar et al. 1991b). 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.

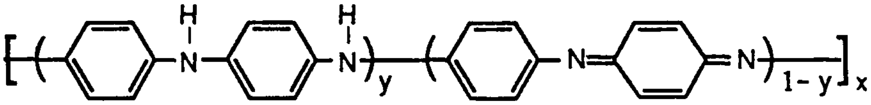
The above reaction can be used in a novel process to produce block co-polymers of aniline. For example, if, instead of adding additional aniline in cycle 1, o-toluidine, $CH_3(C_6H_4)NH_2$ is added, the resulting polyaniline hydrochloride (emeraldine oxidation state) is consistent with solubility, elemental analysis and spectroscopic studies as being a block co-polymer containing ≈10% of polytoluidine and ≈90% polyaniline (Manohar et al. 1991a).

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 (Manohar et al. 1991b). This is accomplished by having relatively insoluble solid anilinium hydrochloride, $C_6H_5NH_2.HCl$, present in the reaction vessel. The concentration of free aniline in solution in 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 ≈ −9°C the anilinium hydrochloride precipitates. Molecular weights up to $\overline{M}_n$ =127,000, $\overline{M}_w$ ≈ 440,000 and $\overline{M}_w/\overline{M}_n$ ≈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 $\overline{M}_w$ values (GPC) are approximately twice those obtained from light scattering studies. Hence, the $\overline{M}_W$ values obtained by GPC studies on polyaniline should be divided by two to obtain more accurate values (Manohar et al. 1991c).

(2) Allowed Oxidation States

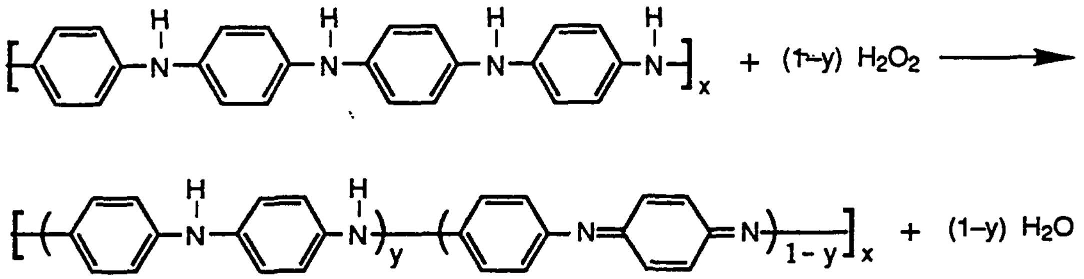
As can be seen from the generalized formula of polyaniline base,



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 studies (MacDiarmid and Epstein 1990b) 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 (Masters et al. 1991).

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 in the (1–y)=0.5 to (1–y)=1 oxidation state range. Within each of these ranges all intermediate oxidation states consist, at the molecular level, only of mixtures of the chromophores characteristic of the two states defining the beginning and end of each range (Masters et al. 1991).

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.,



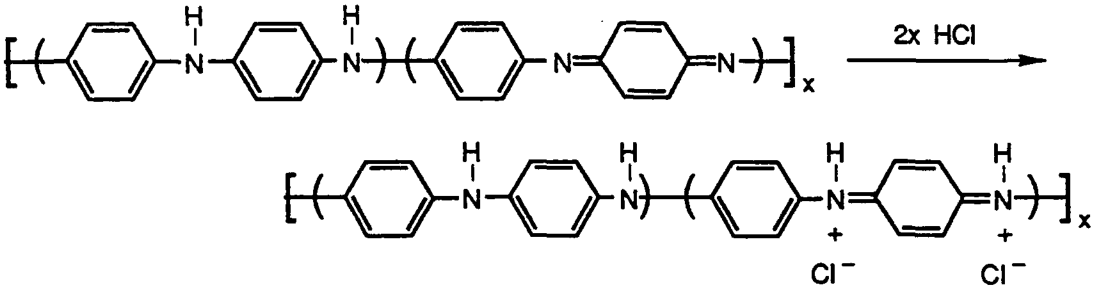
(9)

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. 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.

The chromophore associated with emeraldine base oxidation state, (1–y)=0.5, and pernigraniline oxidation state, (1–y)=1, is certainly no greater than eight ring–N units in length since the octomer and polymer in these oxidation states have identical vis/uv spectra (Lu et al. 1986; Sun et al. 1990). 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.

(3) Doping

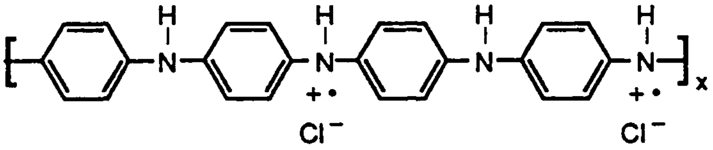
Polyaniline holds a special position amongst conducting polymers in that its most highly conducting doped formed can be reached by two completely different processes – protonic acid doping and oxidative doping. Protonic acid doping of emeraldine base units with, for example 1M aqueous HCl results in complete protonation of the imine nitrogen atoms to give the fully protonated emeraldine hydrochloride salt (Chiang and MacDiarmid 1986; MacDiarmid et al. 1987a):



(10)

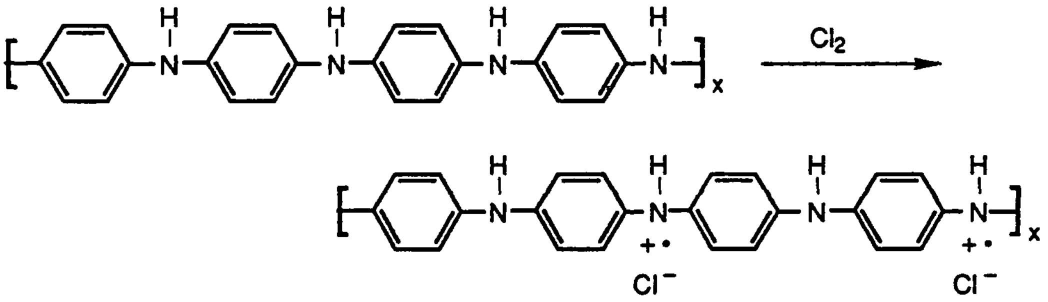
As shown in FIGURE 4, protonation is accompanied by a 9 to 10 order of magnitude increase in conductivity (to 1–5 S/cm; 4 probe; compressed powder pellet) reaching a maximum in ≈1M aqueous HCl.

If this fully protonated emeraldine base should have the above dication, i.e. bipolaron constitution as shown in Equation 10, it would be diamagnetic. However, extensive magnetic studies (MacDiarmid and Epstein 1989) 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 (McManus et al. 1985; Wnek 1985) show that the protonated polymer is actually a poly–semiquinone radical cation, one resonance form consisting of two separated polarons:



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 are 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.

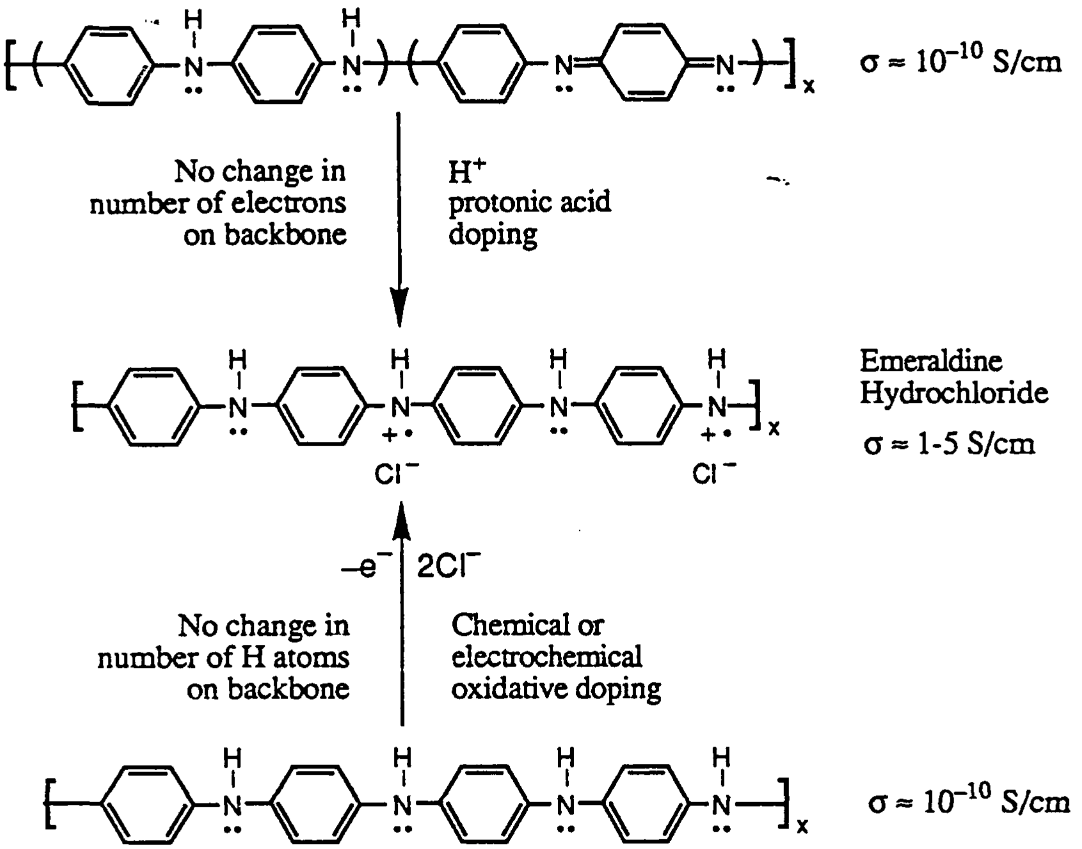
The same doped polymer can be obtained by chemical oxidation (p–doping) of leucoemeraldine base (MacDiarmid and Epstein 1989). This actually involves the oxidation of the σ/π system rather than just the π system of the polymer as is usually the case in p–type doping. Its reaction with a solution of chlorine in carbon tetrachloride proceeds to give emeraldine hydrochloride:



(11)

The leucoemeraldine base form of polyaniline can also be anodically oxidized electrochemically to the poly–semiquinone radical cation in aqueous HCl (MacDiarmid and Epstein 1989).

The relationship between protonic acid doping and oxidative doping of different forms of polyaniline to give the same conducting material is illustrated diagrammatically below:



(12)

The versatility of the polyaniline system is illustrated in FIGURE 5 (Salaneck et al. 1986) where it is shown that the most highly conducting form of polyaniline, the emeraldine salt, can in principle, be obtained either by oxidizing leucoemeraldine base to emeraldine base, followed by protonation of emeraldine base, or by protonation of leucoemeraldine base followed by oxidation to the emeraldine salt. Conductivities intermediate between those of the leucoemeraldine base and emeraldine salt can be obtained by an appropriate combination of protonation and average oxidation state.

(4) Relationship Between Molecular Weight and Conductivity

As–synthesized (MacDiarmid et al. 1987b) 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 ($\overline{M}_{peak} < 5000$) being discarded, since in a separate study it was shown that it contained oxygen–containing impurities (MacDiarmid et al. 1989). 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 (MacDiarmid and Epstein 1990b).

It can be seen from FIGURE 6 that the conductivity of the doped polymer rises monotonically with molecular weight up to a value of ≈150,000 (≈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.

(5) Relationship Between Degree of Stretch–Orientation, Crystallinity, Conductivity and Tensile Strength

"As–synthesized" emeraldine base is very soluble in NMP (Angelopoulos et al. 1988). However, the term "soluble" must be used with caution since it is not clear how much of the polymer in, for example, a viscous ≈20% by weight "solution" is in "true" solution (Angelopoulos et al. 1987, 1988; MacDiarmid and Epstein 1990b). It has been known for some time that emeraldine base is readily solution–processible (Angelopoulos et al. 1987, 1988) and that it may be cast as free–standing, flexible, coppery–colored films from its solutions in NMP. These films can be doped with ≈1M aqueous HCl to give the corresponding flexible, lustrous, purple–blue films ($\sigma \approx$1–4 S/cm) of emeraldine hydrochloride which are partly crystalline.

Aligned Films: The intrinsic properties of a conducting polymer can be approached only through processing. 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 (MacDiarmid and Epstein 1989, 1990b). Samples are observed to elongate by up to four times their original length when stretched above the glass transition temperature (≧110°C) 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.

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 ≈20mm) of various draw ratios can be readily fabricated by stretch–orienting emeraldine base films previously cast from NMP solution at ≈140°C between two metal rollers rotating at different speeds (MacDiarmid and Epstein 1990b; Scherr et al. 1991). As can be seen from FIGURE 7 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_o=1) is, for example, ≈ 90% re–soluble in NMP whereas the highly crystalline film (l/l_o=4) is insoluble in NMP. The conductivity of the HCl–doped uniaxially oriented ribbons increases on stretching (l/l_o=1, $\sigma \approx$5 S/cm; l/l_o=4, $\sigma \approx$80 S/cm). It should be noted that the conductivity of these oriented films 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 (MacDiarmid and Epstein 1990b; Scherr et al. 1991). Their tensile strength also increases significantly with an increase in draw ratio (and crystallinity) as shown in TABLE 2 (MacDiarmid and Epstein 1990b). As expected, biaxially oriented film exhibits significantly greater tensile strength than uniaxially oriented film for the same draw ratio (l/l_o=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 overlaps the lower tensile strength range of commercial polymers such as Nylon 6. Unstretched Nylon 6 has tensile strengths ranging from 69 to 81 MPa (Brandrup and Immergut 1975).

Aligned Fibers: Fibers (≈30–70mm) of emeraldine base can be formed by drawing a ≈20% by weight "solution" of emeraldine base in NMP in a water/NMP solution (MacDiarmid and Epstein 1990b). 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.

The drawn fibers (containing NMP as plasticizer) can be thermally stretch–oriented at ≈140°C up to 4.5 times their original length in a similar manner to emeraldine base films. 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 8. A monotonic increase in apparent crystallinity with draw ratio is observed, as shown in FIGURE 9. 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). As can be seen from FIGURE 10, the conductivity of the HCl–doped drawn fibers increases monotonically with draw ratio, (l/l_o) (MacDiarmid and Epstein 1990b)

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. Since l/l_o 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_o ratios and hence in even higher conductivities. From FIGURES 9 and 10 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 (Fischer et al. 1991; Scherr et al. 1991).

Preliminary studies show that emeraldine base fibers both before and after doping with 1M aqueous HCl exhibit promising mechanical properties (MacDiarmid and Epstein 1990b). Values for 7.6cm gauge length (tensile strength, MPa; initial modulus, GPa) emeraldine base fibers stretch–oriented ($l/l_o \approx 3$–4) at ≈140°C are: 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) (McGraw–Hill chart 1988) the mechanical properties of polyaniline fibers, considering the early stage of development, are most encouraging.

(D) CONCLUSIONS

The concept of doping is the unique, central, underlying and unifying theme which distinguishes conducting polymers from all other types of polymers. The parent, unsubstituted polyanilines hold a unique 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 of the type found in other conducting polymers. These properties, together with the ready processibility of polyaniline into oriented films and fibers, with concomitant increase in conductivity, crystallinity and tensile strength (already approaching that of some commercial polymers) offer a richness of chemistry and physics unparalleled in most 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 increased appreciation of the relationship of these properties to the nature of the chemical substituent. An understanding of the basic 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.

(E) ACKNOWLEDGEMENTS

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TABLE 1.

Characterization of Fractions of Emeraldine Base

From Preparative G.P.C. Studies (a)

Fraction	$\overline{M}_{peak}$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	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 (MacDiarmid and Epstein 1990b).

TABLE 2.

Tensile Strength (MPa)[a] Of Emeraldine Base Ribbons

As A Function Of Draw Ratio (l/l_o).

		Uniaxial Orientation:				Biaxial Orientation[b]:
		$l/l_o = 1$	$l/l_o = 2$	$l/l_o = 3$	$l/l_o = 4$	$l/l_o = 2$
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) $l/l_o = 2$ in both directions (MacDiarmid and Epstein 1990b).

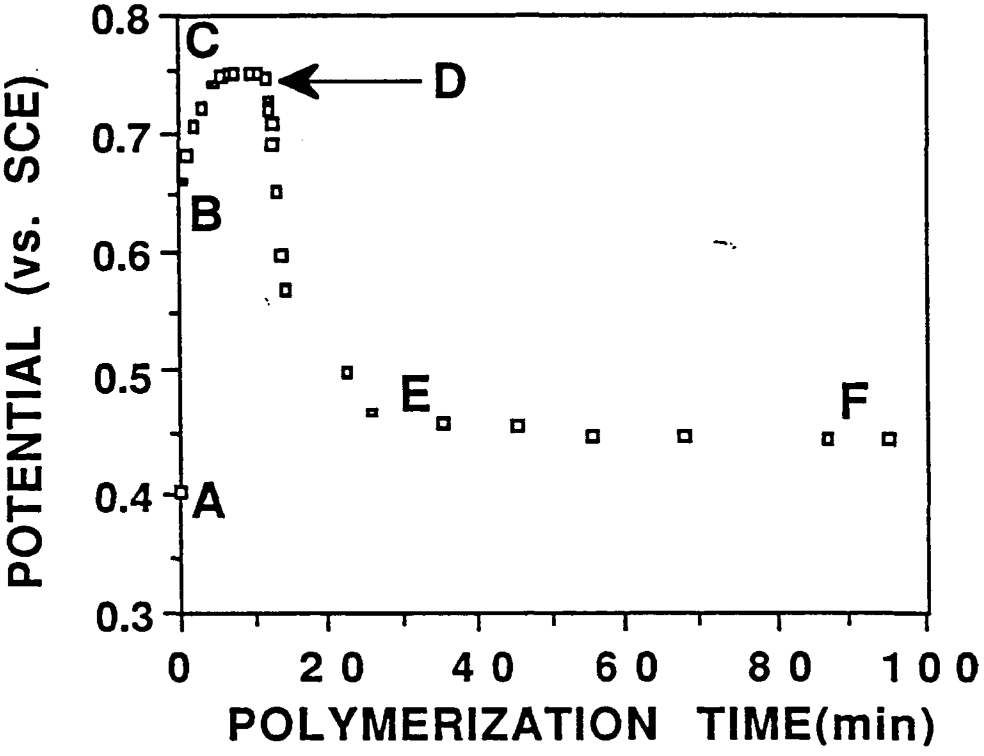

FIGURE 1. Potential–Time Profile of a Conventional Chemical Oxidative Polymerization of Aniline Using Ammonium Peroxydisulfate in Aqueous 1.0M HCl (Pt electrode; SCE reference) (MacDiarmid and Epstein 1990b).

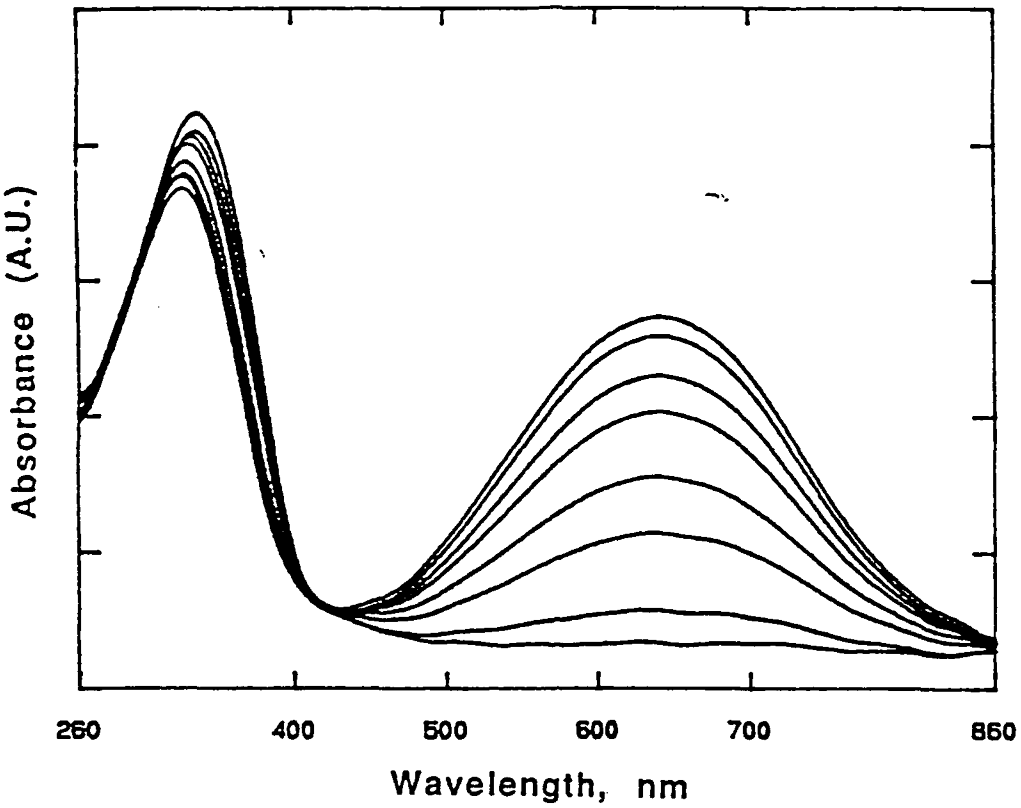

FIGURE 2. Vis/uv Spectra of Films of Polyaniline Bases in Average Oxidation States Intermediate Between Those of Leucoemeraldine, (1-y)=0 and Emeraldine, (1-y)=0.5 (Masters <u>et al.</u> 1991).

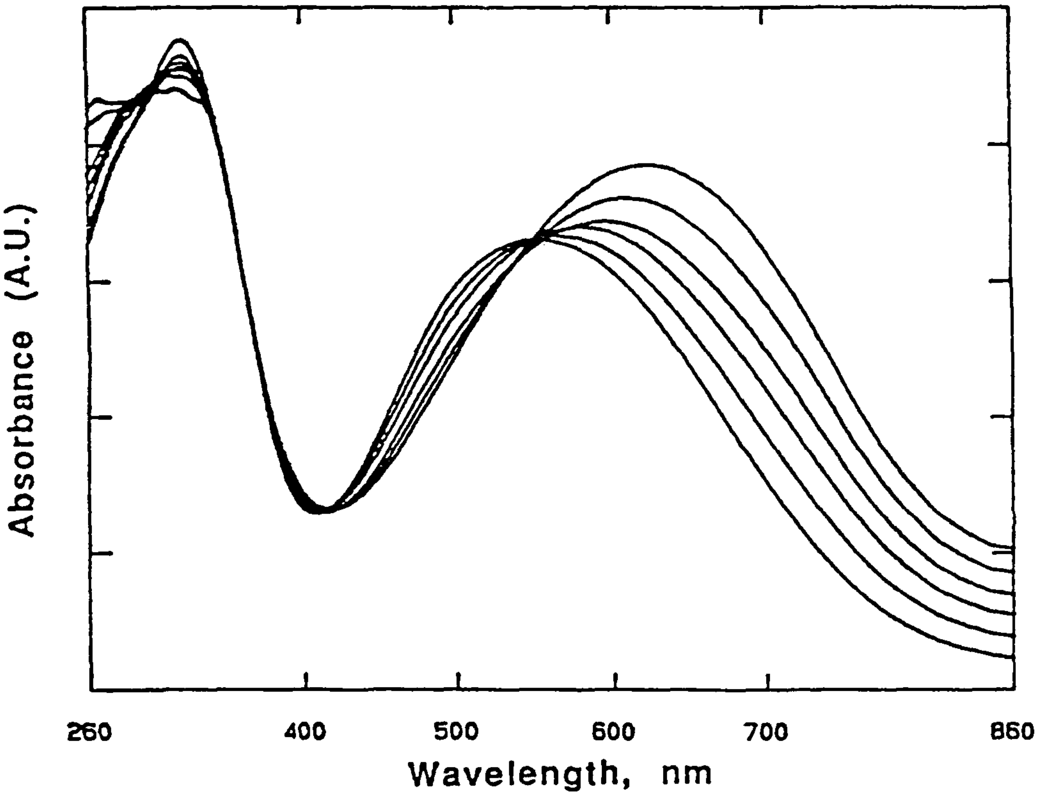

FIGURE 3. Vis/uv Spectra of Films of Polyaniline Bases in Average Oxidation States Intermediate Between Those of Emeraldine, (1-y)=0.5 and Pernigraniline, (1-y)=1.0 (Masters et al. 1991).

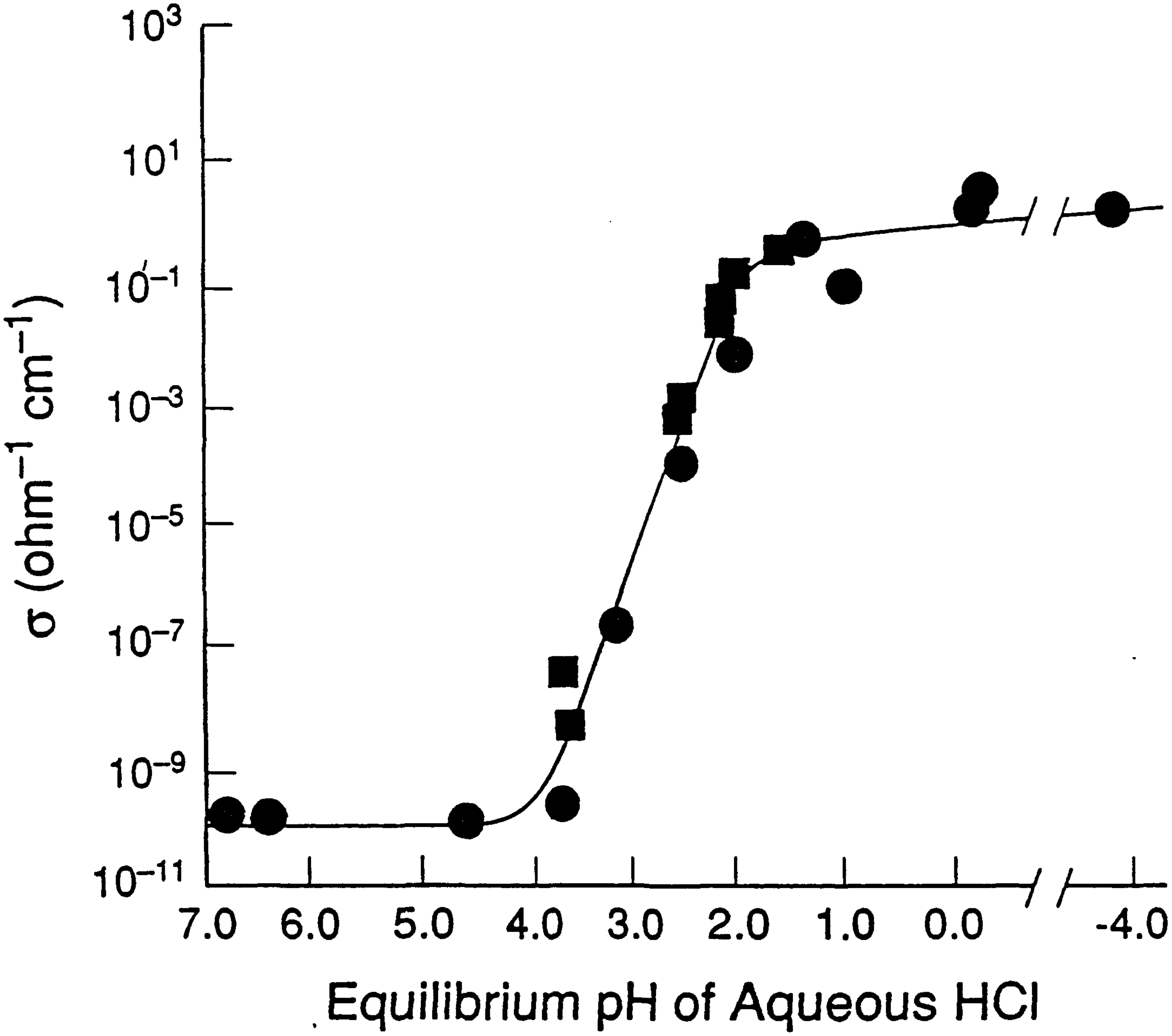

FIGURE 4. Conductivity of emeraldine base as a function of pH of HCl dopant solution as it undergoes protonic acid doping (● and ■ represent two independent series of experiments) (Chiang and MacDiarmid 1986; MacDiarmid <u>et al.</u> 1987a).

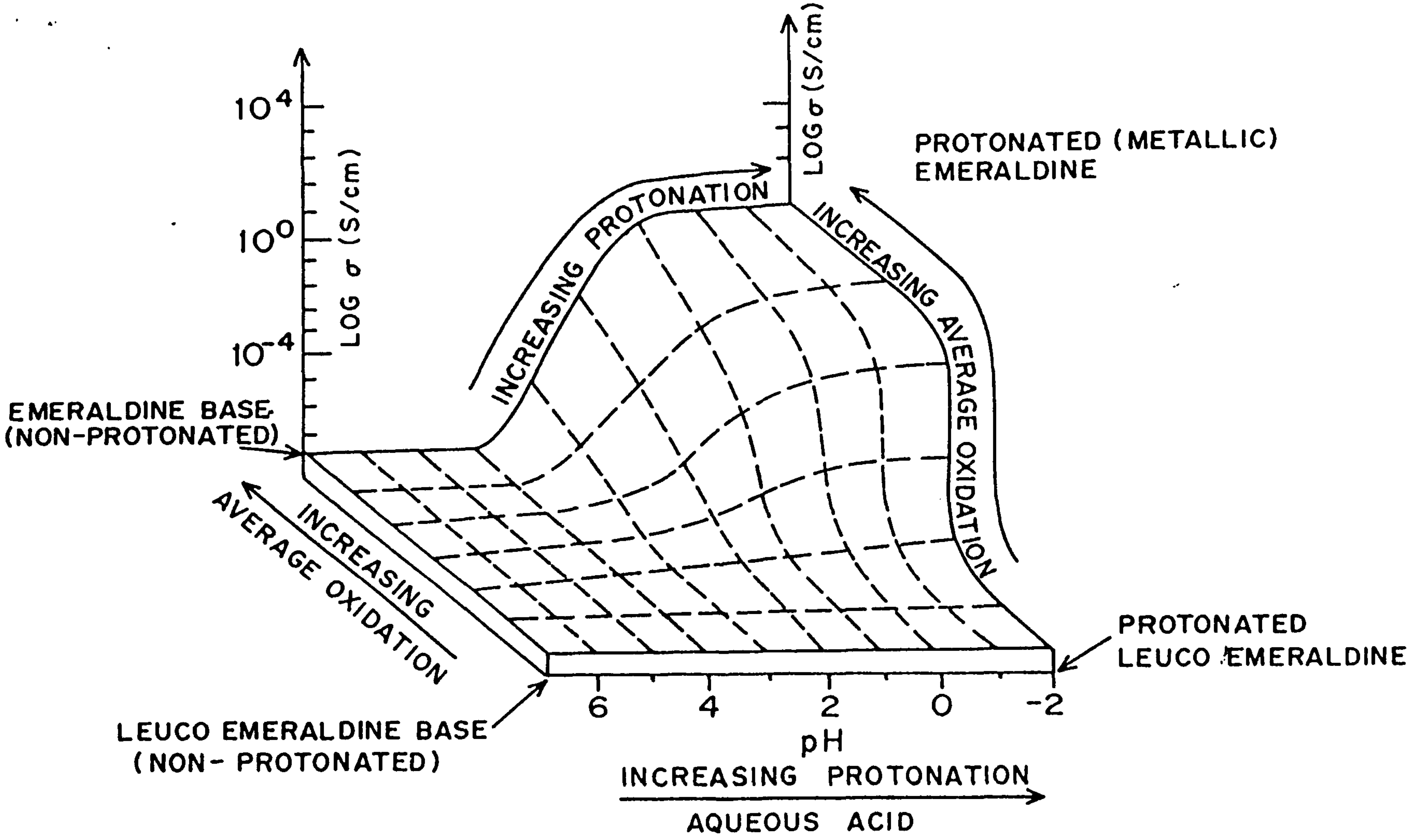

FIGURE 5. Relationship Between Conductivity, Average Oxidation State and Degree of Protonation of Polyaniline (as modified from Salaneck et al. 1986).

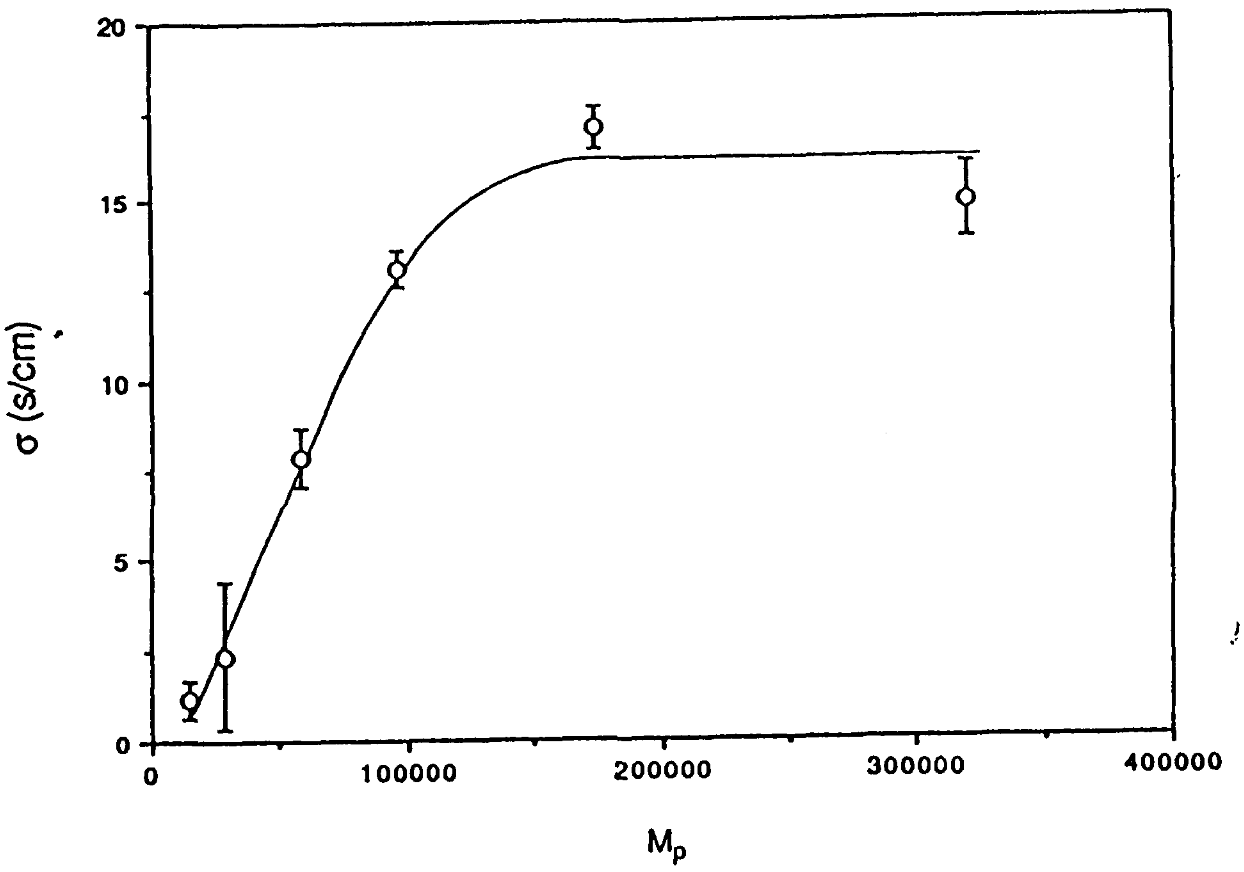

FIGURE 6. Dependency of Conductivity (σ) of Doped Polyaniline (Emeraldine Oxidation State) on Molecular Weight (MacDiarmid and Epstein 1990b).

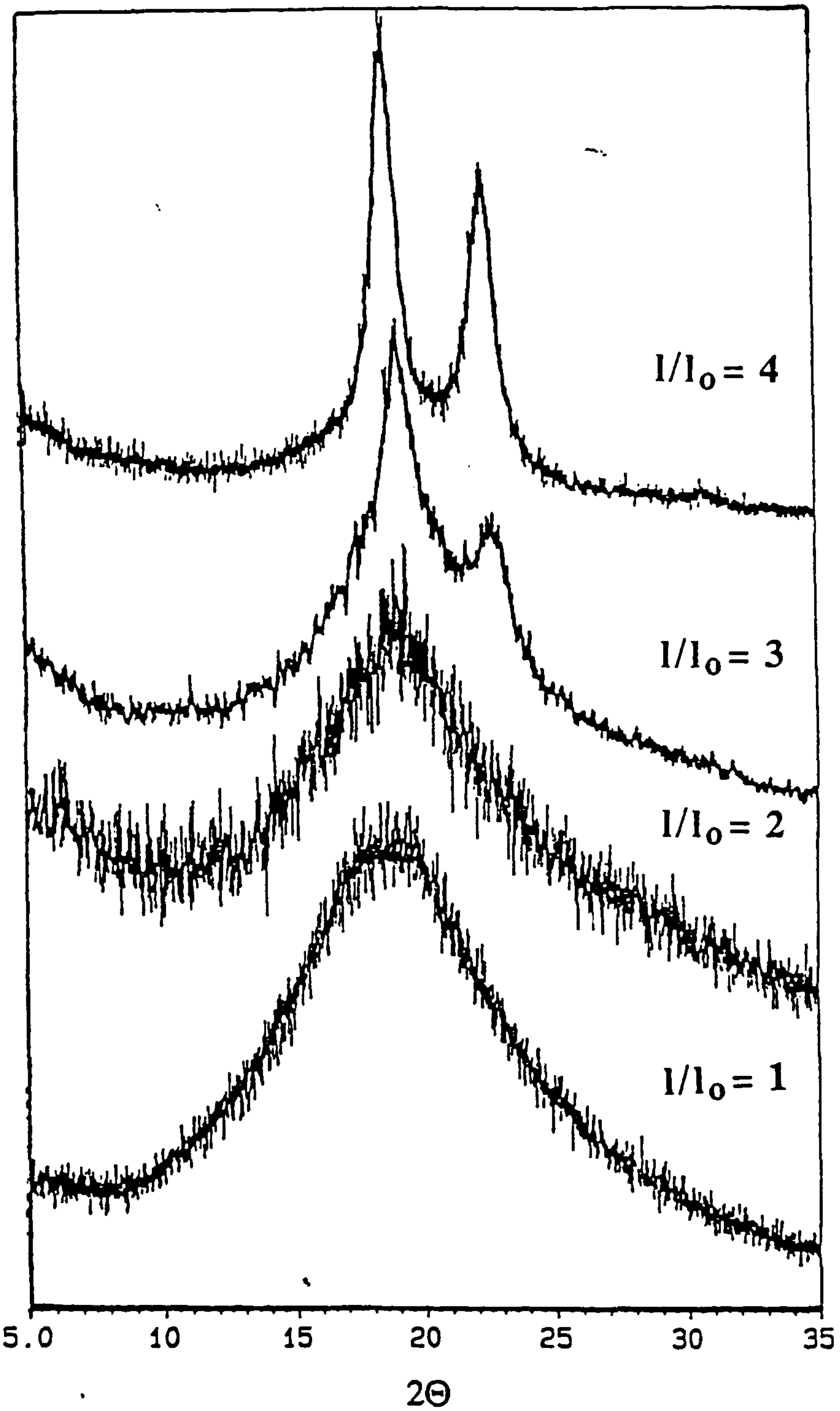

FIGURE 7. X–Ray Diffraction Spectra of Ribbons of Emeraldine Base of Increasing Draw Ratio, (l/l_o; l = final length; l_o = original length before stretching) (MacDiarmid and Epstein 1990b; Scherr et al. 1991).

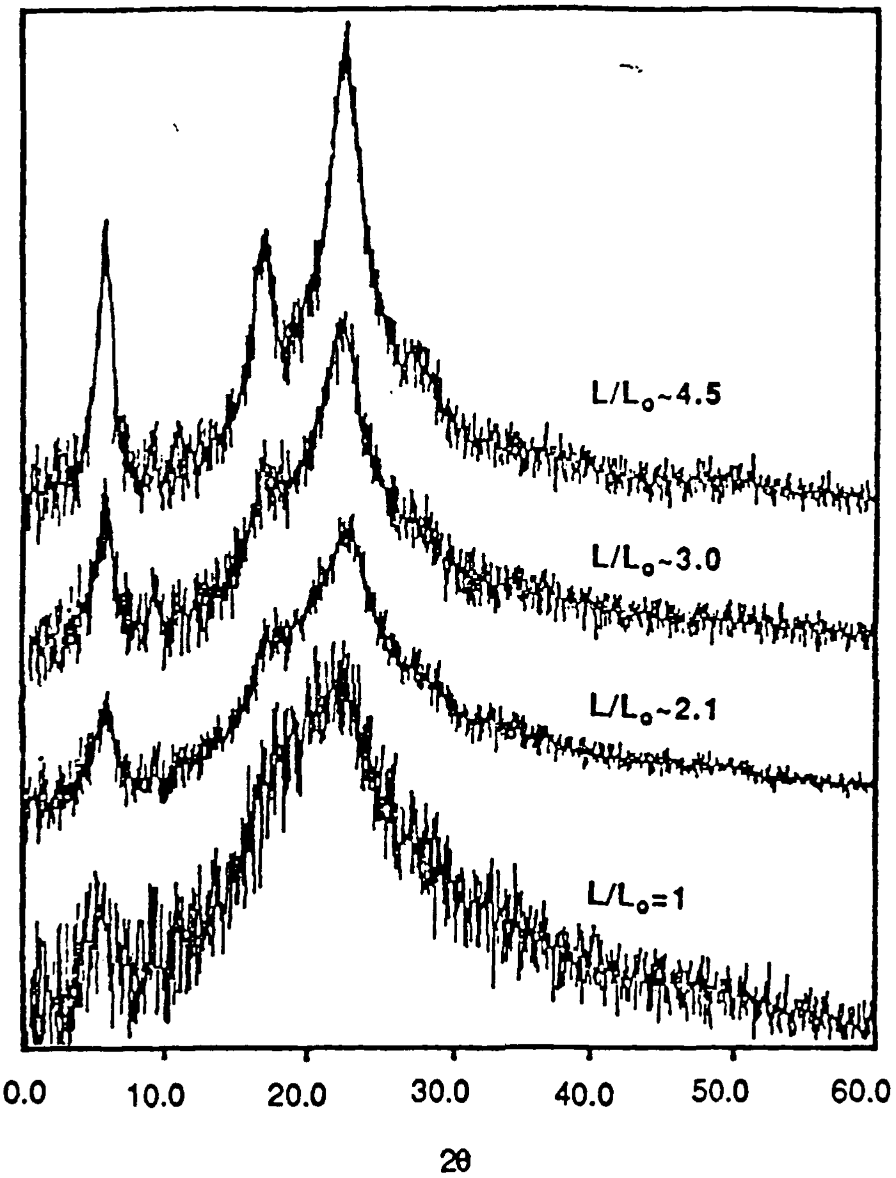

FIGURE 8. Change in X–ray Diffraction Spectra of Stretch–Oriented Fibers of Emeraldine Base Drawn in Aqueous/NMP to Selected Values After Doping in 1M HCl, (l_o = original length, l = final length) (MacDiarmid and Epstein 1990b).

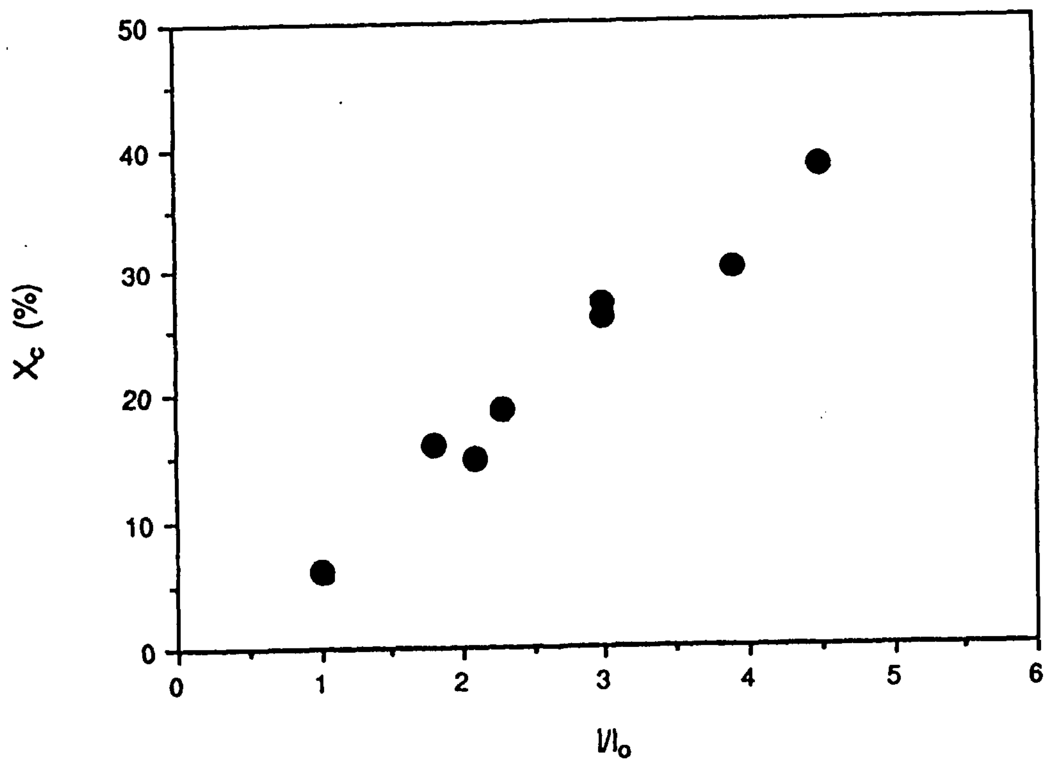

FIGURE 9. Crystallinity vs. Draw Ratio (l/l_o) for Emeraldine.HCl Fibers [X_c = fractional integrated radial intensity (sum of 010, 012, 200 crystal peaks)] (MacDiarmid and Epstein 1990b).

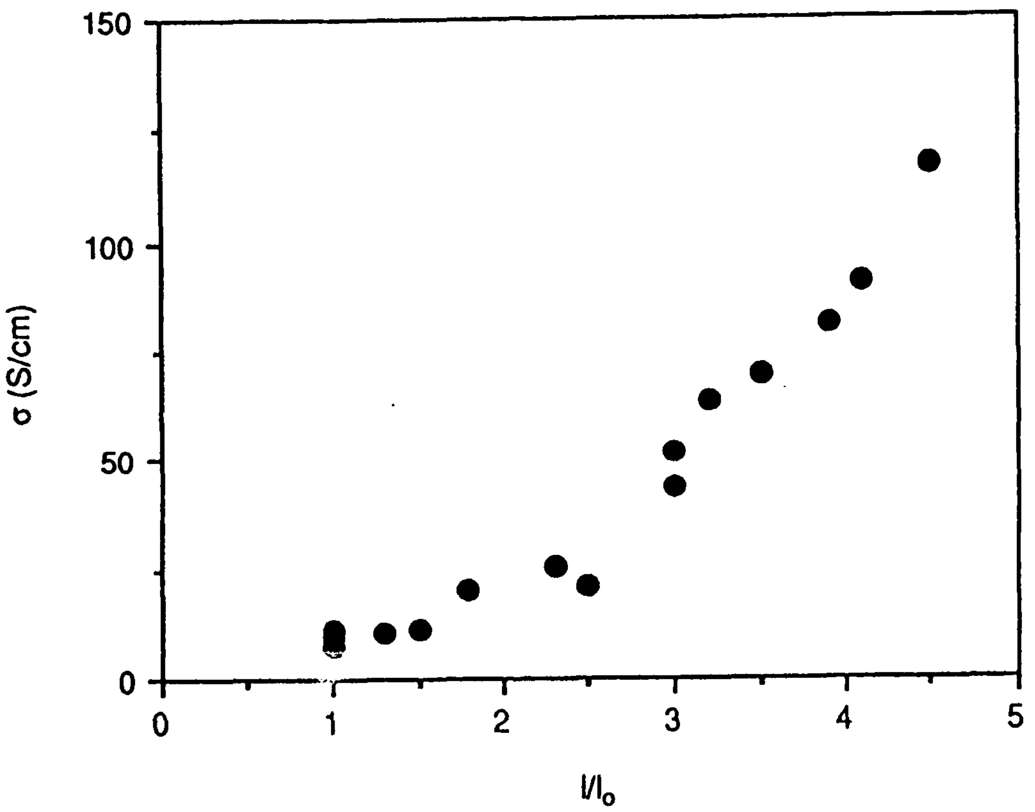

FIGURE 10. Conductivity (σ) of the HCl-doped Drawn Fibers vs. Draw Ratio (l/l_o) (MacDiarmid and Epstein 1990b).