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The conductivity (doped form), degree of crystallinity, tensile strength, solubility and swellability (as a gel) of polyaniline (emeraldine oxidation state) is found to be greatly dependent on the past chemical and/or mechanical history of the polymer which significantly affects the ultra-structure of the material. The conductivity and tensile strength of polyaniline films and fibers can be greatly enhanced by stretch orientation which is also accompanied by a monotonic increase in crystallinity. The solubility of the emeraldine base in NMP is greatly decreased as the degree of crystallinity is increased. The conductivity shows relatively little dependency on molecular weight as compared to crystallinity; it first rises monotonically with increase in molecular weight and then remains essentially independent of molecular weight. Gels of oriented emeraldine base exhibit a remarkable anisotropic swelling in NMP and in mixtures of NMP/CH₃OH.			
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"POLYANILINE: INTER-RELATIONSHIP BETWEEN ULTRA-STRUCTURE
AND PROPERTIES"

by

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POLYANILINE: INTER-RELATIONSHIP BETWEEN ULTRA-STRUCTURE AND PROPERTIES

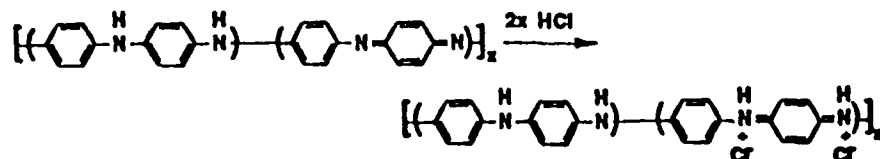
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INTRODUCTION

Polyaniline is an organic polymer which can exist in several different oxidation states¹. The base form of the emeraldine oxidation state can be protonated ("doped") with a concomitant increase in conductivity of $\sim 10^{10}$, viz.,



The conductivity (doped form), degree of crystallinity, tensile strength, solubility, and swellability of polyaniline gel (emeraldine oxidation state) is found to depend greatly on its ultra-structure as determined by its previous chemical and mechanical history.

Effect of Chemical Treatment

The "as-synthesized" emeraldine base powder is essentially amorphous and is soluble in N-methyl-pyrrolidinone (NMP) and concentrated sulfuric acid. Extraction with THF followed by extraction with NMP at room temperature until the NMP is colorless greatly increases its degree of crystallinity and decreases its degree of solubility rendering it essentially insoluble. Approximately 20% of the polymer is dissolved by this process. Protonation of the material with 1M aq. HCl followed by deprotonation with 0.1M NH_4OH reconverts it to the amorphous, soluble polymer.

Effect of Alignment

Large flexible films or ribbons of emeraldine base can be cast from NMP solution and subsequently stretch-aligned at $\sim 140^\circ\text{C}$. The change in crystallinity with stretching is shown in Figure 1.

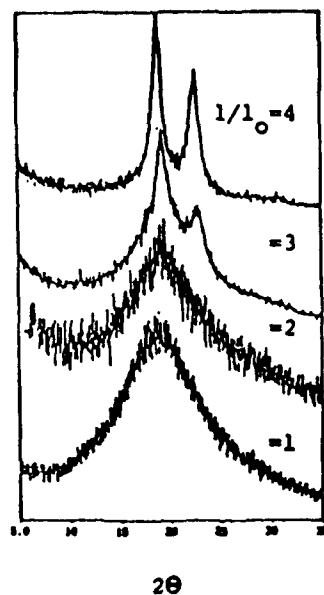


Fig. 1. X-ray diffraction spectra of emeraldine base of increasing draw ratio (l/l_0 ; l =final length; l_0 =length before stretching).

Upon doping with HCl, the conductivity is found to increase markedly with degree of stretching ($l/l_0=1$, $\sigma \sim 5$ S/cm; $l/l_0=4$, $\sigma \sim 80$ S/cm). It should be noted that the conductivity of the oriented films is greatly dependent on their method of drying; conductivities of ~ 400 S/cm can be obtained for films which have not been dried to any great extent. The tensile strength of the ribbons also increases significantly (up to 144.8 MPa for $l/l_0=4$) with increased draw ratio (and crystallinity). As expected, biaxially oriented films exhibit significantly greater tensile strength than uniaxially oriented films having the same draw ratio.

Fibers (~ 30 - $70\mu\text{m}$) of emeraldine base can be formed by drawing a $\sim 20\%$ by weight "solution" of emeraldine base in NMP in a water/NMP solution. Fibers can also be spun from NMP solution. The drawn fibers (containing NMP as plasticizer) can be thermally stretch-aligned at $\sim 140^\circ\text{C}$ up to 4.5 times their original length. X-ray diffraction studies show directional enhancement of the Debye-Scherrer rings. A monotonic increase in apparent crystallinity with draw ratio is observed as shown in Figure 2.

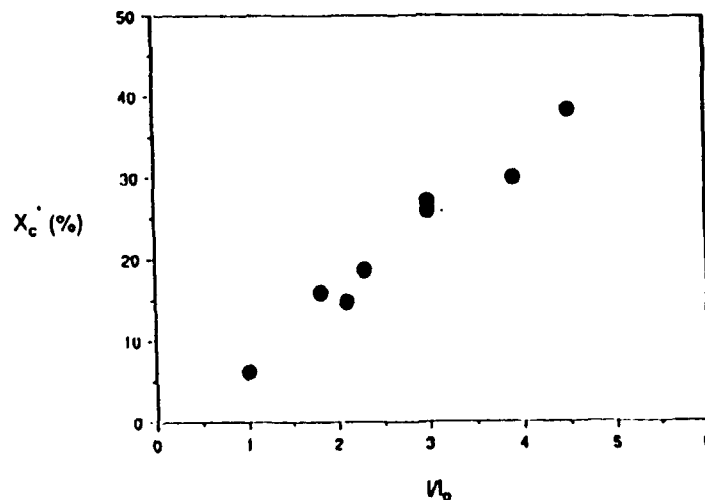


Fig. 2. Crystallinity vs. draw ratio (l/l_0) for emeraldine.HCl fibers [X_c = fractional integrated radial intensity (sum of 010, 012, 200 crystal peaks)]²

This is paralleled by a monotonic increase in conductivity (up to ~ 170 S/cm) after doping with 1M HCl. Preliminary tensile strength studies (366 MPa for $l/l_0 \sim 3-4$) show that emeraldine base fibers both before and after doping with 1M HCl exhibit promising mechanical properties overlapping the lower tensile strength range of commercial fibers such as those of Nylon 6.

Polyethoxyaniline fibers ($\sim 24-30 \mu\text{m}$) can be drawn or spun from CH_2Cl_2 solution and stretch-aligned at $\sim 140^\circ\text{C}$ to $l/l_0 \sim 6$. They have an average tensile strength of ~ 275 MPa and after doping with 1M HCl a conductivity of ~ 54 S/cm which is almost 10^4 higher than that of the doped polymer in the form of a powder!

Molecular Weight

The ability to process a polymer into oriented films and fibers depends greatly on its molecular weight; hence a knowledge of the molecular weight of the polyaniline which is being processed is of considerable importance. A solution of "as synthesized" emeraldine base in NMP (containing 0.5 wt. % LiCl) gave a symmetrical monomodal molecular weight distribution curve by G.P.C. (polystyrene standard) resulting in values of $M_p \sim 38,000$, $M_w \sim 78,000$, $M_n \sim 26,000$, $M_w/M_n \sim 3.0$. It can be separated into six molecular weight fractions varying from: $M_p \sim 15,000$, $M_n \sim 12,000$, $M_w \sim 22,000$, $M_w/M_n \sim 1.8$ to $M_p \sim 320,000$, $M_n \sim 264,000$, $M_w \sim 380,000$, $M_w/M_n \sim 1.4$ using a preparative GPC column. All samples were slightly crystalline and exhibited the same degree of crystallinity after doping. The conductivity of the doped (1M HCl) polymer rose monotonically with increasing molecular weight from 1.2 S/cm to 17 S/cm ($M_p \sim 174,000$) after which it changed relatively little as shown in Figure 3.

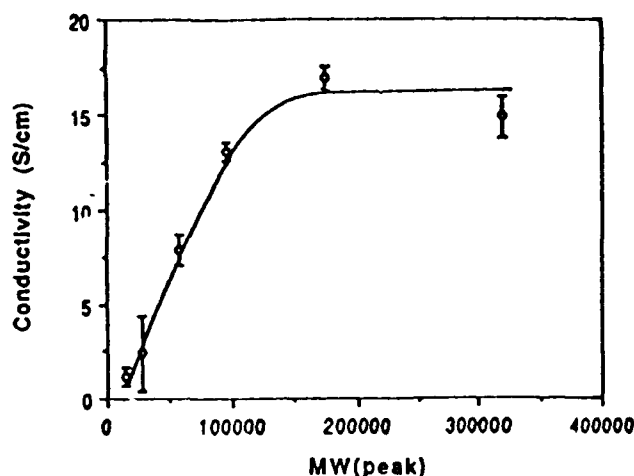


Fig. 3. Dependency of conductivity of doped polyaniline (emeraldine oxidation state) on molecular weight.

The conductivity, therefore, shows relatively little direct dependency on molecular weight as compared to its large dependency on degree of crystallinity/alignment. However, it is indirectly related to molecular weight, since in general, the higher the molecular weight of a polymer, the more extensively can it be stretch aligned.

Polyaniline Gels

Polyaniline (emeraldine base) gels can be produced by first making a ~20 wt. % "solution" of emeraldine base and then casting on a substrate or pouring into a container. It solidifies to a jelly-like material after ~15 min. at room temperature. When cast on a substrate, after heating at ~60 °C (under N₂) for ~1.5 hrs., extraction with NMP until

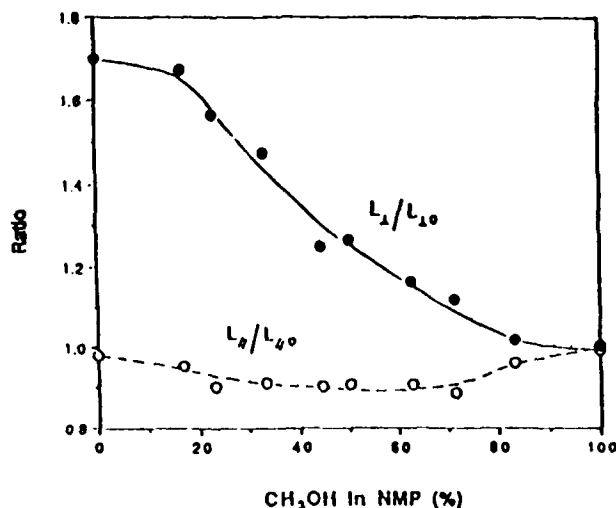


Fig. 4. Change in Dimensions of Stretch-Aligned Emeraldine Base Film ($L/L_0 \sim 1.5$) As a Function of NMP/CH₃OH Concentration. $L_{\perp 0}$: initial length in the direction perpendicular to stretching direction; $L_{\perp}$: length in the direction perpendicular to stretching direction in NMP/CH₃OH; $L_{\parallel 0}$: initial length in the direction parallel to stretching direction; $L_{\parallel}$: length in the direction parallel to stretch direction in NMP/CH₃OH.

colorless yields an insoluble gel film. When placed in methanol, it shrinks to ~0.2 its original size, returning to its previous dimensions when placed in NMP. The gel film can, however, be made completely soluble again in NMP by doping with 1M HCl followed by dedoping with 0.1M NH₄OH on several occasions. After heating at ~60 °C as described above, the film can be stretch oriented. Such film shows a remarkable (reversible) anisotropic change in dimensions when placed in NMP/CH₃OH mixture, (Figure 4). It is concluded that the gel owes its existence to microcrystalline crosslinks between chains.

CONCLUSIONS

Such diverse properties as conductivity, crystallinity, tensile strength, and swellability of polyaniline show a remarkable dependency on the past chemical and/or mechanical history of the polymer which significantly affects the ultra-structure of the material.

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