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E.M. Scherr, A.G. MacDiarmid, S.K. Manohar, J.G. Masters, Y. Sun, X. Tang,  
M.A. Druy, P.J. Glatkowski, V.B. Cajipe, J.E. Fischer, K.R. Cromack,  
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## POLYANILINE: ORIENTED FILMS AND FIBERS

E.M. SCHERR, A.G. MACDIARMID, S.K. MANOHAR, J.G. MASTERS, Y. SUN, X. TANG  
Department of Chemistry, University of Pennsylvania, Philadelphia, PA (USA)

M.A. DRUY and P.J. GLATKOWSKI  
Foster-Miller Co, Inc. Waltham, MA (USA)

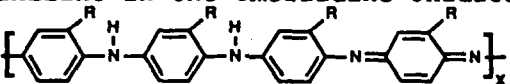
V.B. CAJIFE and J.E. FISCHER  
Laboratory for the Research on the Structure of Matter, University of  
Pennsylvania, Philadelphia, PA (USA)

K.R. CROMACK, M.E. JOZEFOWICZ, J.M. GINDER, R.P. McCALL, A.J. EPSTEIN  
Department of Physics, The Ohio State University, Columbus, OH (USA)

### ABSTRACT

The dependency of the conductivity of polyaniline (emeraldine oxidation state) on its molecular weight has been determined. Uni- and biaxially oriented films and uniaxially oriented fibers of emeraldine base have been studied and the dependency of their degree of crystallinity, tensile strength, and conductivity (after doping) on draw ratio has been determined.

### INTRODUCTION

The base form of polyaniline in the emeraldine oxidation state is represented by the general formula:  where R=H (parent emeraldine base), CH<sub>3</sub>, CH<sub>3</sub>O, C<sub>2</sub>H<sub>5</sub>O, etc. [1]. These base forms can be protonated at the imine nitrogen atoms by aqueous acids to form a polysemiquinone radical cation with a concomitant increase in conductivity of up to ~10 orders of magnitude [1].

It has been known for some time [2] that emeraldine base is readily solution processible and that it may be cast as free-standing, flexible, copper-colored films from its solutions in NMP. These films can be doped with 1M aqueous HCl to yield flexible, lustrous blue films ( $\sigma=1-4$  S/cm) of emeraldine hydrochloride [2]. This processibility makes it possible to determine the intrinsic electrical and mechanical properties of polyaniline both in its undoped and doped forms as previously demonstrated in preliminary studies [1].

## RESULTS

### 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:  $M_p = 15,000$ ,  $M_n \sim 12,000$ ,  $M_w \sim 22,000$ ;  $M_w/M_n \sim 1.8$  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. 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 changes relatively little as shown in Fig. 1.

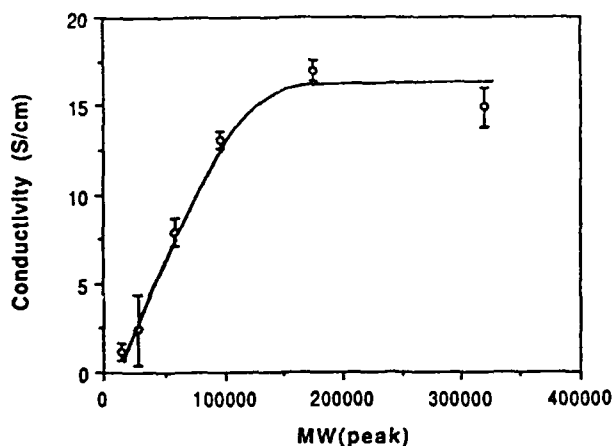


Fig. 1. Dependency of conductivity of doped polyaniline (emeraldine oxidation state) on molecular weight.

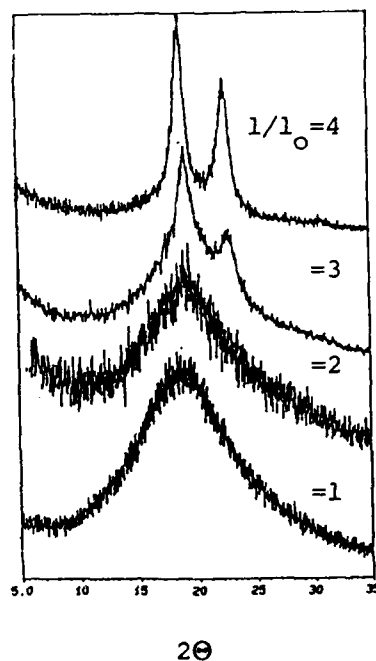


Fig. 2. X-ray diffraction spectra of emeraldine base of increasing draw ratio ( $l/l_0$ ;  $l$ =final length;  $l_0$ =length before stretching).

### Oriented Films

Uniaxially oriented, partly crystalline emeraldine base films were obtained by simultaneous heat treatment and mechanical stretching of films of emeraldine base containing ~15 wt.% plasticizer such as NMP. Samples were observed to elongate by up to four times their original length when stretched above the glass transition temperature ( $> \sim 110^\circ\text{C}$ ) [1]. The resulting films have 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 in length and 2.5 cm in width (thickness  $\sim 20\mu\text{m}$ ) of various draw

ratios can be readily fabricated by stretch-orienting an emeraldine base film cast from NMP solution by passing it between two pinch rollers and then across a heated (~140°C) Teflon coated roller and then finally between a second set of pinch rollers rotating at a higher speed than the first set. The apparent degree of crystallinity is greatly increased by processing of this type as shown in Fig. 2.

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). The conductivity of the HCl-doped uniaxially oriented ribbons increases on 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. As expected, biaxially oriented films exhibit significantly greater tensile

strengths than uniaxially oriented films having the same draw ratio.

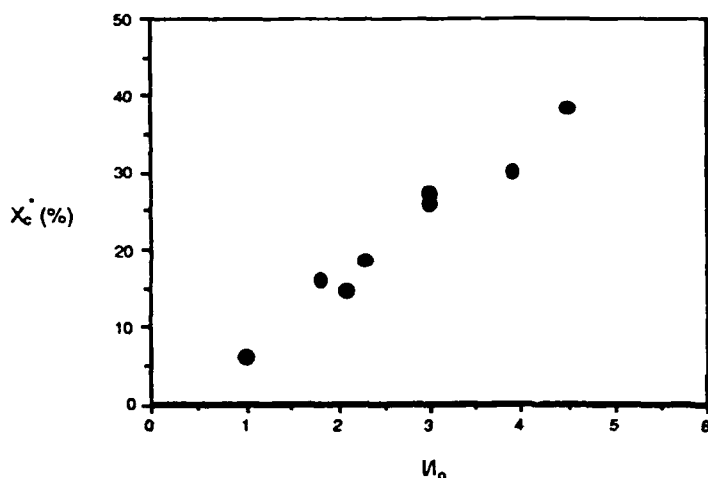


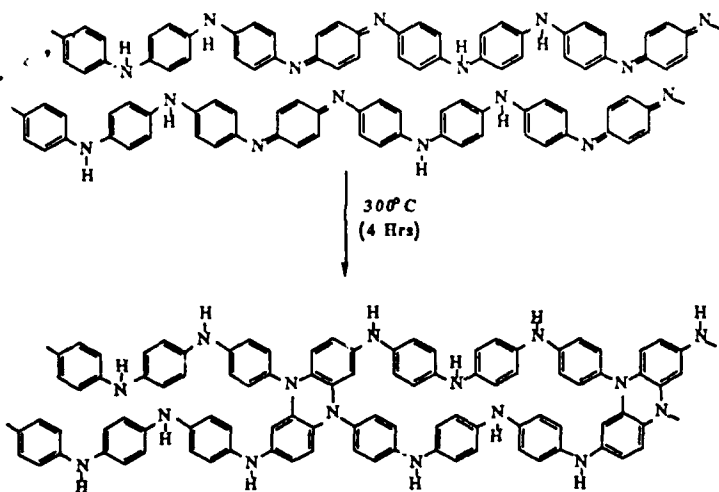
Fig. 3. Crystallinity vs. draw ratio ( $l/l_0$ ) for emeraldine.HCl fibers [ $X_c$ =fractional integrated radial intensity (sum of 010, 012, 200 crystal peaks)]

#### Oriented Fibers

Fibers (~30-70 $\mu$ m) of emeraldine base can be formed by drawing a ~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-oriented at ~140°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 Fig. 3. This is paralleled by a monotonic increase in conductivity (up to ~170 S/cm) after doping with 1M HCl. Preliminary tensile strength studies (366MPa for  $l/l_0=3-4$ ) 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 (~24-30 $\mu$ m) can be spun from  $CH_2Cl_2$  solution and stretch-oriented at ~140°C to  $l/l_0 \sim 6$ . They have an average tensile strength of ~275 MPa and a conductivity of ~54 S/cm after doping in 1M HCl.



## 2D/3D Polyaniline

Emeraldine base can be controllably converted at 300°C under inert conditions into an "isomeric" 2D/3D electroactive polymer involving crosslinking between chains as shown in Fig. 4.

## CONCLUSIONS

The improved ability to process pure polyaniline by conventional methods in the form of oriented films and fibers having greatly increased conductivities and having

Fig. 4. Thermal crosslinking of polyaniline (emeraldine base).

tensile strengths overlapping those of conventional commercial polymers is most encouraging from the point of view of its technological potential. The data obtained show that its intrinsic properties can only be approached through processing and that increases in its conductivity and mechanical properties are controlled by the same fundamental factors, principally, molecular weight and degree of crystallinity.

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