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DIELECTRIC PROPERTIES OF ALIGNED CONDUCTING POLYMERS

FINAL REPORT FOR THE PERIOD
March 1, 1989 through February 28, 1991

CONTRACT NO. N00014-89-C-0075

Prepared for:

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Washington D.C. 20375

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OCTOBER 1991

91-17727



Rockwell International
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91 10 29 124

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ABSTRACT

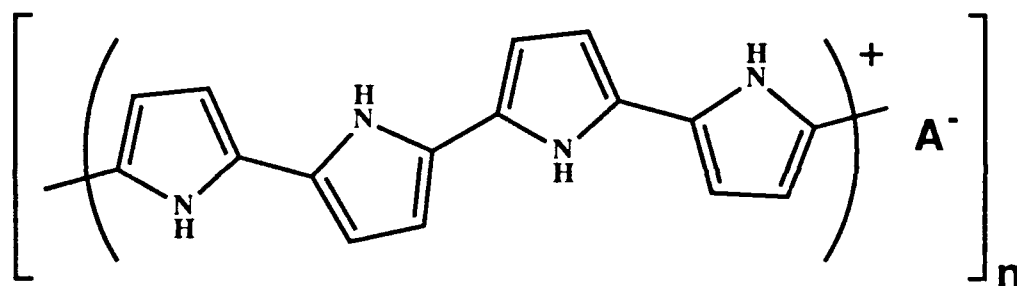
Attempts to align electrically conducting polypyrrole (PPy) were made using various electrochemical methods. Rotating cylinder anode electropolymerization was found to induce partially aligned deposits of PPy films when they were prepared in the presence of a soap supporting electrolyte or a soluble polymer additive. Degrees of dc electrical anisotropy up to 60 to 1 were observed. SEM and UV-vis results indicated that soluble pyrrole oligomers generated in the rotating anode cell result in film alignment. Electrochemically prepared PPy/poly(ethylene oxide) composites were stretchable, resulting in conductivity enhancement, but with little electrical anisotropy. Pyrrole electropolymerization in a magnetic field was also evaluated, but electrical anisotropy was not detected in any of the films. However, an unusual uniform rotational hydrodynamic motion, depending on the disposition and polarity of the electrodes, was observed with submersed electrodes in which the electric field was parallel to the magnetic field.



1.0 INTRODUCTION

Alignment of intrinsically conducting polymers (CPs) has been the subject of intense research interest.^{1,2} It has been demonstrated that aligned polyacetylene and polyaniline possess remarkably enhanced conductivities. The increase in crystallinity and orderliness in their backbone chains enhance not only charge mobility along individual polymer chains but electron hopping between the chains, which increases overall bulk conductivity as well as electrical anisotropy. Because of their unique electrical properties, aligned conducting polymers can find new applications, including devices that can anisotropically absorb electromagnetic energy.

Polypyrrole (PPy) has been studied extensively, as it is the most chemically stable of the CP's in its conducting form.³



Oxidized/conducting form of PPy with dopant anion A^-

It is prepared from pyrrole monomer, which can be easily polymerized using electrochemical,⁴ photochemical,⁵ or chemical oxidation methods.⁶ As formed, conducting PPy incorporates 25-30% of an anion species (A^-) to compensate its positive charge. PPy typically exhibits higher conductivities and greater environmental and thermal stability compared to other CPs such as polyacetylenes, polythiophenes, and polyaniline. These favorable properties and the commercial availability of the monomer make PPy one of the most attractive conductive materials for practical applications, and we therefore selected it as the material of choice for our study. However, PPy is very intractable. Conventional processing techniques such as extrusion and spinning have proven to be ineffective with PPy, and unique approaches are required to produce aligned material. A few successful attempts have been reported, and these include stretch-orientation of BF_4^- -doped PPy films electrochemically deposited at $-30^\circ C$,⁷ pyrrole electropolymerization at a xylene/water interface,⁸ and polymerization within the mesoscopic pores of a membrane.⁹



The objective of this program has been to develop a practical *in-situ* polymerization technique producing free-standing oriented PPy films and to characterize their electrical properties and polymer morphology. During this contract, a variety of alignment approaches were evaluated. Methods described in the literature which were not amenable to fabrication of centimeter-sized free-standing films were not pursued. A method which purported to generate electrically anisotropic films by employing titanium strip anodes¹⁰ was simply not repeatable in our hands. The above-mentioned interfacial electropolymerization method,⁸ likewise, did not produce anisotropic films. The new techniques investigated in this program are listed below:

- (1) rotating cylinder electropolymerization,
- (2) stretch orientation of electrochemically prepared
PPy/poly(ethylene oxide) blends, and
- (3) pyrrole electropolymerization in a magnetic field.



2.0 EXPERIMENTAL

Pyrrole was purchased from Aldrich Chemical Co. and was purified by distillation in an inert atmosphere over molecular sieves and stored in a refrigerator under nitrogen before use. Cetyltrimethylammonium *p*-toluenesulfonate (CTMATos, Research Plus Inc.), tetraethylammonium *p*-toluenesulfonate (TEATos, Fluka Chemie AG), polyacrylonitrile (PAN, MW 23000; Aldrich), poly(ethylene oxide) (PEO, MW 8000-900000; Aldrich), and poly(propylene carbonate) (PPC, MW 50000, Air Products) were purchased and dried under vacuum before use. Silver *p*-toluenesulfonate (Eastman Kodak Co.) and poly(styrenesulfonic acid) (PSS, MW 70,000; Polysciences Inc.) were used as received. Polyanilinesulfonate (PaniS) was prepared according to a published procedure.¹¹

In the rotating cylinder electropolymerization technique, illustrated schematically in Fig. 1, the inner rotating anode was comprised of a 1 cm wide ring ($\sim 10 \text{ cm}^2$ area) of polished stainless steel or gold-plated copper with flush Kel-F spacers (see diagram) and was equipped with a variable speed rotator (Pine Instrument Co.). The anode was positioned in the cell so as to maintain a uniform gap, $\sim 2.5 \text{ mm}$, between it and the surrounding stainless steel shim cathode. In a typical experiment, a mixture of a supporting electrolyte and neat pyrrole was charged in the cell, and nitrogen was bubbled through the resulting solution to remove the dissolved oxygen. During electropolymerization, a nitrogen blanket was maintained at the top of the cell to minimize the intrusion of water and oxygen. PPy films deposited on the rotating anode were readily removed from the electrode by soaking in water, washing thoroughly with water and methanol, allowing to dry at ambient, and then storing in sealed plastic bags.

Electrical conductivities were measured by the Montgomery method using mounting procedures and a gold-dot four-probe technique described elsewhere.¹² This technique, which is illustrated in Fig. 2, is a reliable one for measuring electrical anisotropy within the plane of a thin film. Most of the literature results reporting anisotropy data do not provide sufficient experimental detail on the measurement techniques used and are therefore suspect in our eyes. Care was taken to insure ohmic contacts and a uniform electric field across the samples. Film thicknesses were measured either microscopically or with a micrometer. Surface resistance of the films was also measured using a standard four-point probe apparatus (Alessi Industries).

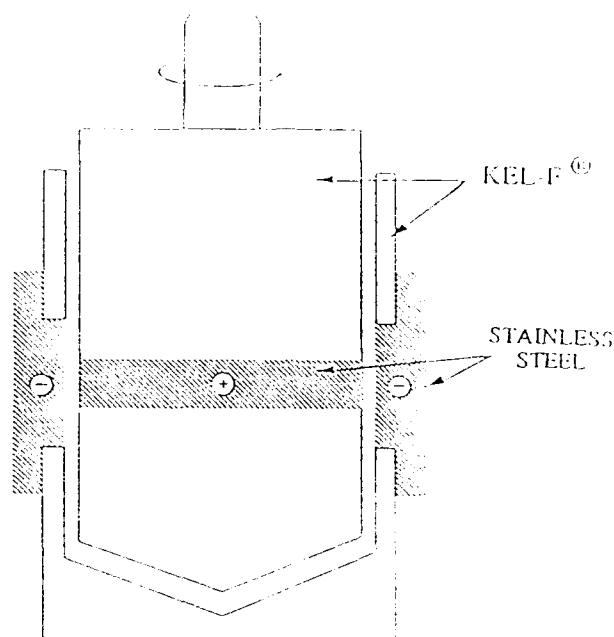


Fig. 1 Schematic representation of the rotating electrode electropolymerization cell.

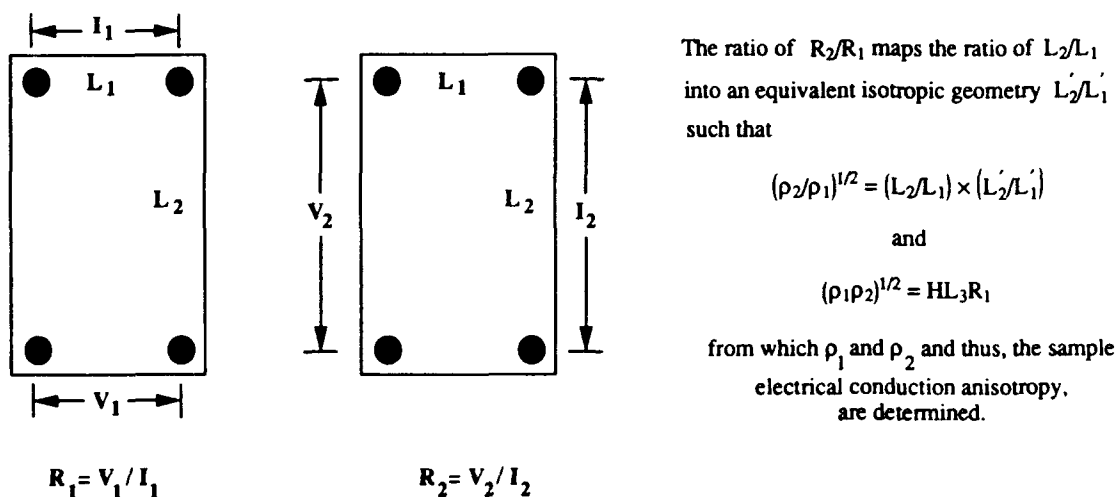


Fig. 2 Method of determining dc conduction anisotropy using the Montgomery method.

Electropolymerization of pyrrole under static conditions or in a magnetic field was carried out using a single-compartment cylindrical Pyrex glass cell (2 in. diameter, 3 in. height) under a



nitrogen blanket. Platinum or stainless steel strips (0.5 in. width, 4 in. length) were used for both anodes and cathodes. The magnet employed, 15 in. diameter, 3 in. gap, was manufactured by O.S. Walker Scientific Inc. and was capable of operating at fields up to 18000 G.

DSC analysis was performed using a Perkin-Elmer DSC-2C. UV-vis spectra were measured with a Beckman Spectrophotometer UV 5230, and electron micrographs of PPy films were taken with SI-40 scanning electron microscope (SEM).



3.0 RESULTS AND DISCUSSTION

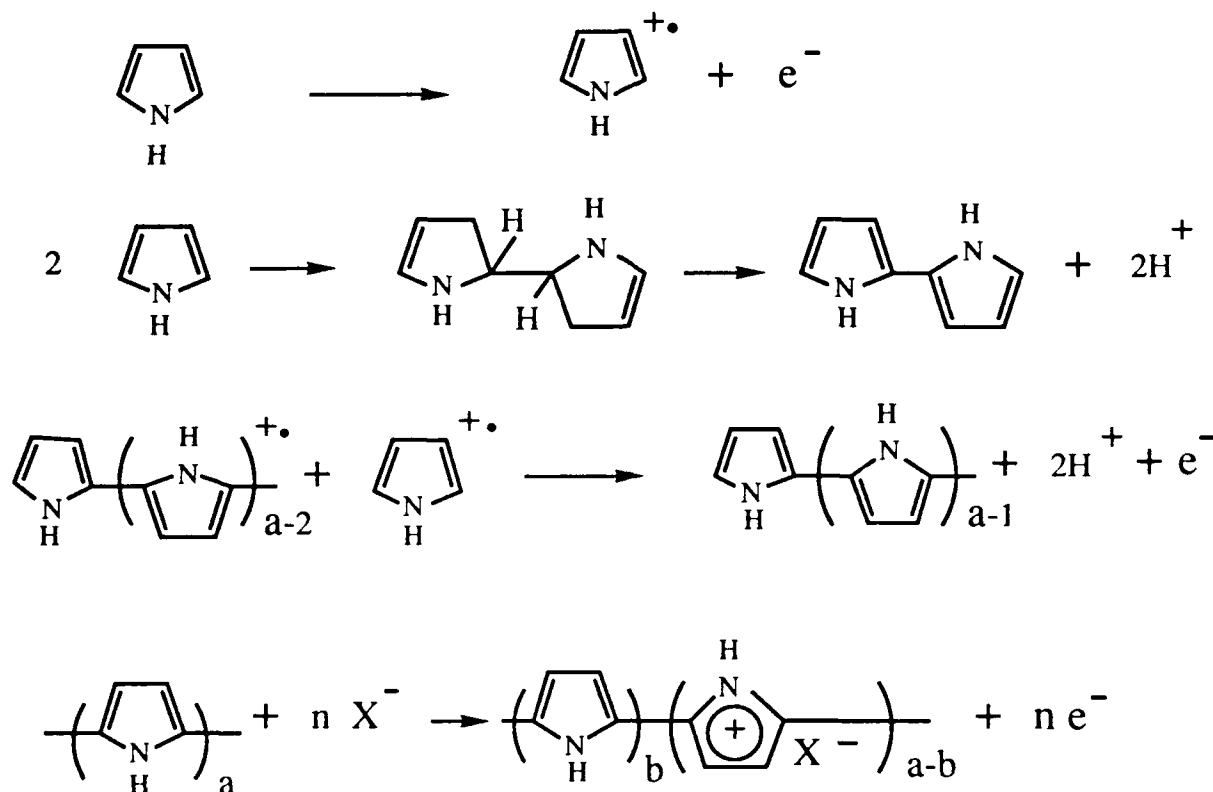
3.1 Rotating Cylinder Electropolymerization of Pyrrole

It is known that shear flow in a liquid medium can orient solute linear polymer chains along the force direction. In general, two criteria must be met to achieve a high degree of orientation by this method. First, the polymer must be easily oriented by shear or elongational flow, and second, this orientation must be preserved until the chain mobility is frozen by processing (i.e., a relatively long relaxation time is required). Obviously, polymers having relatively rigid backbone chains (e.g., liquid crystal polymers, high molecular weight polyethylene) are expected to respond more favorably than low molecular weight elastomers. This technology has been successfully employed to produce a variety of oriented polymer films and fibers by spinning and extrusion. We therefore investigated for the first time a new rotating cylinder anode technique for electropolymerization of pyrrole in the hope that shear flow generated by the anode rotation may induce *in situ* aligned PPy film formation.

3.1.1 Polymerization in Conventional Electrolyte Media

The electropolymerization of pyrrole is very complex, and the widely accepted mechanism⁴ is shown in Scheme 1. The reaction proceeds via a radical coupling reaction of oxidized pyrrole radical cations, followed by deprotonation and one-electron oxidation in order to generate the aromatic (i.e., 6 pi-electron) system. The highly oxidizable polypyrrole subsequently further reacts at the anode to give a positively charged polymer species which is charge compensated by a supporting electrolyte anion to form an insoluble PPy film.

It was hoped that the electropolymerization of pyrrole using a rotating cylinder anode would enable orientation of the soluble lower molecular weight polymer species, and that these will be deposited onto the anode in an aligned state as polymerization proceeds.



SCHEME 1 ELECTROPOLYMERIZATION OF PYRROLE

In this program, pyrrole electropolymerization was carried out in the "conventional" solvents acetonitrile, propylene carbonate, and water using the rotating cylinder anode technique. The concentration of pyrrole monomer was varied from 0.1-1.0 M. Supporting electrolytes employed include several organic sulfonate salts with various cations: (i) tetraethylammonium tosylate, TEATos, (ii) tetrabutylammonium tosylate, TBATos, (iii) cetyltrimethylammonium tosylate, CTMATos, (iv) sodium tosylate, NaTos, (v) sodium dodecylsulfate, NaDDS, (vi) polystyrenesulfonic acid, PSS, and (vii) polyanilinesulfonic acid, PaniS. The structures of these ions are shown below.



rotation (~ 200 rpm) conditions. In the case of the polymer dopants PSS and PaniS, the stainless steel anode surface gave spotty PPy deposits which were accompanied by severe electrode erosion. Use of a gold-plated anode provided more uniform films but film conductivities remained low.

These results indicated that the mass transport mechanism under hydrodynamic flow conditions is quite different from that under static conditions in which the diffusional flow of pyrrole monomer to the electrode surface is operational. Under rotational flow conditions, the monomer is brought to the electrode surface by rotation; however, the residence time of the monomer at or near the surface is dependent on the flow rate, i.e., the higher the flow rate, the shorter the residence time of the monomer. Therefore, we attributed the film conductivity decrease to the formation of short molecular weight PPy. One way to potentially overcome this problem is to use neat pyrrole as the electrolyte medium and thus avoid monomer diffusional limitations.

3.1.2 Neat Pyrrole Electropolymerization Under Static Conditions

Neat pyrrole exhibits unique solvent properties. Unlike other aromatic-based monomers such as benzene and thiophene, it can readily dissolve certain polar supporting electrolytes as well as some polymers. This is probably due to its NH functionality which enhances its solvation power by hydrogen-bond formation with appropriate solutes. Neat pyrrole electropolymerization was first reported by Lindsey and Street (see Ref. 3), who observed that PPy films from a pyrrole electrolyte containing TEABF₄ exhibited low conductivity (ca. 5 S/cm) and poor mechanical properties.

We evaluated for the first time neat pyrrole containing the novel CTMATos supporting electrolyte, which has an amphiphilic or soap-like cation. (CTMATos forms a gel in water, and DSC analysis showed endothermic peaks at 43, 118, and 128°C upon heating from 20 to 180°C, indicating multiple phase changes.) This unusual salt was very soluble in neat pyrrole and formed a homogeneous solution, in spite of the fact that it was not soluble in other polar organic solvents such as acetonitrile, propylene carbonate, or N-methylpyrrolidinone. Static electropolymerization in neat pyrrole containing CTMATos produced flexible films having high conductivities (ca 100 S/cm). Polymerizations were carried out by varying the ratio of pyrrole and CTMATos as well as current density under static conditions. As shown in Fig. 3, the optimized Py/CTMATos ratio was found to be 1.5. The variation in current density (0.2 -5.0 mA/cm²) seldom affected the conductivity.

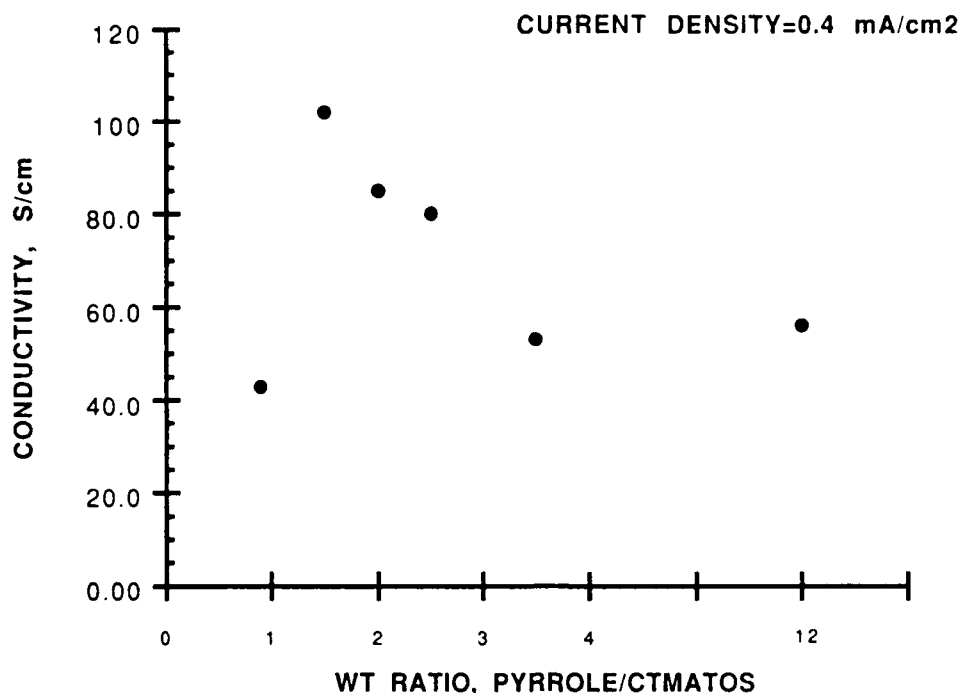


Fig. 3 The effect of CTMATos supporting electrolyte concentration on conductivity of PPy films electropolymerized from neat pyrrole under static conditions, current density 0.4 mA/cm².

The effect of water on PPy film conductivity was also examined. Results shown in Table 1 indicate that little or no water is required for formation of high conductivity films from neat pyrrole electrolytes. This contrasts with data from conventional organic solvents, where about 1-5% water is required to optimize film conductivity. It was also observed that adhesion of PPy to the anode was enhanced with increasing water concentration. In fact, separation of an intact film deposited from a neat pyrrole electrolyte containing 1.5 wt % water was not successful.

Table 1
The Effect of Water Concentration on PPy Film Conductivity
from a Neat Pyrrole Electrolyte*

Water conc., wt %	Conductivity, σ (S/cm)
0	102
0.3	112
0.9	79
1.5	**

* Pyrrole/CTMATos = 1.5 (wt ratio), static conditions, 0.4 mA/cm².

** PPy film did not separate from anode.



3.1.3 Rotating Cylinder Electropolymerization - Neat Pyrrole

CTMATos as Supporting Electrolyte. Rotating cylinder anode polymerization was performed using a Py/CTMATos (1.5/1.0) electrolyte, since this ratio provided the highest conductivity under the static conditions. Figure 4 plots conductivities of PPy films deposited at a constant voltage of +4 V (vs. the counterelectrode) at various anode rotation rates. Electrical conductivities of these films in the direction parallel to the rotational flow were higher than those perpendicular to the flow direction, and the maximum anisotropy under these conditions was ca 10 at a rotational rate of 2000 rpm. Morphologies of these partially aligned films were examined by SEM, and Figs. 5 and 6 show a growing surface and an intersection fractured parallel to the flow, respectively. Submicron aligned layers along the flow direction can be seen, indicating the polymer chain orientation along the flow direction. SEM of a fractured surface perpendicular to the flow direction is also shown in Fig. 7. This SEM suggests that the film grows rather isotropically in the initial stages, then gradually changes to a columnar-like texture in the direction of the growing surface. Unfortunately, none of the anisotropic films were suitable for microwave resistivity measurements.

The reproducibility of the electrical anisotropy in these rotating anode electrodeposited PPy films was poor, and this was subsequently found to depend on the age and prior use of the neat pyrrole electrolyte. Electrodeposition in fresh pyrrole solutions at low current densities ($< 1.0 \text{ mA/cm}^2$) produced PPy films having very little electrical anisotropy and low overall conductivities (ca 10 S/cm). However, older solutions, from which a number of films had been deposited at high current densities ($> 5 \text{ mA/cm}^2$) produced much higher anisotropies. In fact, our initial results with unpurified pyrrole provided the highest anisotropy with fiber-like PPy deposits prepared using the rotating cylinder anode -- up to 60:1, highest conductivity 200 S/cm . Repeated efforts to reproduce this result were unsuccessful, due primarily to the critical chemical makeup of the pyrrole prior to electropolymerization.

This feature of the neat liquid pyrrole was examined further by oxidatively pregenerating soluble pyrrole oligomers (i.e. low molecular weight polymers) using a separated compartment three-electrode cell as illustrated in Fig. 8. With a stainless steel spindle anode rotated at 1500 rpm and held at a constant voltage of $> +3 \text{ V}$ (vs $\text{Ag}/0.1\text{M AgNO}_3/\text{pyrrole}$ reference electrode), a reddish orange species which rapidly converted to a yellowish green color formed in the anode compartment. At the same time, the cathode compartment turned pale blue. A UV-visible spectrum of the anode solution showed a family of peaks between 400 nm to 600 nm which, in

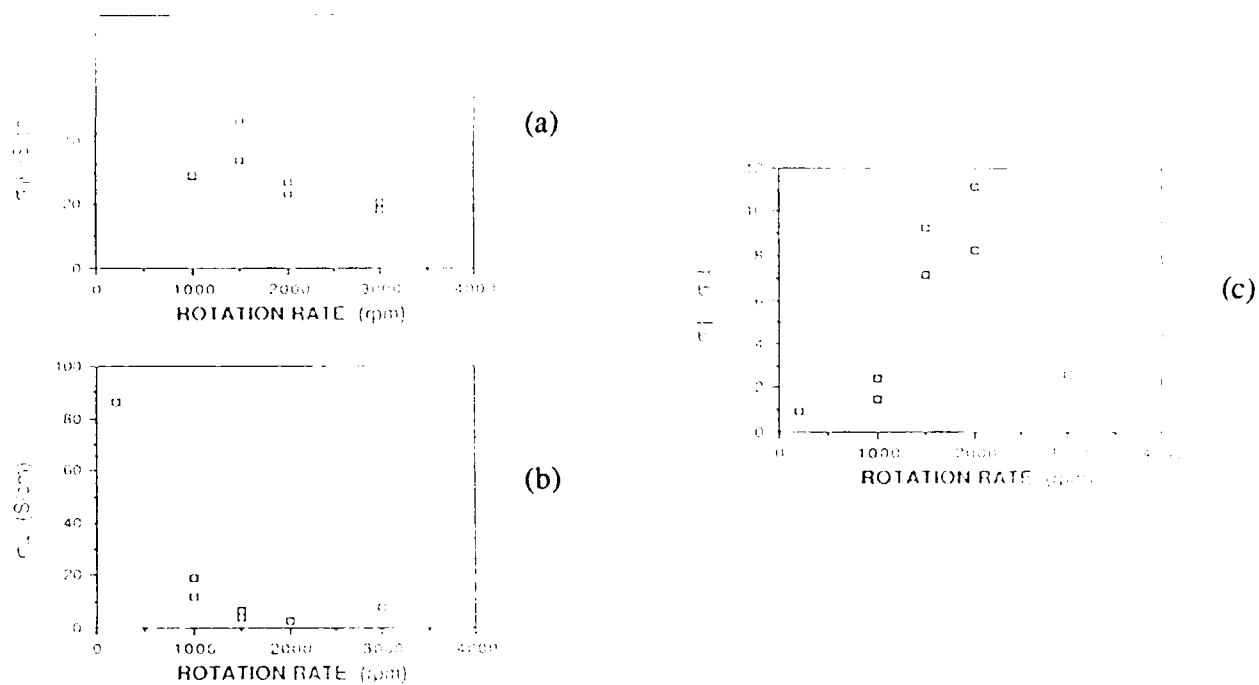


Fig. 4 Room temperature conductivity vs anode rotation rate for PPy films produced via rotating electrode polymerization in neat pyrrole electrolyte containing CTMATos. Pyrrole/CTMATos = 1.5; constant voltage deposition at +4.0 V. $\sigma_{\parallel}$ = film conductivity parallel to the shear force direction, $\sigma_{\perp}$ = conductivity perpendicular to the shear force direction.

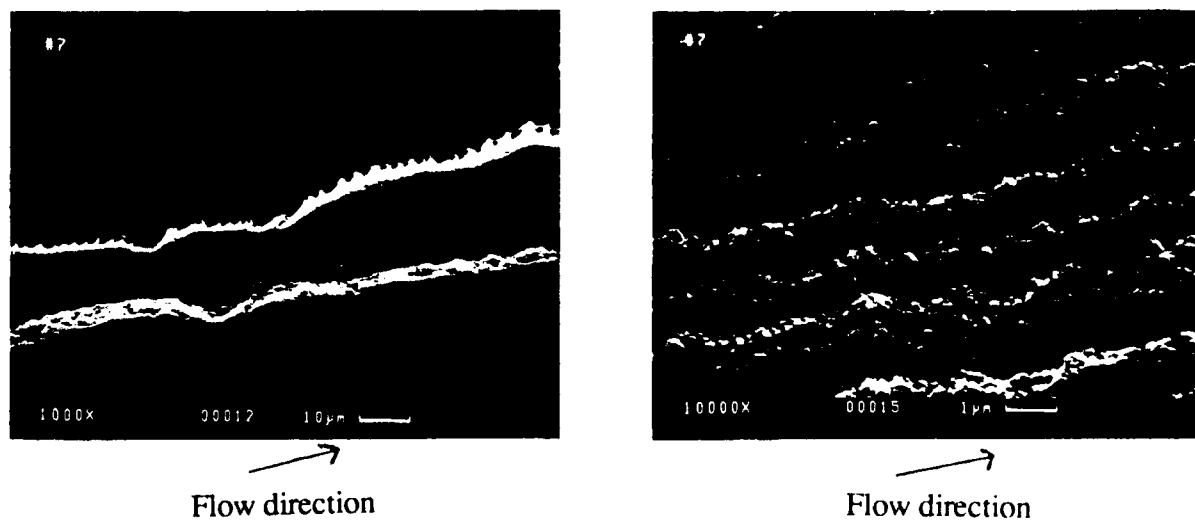


Fig. 5 SEM micrographs of aligned PPy film (solution side).

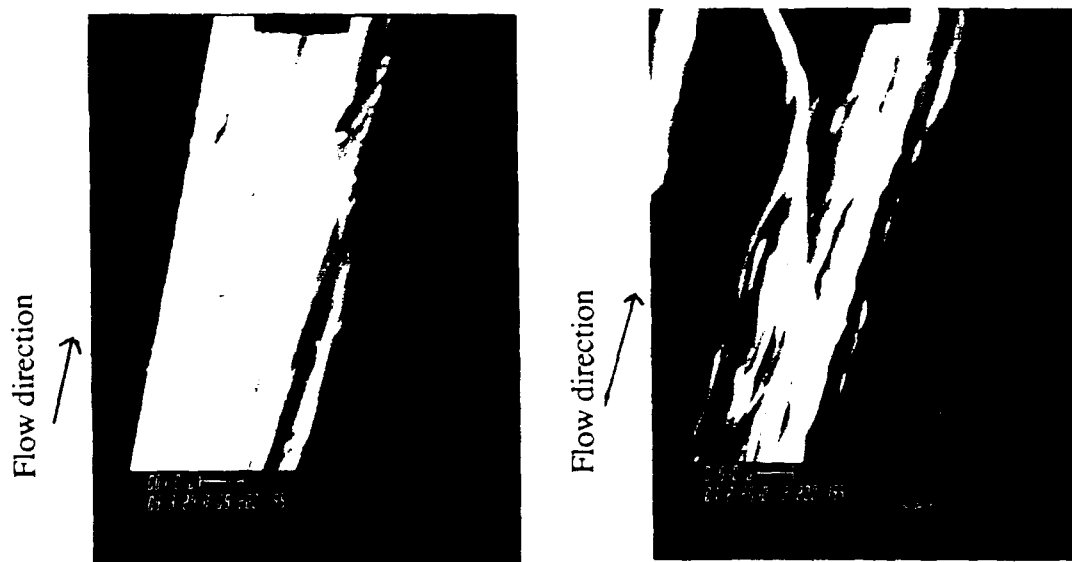


Fig. 6 SEM micrographs of aligned PPy film (cross section along flow direction).

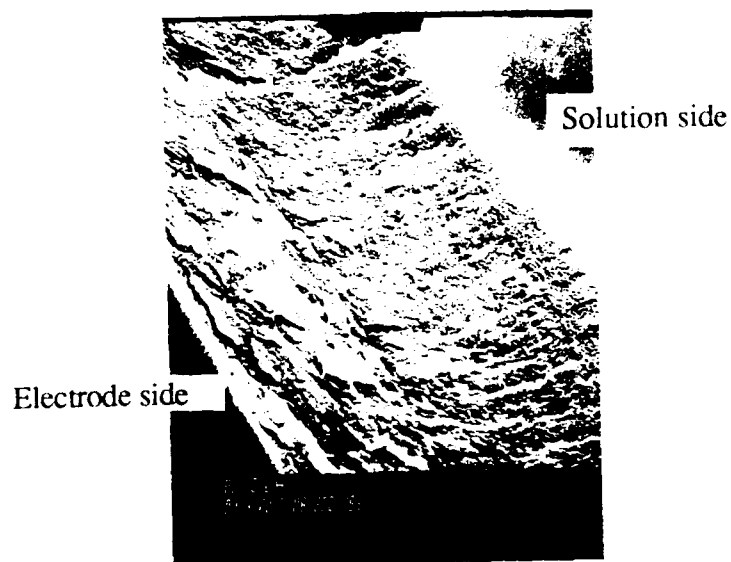


Fig. 7 SEM micrograph of aligned PPy film (cross section perpendicular to flow direction).



time, gradually decreased in intensity with concomitant growth of a broad peak as shown in Fig. 9. Exposure of these solutions to atmospheric oxygen accelerated this conversion, resulting in blue-green solutions from which black PPy gradually deposited upon standing at room temperature. Similar UV-visible spectra were obtained when neat pyrrole was treated with chemical oxidants namely Cu(II) and Ag(I) salts (see Fig. 9). These results *are consistent with the formation of soluble pyrrole oligomers which appear to be responsible for the orientation of PPy films electrodeposited from neat pyrrole electrolytes under shear flow conditions*. This is the first time that such species have been observed and invoked in PPy film orientation.

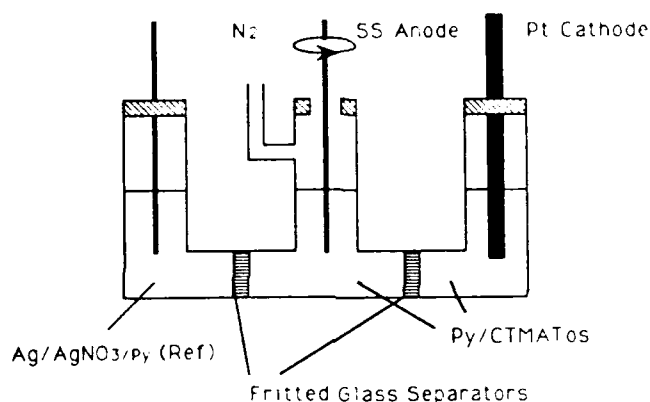


Fig. 8 Separated compartment three electrode cell.

CTMA vs TEA. We attributed the decrease in PPy film conductivity with increasing spin rate to the formation of low molecular weight PPy, most likely caused by the low ionic conductivity of the neat pyrrole electrolyte containing the bulky CTMATos. We therefore examined electropolymerization in the presence of the smaller supporting electrolyte TEATos to determine if a more (ionically) conductive electrolyte could improve the conductivity of PPy films. Results are shown in Fig. 10. With TEATos, the increase in film conductivity with increasing current density was much more rapid than observed in CTMATos electrolytes, with the conductivities reaching values of ca. 100 S/cm. Conductivity differences may be a result of chain lengths of PPy in the films; that is, the lower the current density and faster the rotation rate, the shorter the PPy polymer chains in the films. The higher film conductivities in TEATos media may be attributed to the less hydrophobic, more ionically conductive nature of TEATos as compared to CTMATos. However, with TEATos *no electrical anisotropy was observed, indicating the important role of the large CTMA cation in the generation of aligned PPy deposits*. At this stage,

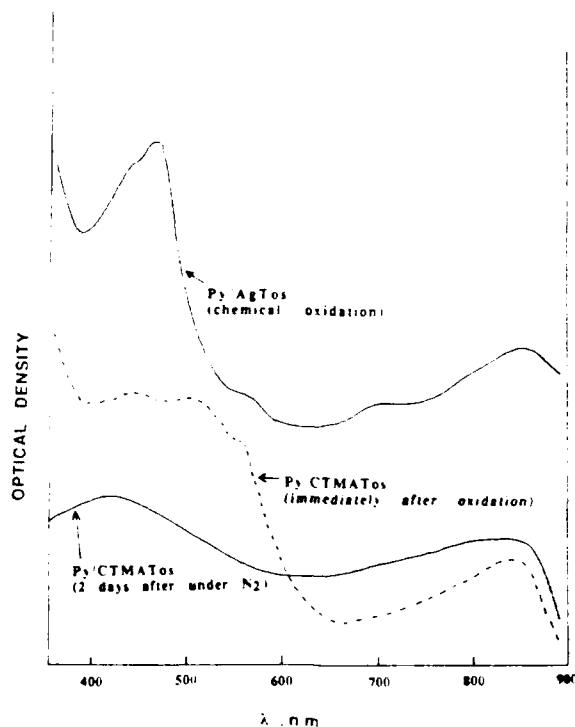


Fig. 9 UV-vis spectra of soluble oxidation products of neat pyrrole by electrochemical and chemical methods.

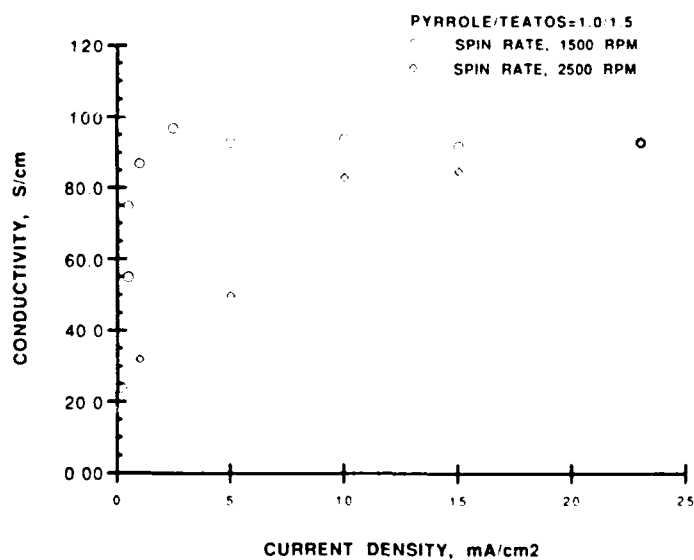
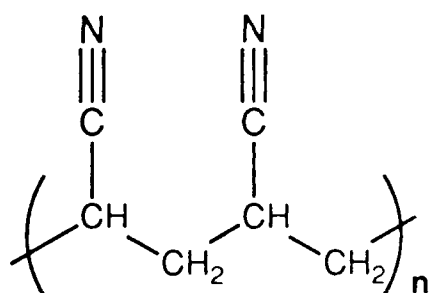


Fig.10 The effect of current density on conductivity in neat pyrrole/TEATos electrolyte; pyrrole/TEATos ratio 1:1.5.

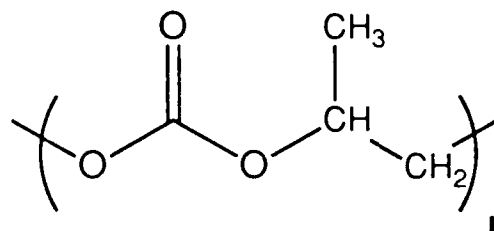


we speculate that the surfactant-like properties of the CTMA cation enables orientation on the anode by shear flow, thus inducing the alignment of PPy oligomers before deposition.

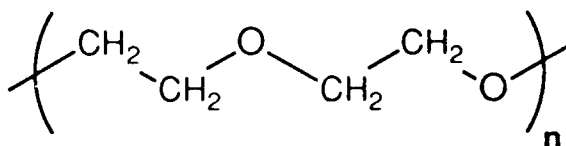
Inert Polymer Additives. We also carried out neat pyrrole polymerization in the presence of uncharged, electrochemically inert polymers and found that the increased electrolyte viscosity could induce PPy orientation using the rotating anode. The specific polymers which were evaluated were poly(ethylene oxide) (PEO), poly(acrylonitrile) (PAN), and poly(propylene carbonate) (PPC).



PAN



PPC



PEO

Both PEO and PPC were readily soluble in neat pyrrole, and PAN was slightly soluble (up to 4 wt%). However, in the case of PPC and PAN, poor compatibility with the TEATos supporting electrolyte did not result in homogeneous viscous solutions, and efforts were concentrated on the PEO additive. [Note: It is worthwhile to point that isotropic PPy films (i.e., without anode rotation) produced in the presence of PPC (3-8 wt %) exhibited substantially higher conductivities (150-170 S/cm) compared to films without PPC.]

Table 2 presents conductivities of PPy films deposited in the presence of PEO (MW 300,000) under various anode rotation rates. Film conductivities parallel to the flow direction were consistently higher than those perpendicular to the flow, although the anisotropies were low. It was also found with these films that the sheet resistivities of the growth surfaces were substantially higher than those of the electrode-facing surfaces. These results are consistent with our previous



observations and indicate that *film growth morphology changes from isotropic to anisotropic with increasing film thickness.*

Table 2
Rotating Cylinder Electropolymerization of Neat Pyrrole in the
Presence of Poly(ethylene oxide)

Sample No.	Rotation Rate (RPM)	Current Density (mA/cm ²)	Conductivity Parallel to Flow (S/cm)	Conductivity Perpendicular to flow (S/cm)	Parallel: Perpendicular Conductivity Ratio	Sheet Resistivity (ohms/sq.)
1	500	2	105	87	1.21	
2	1000	2	100	94	1.06	
3	1500	2	112	92	1.22	
4	2500	2	60 ^a	44	1.37	4.0
			80 ^b	51	1.56	6.8

* Pyrrole/TEATos/PEO, mw 300,000 = 8/5/0.5

a electrode side of film

b growing side of film

3.1.4 Stretching of PPy/PEO Blend Films

PPy films are generally non-stretchable due to their intractability, although BF₄⁻-doped PPy films deposited at low temperature are reported to be stretchable.⁷ We examine the stretchability of PPy/PEO films produced from neat pyrrole containing TEATos in the presence of PEO by rotating the anode at 200 rpm. [Note: at this low rotation rate, electrical anisotropy would not be expected in the deposited film]. Two PEO polymer samples having molecular weights of 8000 and 300,000 were employed. The resulting flexible, shiny PPy films (10 micron thickness, 1 cm width, and 5 cm length) were soaked in propylene carbonate. The wet films were subsequently stretched by hanging vertically using a steel weight (300 grams) and heating to 60-80°C for 10-20 sec with an infrared reflector heater. Films typically stretched up to 10-20% of their original length. These results, presented in Table 3, appear to indicate that films containing high molecular weight PEO are more stretchable than those containing low molecular weight PEO, with conductivities increasing ca. 50 %, however, with no measurable anisotropy. We feel that improvement of the stretching method along with evaluation of other compatible PPy/elastomer blends could lead to further enhancement of stretchability of the films.



Table 3
Conductivity of Stetched PPy-PEO Blends

System	Conductivity (S/cm) Unstretched	Conductivity (S/cm) Stretched
PPy/Tos/PEO (mw = 8000)	90	115
PPy/Tos/PEO (mw = 300,000)	90	150

Pyrrole/TEATos/PEO = 8/5/1 (Wt ratio); films were prepared by rotating cylinder electropolymerization at a rotation rate of 200 rpm and a current density of 2 mA/cm² at room temperature.

3.2 Pyrrole Electropolymerization in a Magnetic Field

Alignment of certain conducting polymer systems by use of a magnetic field has been demonstrated in the literature. Techniques employed include chemical polymerization of acetylene (to polyacetylene) in an oriented liquid crystal medium^{1,13} and aligned casting of water-soluble lyotropic CPs in a magnetic field.¹⁴ There is also a Japanese patent claiming to enhance CP film conductivities by preparation in a magnetic field;¹⁵ the enhancement was remarkably affected by the angle between magnetic and electric fields.

In this program, we investigated electropolymerization of pyrrole in a magnetic field to determine its effect on film conductivity and alignment. Two electrolyte media were examined: (i) neat pyrrole containing CTMATos or TEATos and (ii) liquid crystalline 4-cyano-4'-n-pentylbiphenyl (or K-15) containing tetrabutylammonium fluoroborate. [Note: pyrrole formed a charge transfer complex with K-15 to produce a hygroscopic colorless solid having a melting point of 58°C]. Magnetic field strengths employed were in the range 4000-18000 G, and in no cases were any enhancements in electrodeposited film conductivities detected, regardless of the electrode configurations --i.e., whether oriented parallel or perpendicular to the applied magnetic field.

3.2.1 Unusual Magnetohydrodynamic Motion Phenomenon

During the magnetic field electrodeposition experiments, we did, however, observe an unexpected uniform horizontal rotational hydrodynamic motion generated in the electrolyte solution



when the electrodes were placed such that the electric field was parallel to the applied magnetic field (Fig. 11). Reversal of the electrode polarity resulted in reversal of the rotational direction. In an attempt to quantify this observation, the upper 3/4 of the strip electrodes were masked, and the unmasked portions were submerged beneath the solution surface. This completely reversed the rotational direction of the motion relative to the unmasked case (see Fig. 11). When the electrodes were placed perpendicular to the applied magnetic field, the motion of the solution became rather complex and included symmetrical vertical convection. This phenomenon appeared to be universal since the same effects were also observed in many other solvent systems, including aqueous electrolytes (e.g., aqueous KCl).

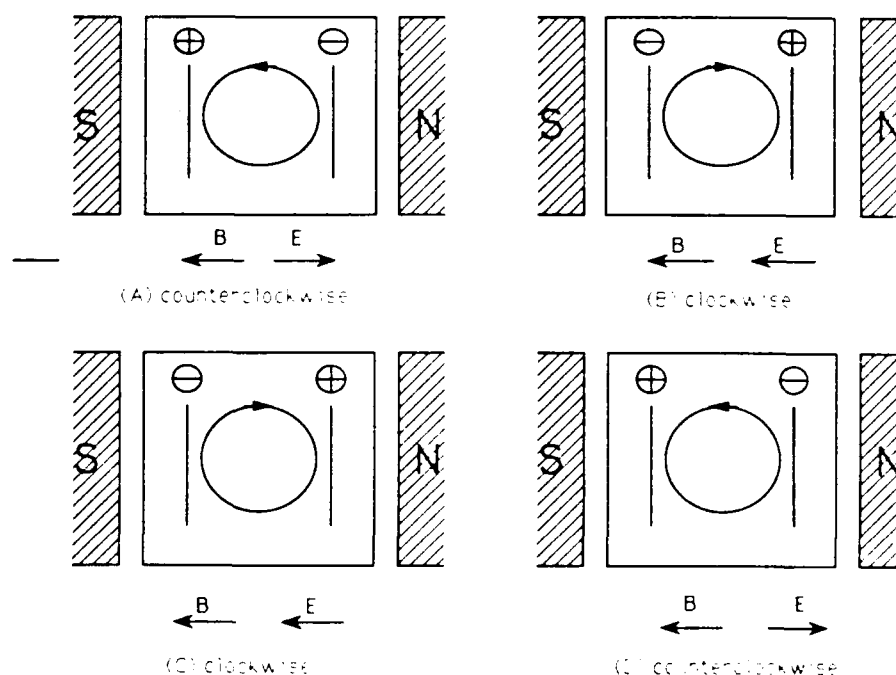


Fig. 11 The rotational hydrodynamic flow generated in an electrochemical cell under the influence of magnetic field; electric field maintained parallel to magnetic field. (A) and (B): bare Pt strip electrodes; (C) and (D): Pt strip electrodes masked with nonconductive adhesive tape from at least 1 cm below liquid surface. Observed from the top of the cell.

Electrochemical generation of hydrodynamic motion generated in the presence of a magnetic field was first reported by F. C. Frary in 1907.¹⁶ Recent attempts have been made to exploit the phenomenon for many applications, including controlled metal plating and agitation.¹⁷ Results have indicated that the shape of the electrodes and the relative electric field directions to the



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applied magnetic field are very important factors with which to control ionic and mass transports. The rather uniform rotational hydrodynamic motion found in our experiments could provide new insight into the phenomenon of magneto/hydrodynamic motion. Further study is needed to elucidate the phenomenon and make it useful for practical applications.



4.0 CONCLUSIONS

The following conclusions have been drawn as a result of this study.

1. Rotating cylinder electropolymerization in neat pyrrole containing a soap supporting electrolyte, CTMATos, in conjunction with high current density can produce aligned PPy films. The key feature in the reproducibility of this method appears to be the presence and/or generation of soluble pyrrole oligomers. Electrical anisotropies up to 60 to one with dc conductivities of 200 S/cm have been observed.
2. Incorporation of inert polymer additives (e.g., PEO) into ionically conductive neat pyrrole electrolyte media can enhance overall PPy film conductivities as well as electrical anisotropies by increasing friction in the rotating cylinder electropolymerization method.
3. Morphology changes with increasing film thickness indicate that soluble pyrrole oligomers (doped or undoped) might be responsible for PPy film alignment; electrical anisotropies are higher on the growing film surfaces than on the electrode surfaces.
4. The mechanism of electrochemical polymerization/deposition of PPy films under hydrodynamic motion is quite different from that under static ones. Further study is needed in order to identify controlling factors for optimization and to potential commercialization. The rotating cylinder anode method should be examined with other conducting polymer systems, such as polyaniline and polythiophenes, which may turn out to be easier to orient. This technique offers many advantages over existing methods of orientation.¹⁸
5. PPy/poly(ethylene oxide) blends are more stretchable than PPy itself, and stretching results in increased film conductivities. Further study is required for this technique to be optimized.



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6. Uniform rotational magnetohydrodynamic motion of the electrolytes takes place when the electrodes are placed in a cell such that the electric field is parallel to an applied magnetic field. The rotational direction of the motion is dependent on electrode polarity and whether unmasked electrodes are completely submerged or not. ¹⁹



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5.0 REFERENCES

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