

AFRL-SR-AR-TR-02-0170

Zwitterionic Electroactive Polymer Actuators

F49620-99-C-0073

Mitchell R. Zakin, Susan T. Pasco, Amy Baldwin
Alan H. Gelb, John C. Magill and Everett B. Anderson

Physical Sciences, Inc.

20020614 176

Approved for public release; distribution unlimited

Air Force Research Laboratory
Air Force Office of Scientific Research
Arlington, Virginia

NL

REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-02-

0170

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing or maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate, suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Avenue, Washington, DC 20540, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE May 15, 2002	3. REPORT TYPE AND DATES COVERED Base Program Final Report, covering the period from 10/99 to 12/01	
4. TITLE AND SUBTITLE Zwitterionic Electroactive Polymer Actuators			5. FUNDING NUMBERS F49620-99-C-0073 JO19-00 JO19-02 62712E	
6. AUTHOR(S) Mitchell R. Zakin, Susan T. Pasco, Amy B. Baldwin, Alan H. Gelb, John C. Magill, and Everett B. Anderson			8. PERFORMING ORGANIZATION REPORT NUMBER PSI-1321/TR-1793	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Physical Sciences Inc. 20 New England Business Center Andover, MA 01810			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) USAF, AFMC 801 N. Randolph St, Rm 732 Arlington, VA 22203-1977			11. SUPPLEMENTARY NOTES	
12a. DISTRIBUTION AVAILABILITY STATEMENT Distribution Statement A: Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE A	
13. ABSTRACT (Maximum 200 words) Physical Sciences Inc. has developed an electroactive polymer-based material that undergoes a reversible conformational transition upon electrochemical reduction/oxidation. The enabling technology is a zwitterionic polyaniline derivative in which generation of +/- charge pairs upon oxidation provides significant conformational distortion along the polymer backbone, and a concomitant change in free volume. This novel actuation mechanism, analogous to that observed in lightly-crosslinked sulfonate gels, was confirmed using circular dichroism spectroscopy of thin supported polymer films. Despite our success in proving the validity of this novel actuation mechanism, the mechanical properties of zwitterionic polyanilines were not suited to the fabrication of polymeric actuators. Molecular mechanics calculations indicated that it may be possible to extend the zwitterionic actuation mechanism to other classes of electroactive polymers. This conjecture will be tested in the Option 1 portion of our proposed effort.				
14. SUBJECT TERMS			15. NUMBER OF PAGES 51	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT	

1. BASE PROGRAM FINAL REPORT

The project objectives, work carried out, results obtained, and estimates of technical feasibility are described in the charts attached as an appendix, presented at the Final Base Program Technical Review held at Physical Sciences Inc. (PSI) on 31 August 2000. DARPA attendees included Dr. Steve Wax, Mr. Randy Sands, Dr. Len Buckley (NRL), and Dr. Charles Lee (AFOSR).

2. PERSONNEL

Mitchell R. Zakin
Susan T. Pasco
Amy B. Baldwin
Alan H. Gelb
John C. Magill
Everett B. Anderson

3. PUBLICATIONS

None.



PHYSICAL SCIENCES INC.

VG02-124

APPENDIX

Zwitterionic Electroactive Polymer Actuators

Physical Sciences Inc.

Base Program Final Report

Contract Number F49620-99-C-0073

Physical Sciences Inc.

20 New England Business Center

Andover, MA 01810

Objective and Technical Approach

Objective

- Develop high-bandwidth, rugged, dry polymeric actuators using an electrostatic-driven mechanism for enhancing conformational changes in polymer structure

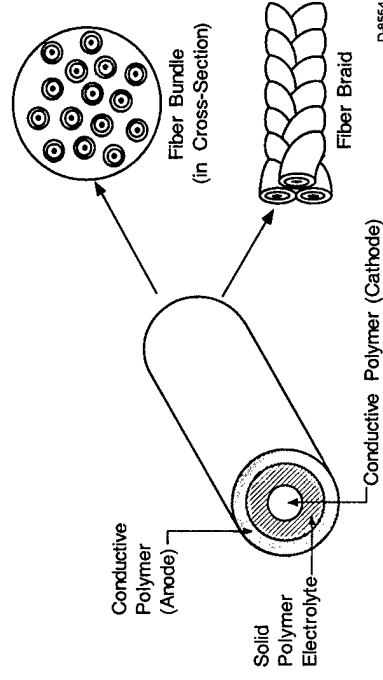
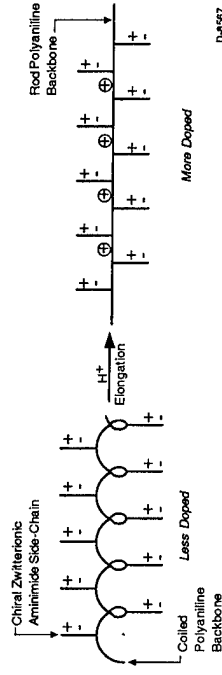
Approach

- Coiled zwitterionic electroactive polymers maximize elongation/contraction for small changes in doping level
- Proton-doping increases speed, eliminates degradative negative counterion transport effects
- Muscle actuation using hydrated solid polymeric ionic conductors including Nafion
- Minimization of device power requirements by minimization of dopant transfer
- Fiber actuator design to “focus” elongation along a single linear dimension

Milestones

- Demonstrate electrostatic “coil-rod” mechanism
- Demonstrate chemical control of actuation mechanism
- Estimate actuator performance

VG02-124-1



ISI

PHYSICAL SCIENCES INC

Key Results

VG02-124-2

- **Were not able to synthesize aminimide-based polyanilines**
- **Demonstrated redox-driven conformational changes for three self-doped polyanilines**
 - self-doped polyanilines exhibit greater electrostatic effects and are easier to synthesize
- **Constructed and tested bender actuators – no actuation observed**
- **Modeled actuator performance and quantified workable ranges for desired material properties**
 - present self-doped polymers lack key properties required for actuator
- **Extended actuator concept to self-doped polythiophenes, which have key advantages over polyanilines**



PHYSICAL SCIENCES INC.

Why Couldn't We Make Aminimide Polyanilines? - 1

VG02-124-3

Synthesis and purification of desired monomers proved problematic

• **Need *electron-donating* aminimides to promote aniline polymerization**

- Common easy-to-make aminimides are electron-withdrawing (carbonyls)
- Well-established one-pot reaction is ineffective for synthesis of electron-donating aminimides
 - low yields
 - products difficult to purify
- Range of applicability of one-pot reaction is much narrower than expected
 - difficult to synthesize desired aminimide variants
 - steric hindrance, electronic effects are strongly deactivating

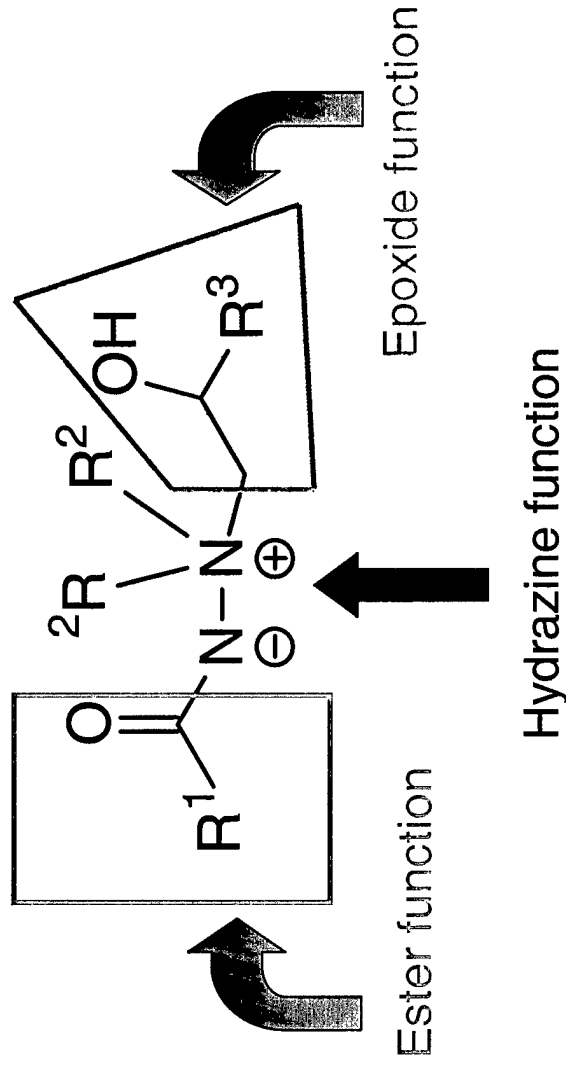
• **Electron-donating aminimides were not prepared in sufficient quantity or quality for polymerization**

PSI

PHYSICAL SCIENCES INC

Anatomy of an Aminimide

VG02-124-4



- Aminimide properties are controlled through variation of the three basic functionalities
- Polymerizable aniline group can be placed on either end (R^1 or R^3)

ESI

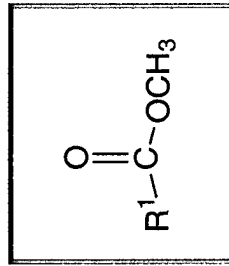
PHYSICAL SCIENCES INC

Aminimide Synthesis

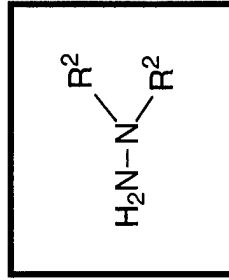
VG02-124-5

- **Best route is simple one-pot reaction for aminimide synthesis**

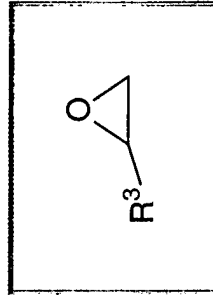
- mix ester, epoxide, 1,1-disubstituted hydrazine in alcohol
- stand at room temperature for ~3 days
- evaporate solvent, recrystallize from ethyl acetate, dry under vacuum
- yield ~ 50-60%



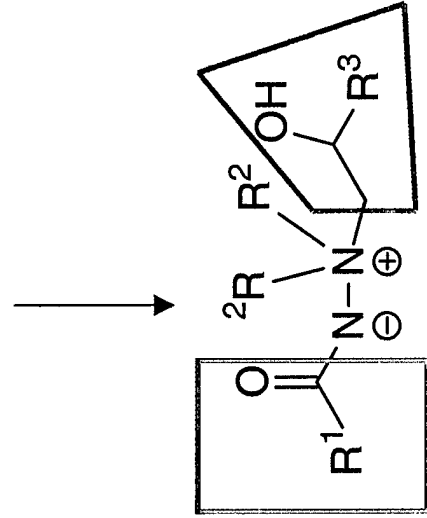
Ester



Hydrazine



Epoxide

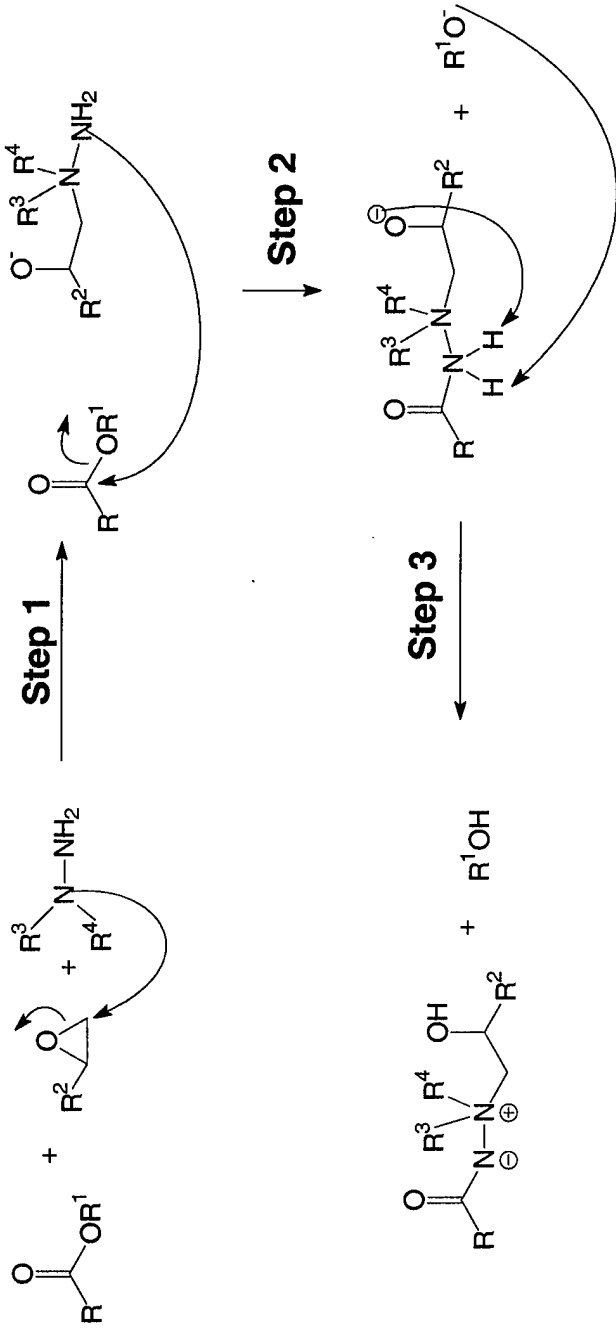


PSI

PHYSICAL SCIENCES INC

Mechanism of One-pot Aminimide Synthesis

VG02-124-6



Step 1: More electron-rich nitrogen on hydrazine attacks less-substituted side of epoxide.
Epoxide opens up.

Step 2: Remaining nitrogen attacks ester. Alkoxide is ejected from ester.

Step 3: Both alkoxides deprotonate nitrogen.

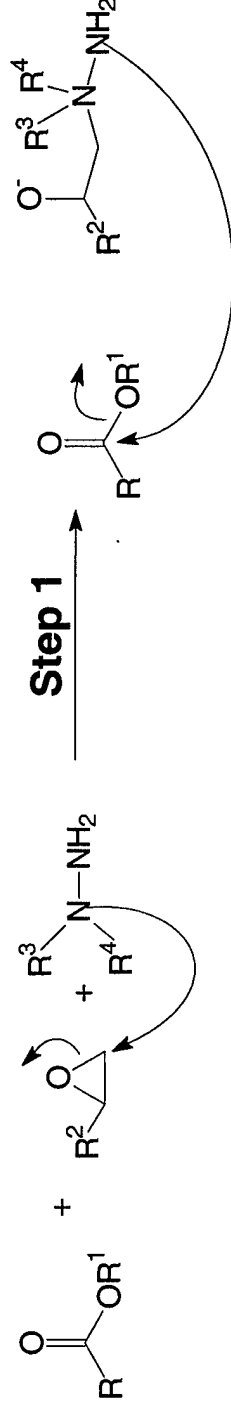
ISI

PHYSICAL SCIENCES INC

What Causes the One-pot Reaction to Fail? - 1

VG02-124-7

- In Step 1:



If R³ and R⁴ are bulky, then attack at the epoxide is sterically hindered

Example:



Dimethyl hydrazine reacts, while diphenyl hydrazine does not.

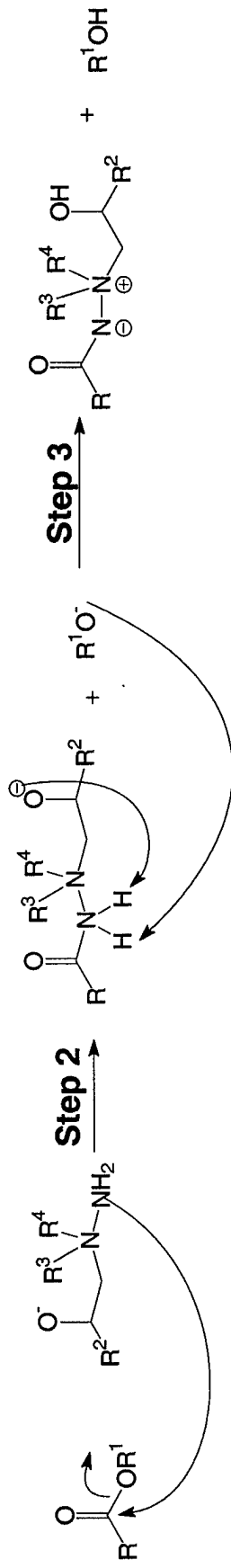
ISI

PHYSICAL SCIENCES INC

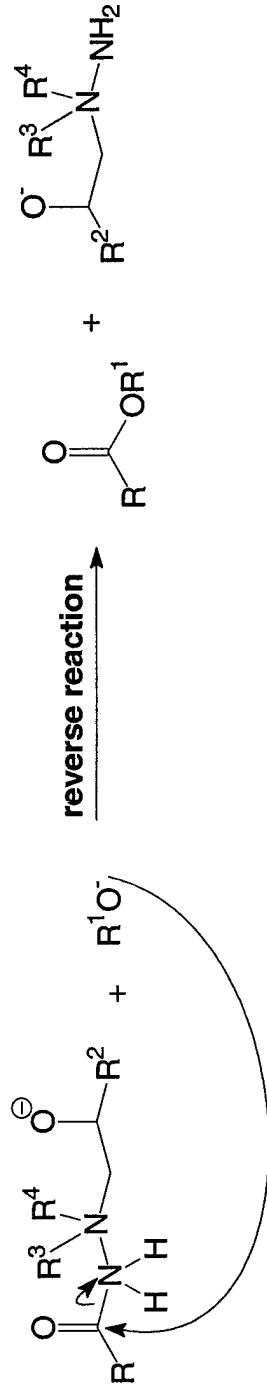
What Causes the One-pot Reaction to Fail? - 2

VG02-124-8

• In steps 2 and 3:



When nitrogen attacks epoxide, deprotonation must occur faster than the reverse reaction:



If R can delocalize charge, then the product is stabilized and the forward reaction is favored. R groups such as phenyl facilitate the forward reaction.

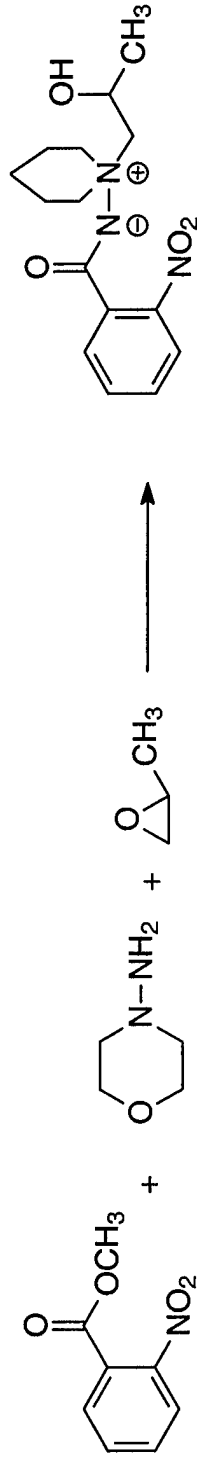
R groups required to synthesize electron-donating aminimide-based aniline monomers cannot delocalize charge sufficiently to drive reaction.

PSI

PHYSICAL SCIENCES INC

Synthesis of Typical Electron-Withdrawing Aminimide Monomer

VG02-124-9



- Reaction was run on a 15 millimole scale
- Purified by recrystallization from ethyl acetate
- Product yield was ~30%

This reaction was successful because the hydrazine is not too bulky and because the negative charge on the final product can be delocalized.

Yield was moderate because the hydrazine derivative is somewhat bulky and because some product is lost in the purification process.

ISI

PHYSICAL SCIENCES INC

Attempted Syntheses of Electron-Donating Aminimide Monomers - 1

VG02-124-10

- Short-chain ester reactant cannot delocalize charge on nitrogen; thus reaction is hindered
- Bulky morpholino hydrazines further slow down reaction
- HPLC of crude product mixture shows 3-15 peaks, indicating incomplete reaction sequence and/or multiple mechanistic pathways
- Literature suggests *one* pathway
- All reactions have a common unknown side-product

ISI

PHYSICAL SCIENCES INC

Attempted Syntheses of Electron-Donating Aminimide Monomers - 2

VG02-124-11

- Longer-chain ester reactant
- Results qualitatively similar to short-chain ester, but with lower product yield
- HPLC analysis indicates that glycidol produces the most side-products, perhaps due to a competing trans-esterification reaction
- All products have a common unknown side-product

ISI

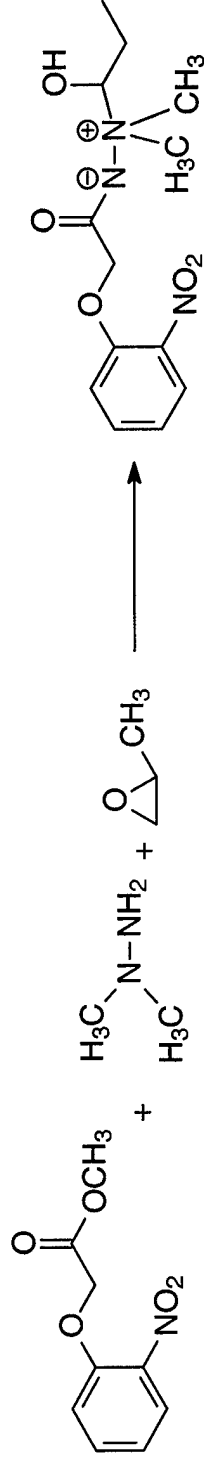
PHYSICAL SCIENCES INC

Purification of Aminimides from Crude Reaction Mixture

VG02-124-12

HPLC and TLC indicate that there are typically 3-15 products and starting materials in reaction mixture

- Low-boiling starting materials can be removed by vacuum
- Recrystallizations from ethyl acetate or *iso*-propanol were unsuccessful
- Chromatography could not separate products

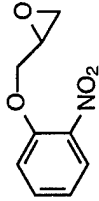
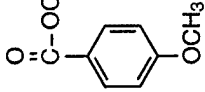
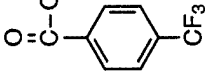
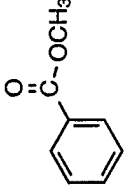
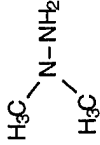
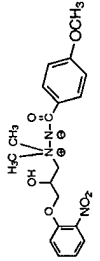
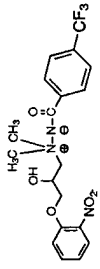
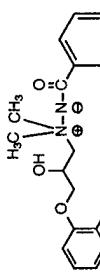
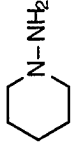
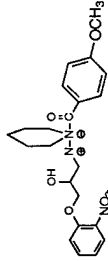
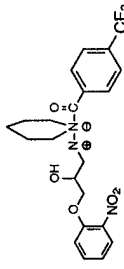
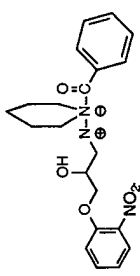


ISI

PHYSICAL SCIENCES INC

Attempted Syntheses of Electron-Donating Aminimide Monomers - 3

VG02-124-13

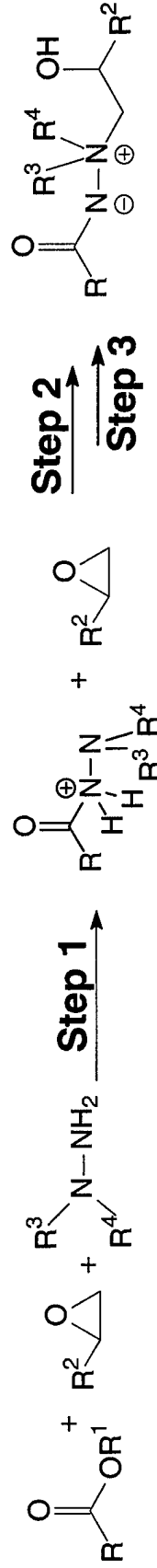
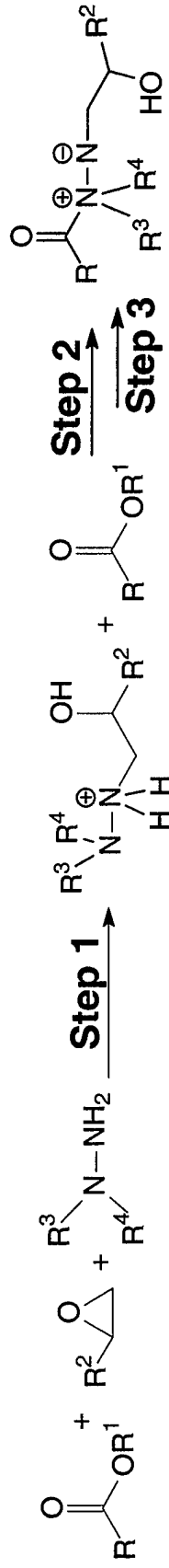
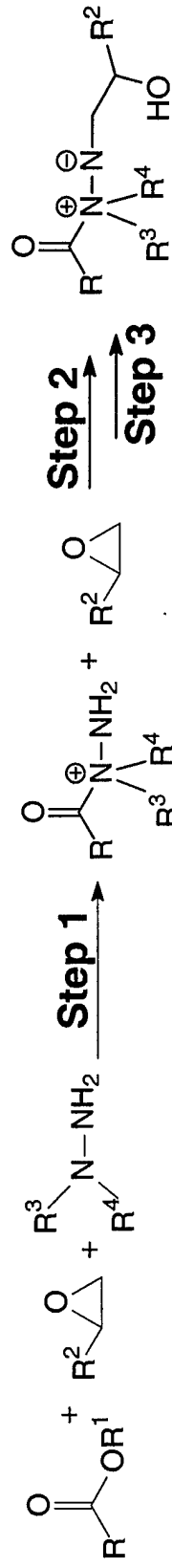
- Epoxide reactant designed to place aniline on opposite end of aminimide moiety
- Reactions “should” work, since esters can delocalize charge
- All reactions yielded at least 6 products according to HPLC analysis
- Results indicative of multiple partially completed mechanistic pathways

ISI

PHYSICAL SCIENCES INC

Alternate Aminimide Mechanistic Pathways

VG02-124-14



ISI

PHYSICAL SCIENCES INC.

Why Couldn't We Make Aminimide Polyanilines? - 2

VG02-124-15

Attempts to polymerize electron-withdrawing aminimide monomers proved unsuccessful

Steric hindrance of bulky aminimide moiety severely inhibits polymerization

- reduces polymerization rate
- lowers MW due to higher probability of chain termination

Electron-withdrawing substituent on aniline ring inhibits oxidation at p-position required for chain propagation

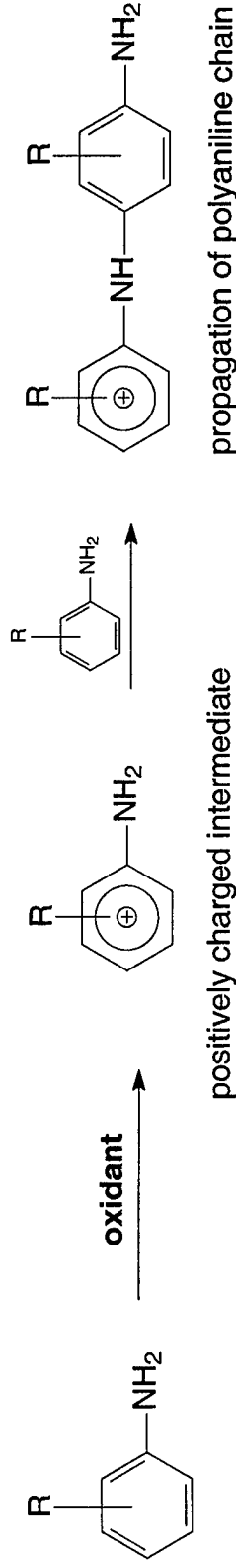
Direct conversion of polyaniline esters to aminimides via the one-pot reaction not feasible due to low polymer purity

The logo for ESI (Electrostatic Interaction) consists of the letters 'ESI' in a stylized, bold, serif font. The 'E' and 'S' are connected at the top, and the 'I' is separate.

PHYSICAL SCIENCES INC

Polymerization of Substituted Anilines

VG02-124-16



Electronics are important:

- Polymerization proceeds via a positively charged intermediate
- If R is electron-withdrawing, then intermediate is destabilized
- If R is electron-donating, then intermediate is stabilized
- Destabilization of intermediate leads to **chain termination**
- Position that is *para* to the NH_2 is most activated \Rightarrow polyaniline is all *para*-linked

Sterics are also important:

- If R is *ortho* to NH_2 then reaction proceeds faster than if R is *meta*
- Reaction is fastest if R is H

Electron-withdrawing aminimide-substituted anilines do not polymerize!!

ISI

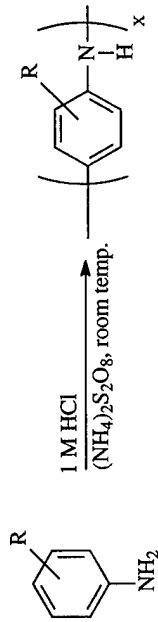
PHYSICAL SCIENCES INC.

Methodology for Polymerization of Substituted Anilines

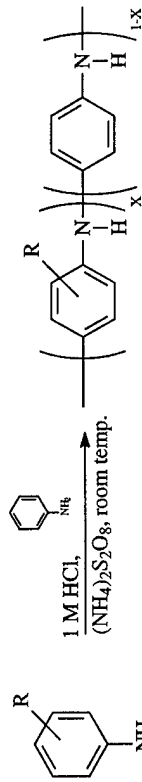
VG02-124-17

Three primary methods – all use $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as oxidant

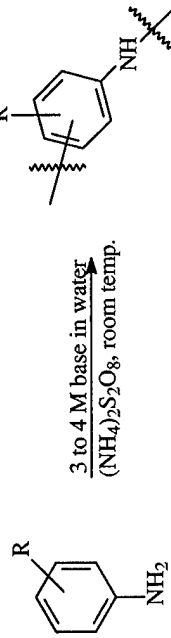
1. Acidic conditions



2. Copolymerization with aniline under acidic conditions



3. Basic conditions

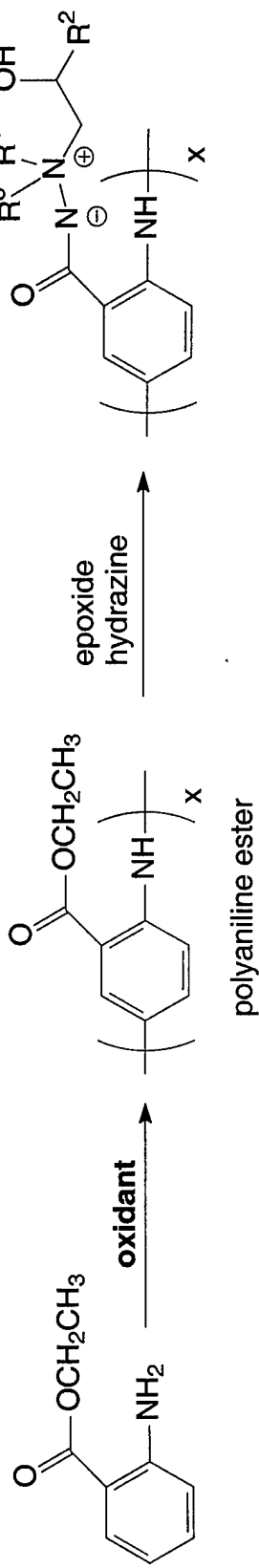


ISI

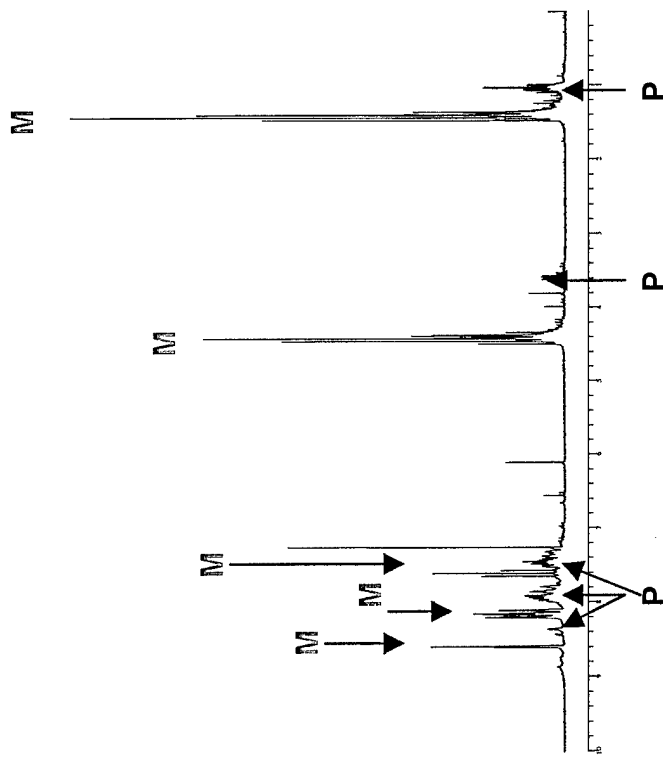
PHYSICAL SCIENCES INC

Alternate Synthesis of Aminimide Polyanilines

VG02-124-18



Polymerization of ester failed due to electron-withdrawing effect on aniline
— yield is 1.3% after 24 hr reaction, but consists mostly of monomer or short oligomer



sample #6, poly(ethyl-3-aminobenzate)

ISI

PHYSICAL SCIENCES INC.

Aminimide-Based Polyanilines - Conclusions

VG02-124-19

- **We never produced aminimide polyanilines**
- **Aminimide-based actuators could not be constructed and characterized**
- **Feasibility of proposed actuation concept could not be evaluated**



PHYSICAL SCIENCES INC

Rationale for Self-Doped Polymers as Actuators

VG02-124-20

- **Actuation mechanism analogous to aminimide polyanilines**
- **Stronger electrostatic interactions should generate enhanced conformational distortion (ion-ion versus ion-dipole)**
- **Synthesis of self-doped polymers is more tractable**

Advantages	Disadvantages
More facile synthetic procedures	May be water-soluble
Processible from organic solvents	Mechanical properties largely unknown
Strong redox-reversible electrostatic forces	Films hard to cast, can be brittle
Compatible with broad range of electrolytes	Lower electrical conductivity than polyaniline
Fixed dopant counterions may increase actuation speed	Redox characteristics largely unknown



PHYSICAL SCIENCES INC.

Actuation Mechanism for Self-Doped EA Polymers

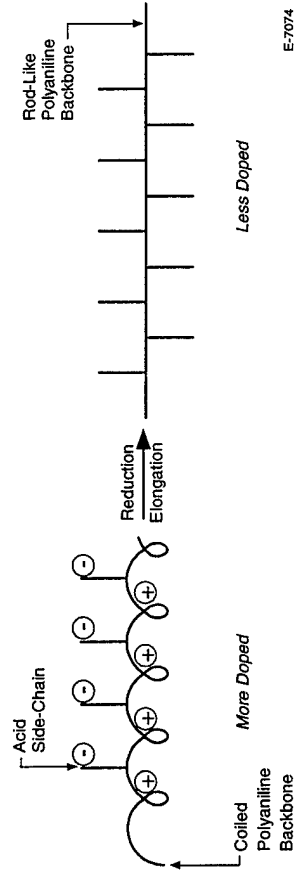
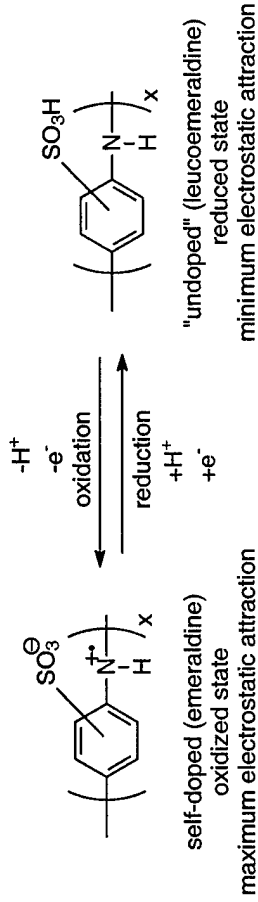
VG02-124-21

• **Strong acid groups (-SO₃H) dope polymer; negative counterions remain fixed to polymer backbone**

- doping creates charge separation
- redox processes cannot uptake/expel counterions
- reversible electrostatic interaction between negatively charged side-chain and + backbone upon redox provides reversible conformational distortion

• **Lack of counterion diffusion should increase actuation speed (rate-limiting step)**

• **Prototypical self-doped EA polymer is SPAN (sulfonated polyaniline)**



ISI

Self-doped EA Polymers Resemble Responsive Gels

VG02-124-22

Four fundamental forces control behavior of most responsive gels

The diagram is divided into four quadrants, each showing a different type of interaction between polymer chains:

- Ionic interactions:** Shows two polymer chains with negatively charged carboxylate groups (COO^-) and a positively charged ammonium group (NH_3^+) interacting.
- Hydrophobic interactions:** Shows a benzene ring and a hydrocarbon chain ($\text{H}_3\text{C}-\text{CH}-\text{CH}_2-\text{CH}_3$) interacting with a water molecule. The hydrocarbon chain is also shown with a methyl group (CH_3) and a methylene group (CH_2).
- Hydrogen bonding:** Shows two polymer chains with amide groups ($\text{C}=\text{O}$ and $\text{N}-\text{H}$) interacting via hydrogen bonds, represented by dashed lines between the oxygen of one chain and the hydrogen of another.
- Van der Waals forces:** Shows two polymer chains with amide groups ($\text{C}=\text{O}$ and $\text{N}-\text{H}$) interacting in a nonpolar solvent.

These forces are responsible for the gel's ability to interconvert between two phases. In one phase, environmental conditions cause the attractive forces to be stronger and the gel collapses, expelling solvent in the other phase. Environmental conditions cause the repulsive forces to be stronger, thus expanding the gel with absorption of solvent.

Source: Toyochi Tanaka, Gel Sciences GmbH

ESI

PHYSICAL SCIENCES INC

How Do We Expect Self-Doped Polymers to Perform?

VG02-124-23

- **Self-doped polymers should exhibit a strong transition from a tightly coiled form in the oxidized (ionized) state to a less coiled form in the reduced (neutral) state**
 - the coiling-uncoiling transition will produce a significant redox-reversible change in polymer dimension (e.g., volume)
- **Linear bending actuators constructed from self-doped polymers will exhibit greater actuation, generated by proton transport, than identical “baseline” polyaniline actuators**



PHYSICAL SCIENCES INC.

Proof-of-Concept Experiments Performed

VG02-124-24

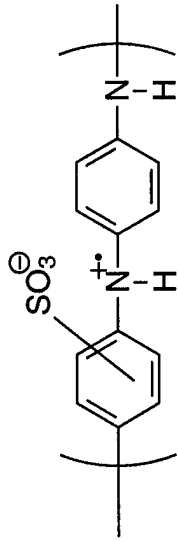
- **Synthesized three self-doped polyanilines with different structural and electronic characteristics**
- **Fabricated thin polymer films for conformational analysis**
- **Characterized redox-induced coiling-uncoiling transition using circular dichroism (CD) spectroscopy**
- **Performed molecular mechanics calculations of polymer coiling and compared to CD results**
- **Built and characterized linear bending actuators from self-doped polymers**



PHYSICAL SCIENCES INC

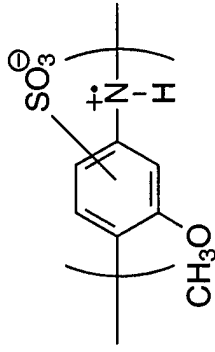
Characteristics of Self-Doped Polyanilines

VG02-124-25



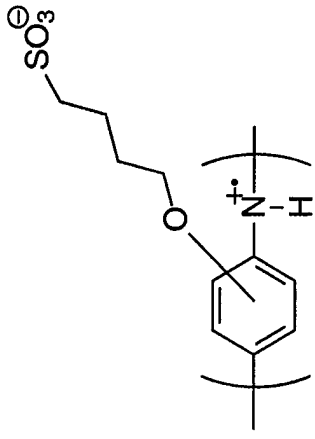
ZPani

- SO_3^- on alternate monomer units



ZPani-activated

- SO_3^- on every monomer unit
- electron-donating $-\text{OCH}_3$ delocalizes + charge
- higher conductivity



ZPani-spacer

- SO_3^- on every monomer unit
- increased distance between SO_3^- and + charge
- lower conductivity

ISI

PHYSICAL SCIENCES INC

Synthesis and Properties of Self-Doped Polyanilines

VG02-124-26

Polymer	ZPani	ZPani - activated	ZPani - spacer
Conductivity	10^{-4} S/cm; 0.01 S/cm	0.1 S/cm	0.005 S/cm
M_w (GPC vs. polystyrene std)	10,000; 84,000 Daltons	10,400 Daltons	10,000 Daltons (est)
Polydispersity	4	1.42	---
Solubility	DMSO, NMP/NEt ₃	Water, DMSO	Water, DMSO
Monomer substituent properties	Strongly electron-withdrawing	Both e-withdrawing and donating; meta and para linkages possible	Electron-donating
Polymerization Method	Sulfonation of PAni with fuming sulfuric acid	Oxidative under basic conditions	Oxidative under acidic conditions



PHYSICAL SCIENCES INC

Polymer Conformational Analysis by CD Spectroscopy

VG02-124-27

- **Circular dichroism (CD) spectroscopy is the only practical method for solid-state polymer conformational analysis**
 - CD signal (ellipticity) is difference in absorbance of right- and left-circularly polarized light by structural features (coils)
 - CD signals arise only at (strong) polymer absorption bands
 - most sensitive to asymmetric (i.e., chiral) conformations
 - technique demonstrated for polyanilines by MacDiarmid and Wallace
- **CD spectrum measures handedness (+ or -) and relative abundance of conformational features**
 - best for comparison of changes in coiling due to redox, chiral processing, etc.
- **Relevant polyaniline spectral absorption features occur in the visible region**

PSI

PHYSICAL SCIENCES INC

Experimental Procedure for Conformational Analysis

VG02-124-28

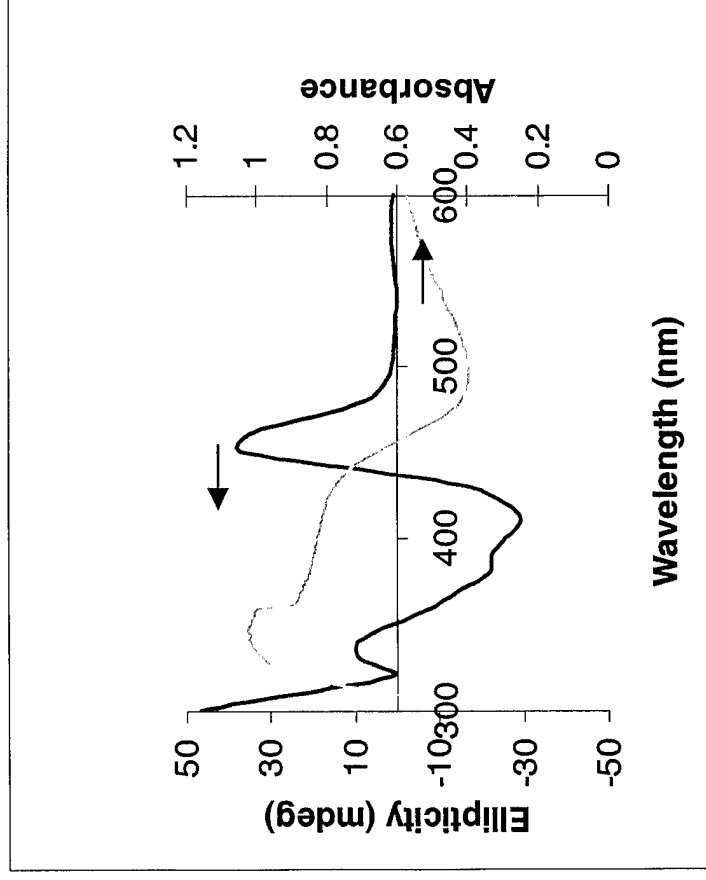
- **Synthesize self-doped polyaniline**
- **Fabricate polymer thin-film from DMSO onto glass slide by casting**
- **Obtain UV-Vis spectrum to confirm oxidation state**
- **Measure CD spectrum to determine polymer coiling**
- **Switch polymer oxidation state (emeraldine to leucoemeraldine) using chemical means**
 - soak polymer film in solution of oxidizer (m-chloroperoxybenzoic acid) or reducing agent (hydrazine) in isopropanol
- **Measure CD spectrum to determine redox-induced change in coiling**

ISI

PHYSICAL SCIENCES INC.

CD Spectrum of Chiral-Doped Polyaniline

VG02-124-29



- Polyaniline does not exhibit native asymmetric backbone coiling (absence of CD spectrum)
- Doping with the chiral dopant camphorsulfonic acid (+CSA) introduces +chiral polymer conformation
- CD bands correlate with UV-Vis absorption features of emeraldine (oxidized) state

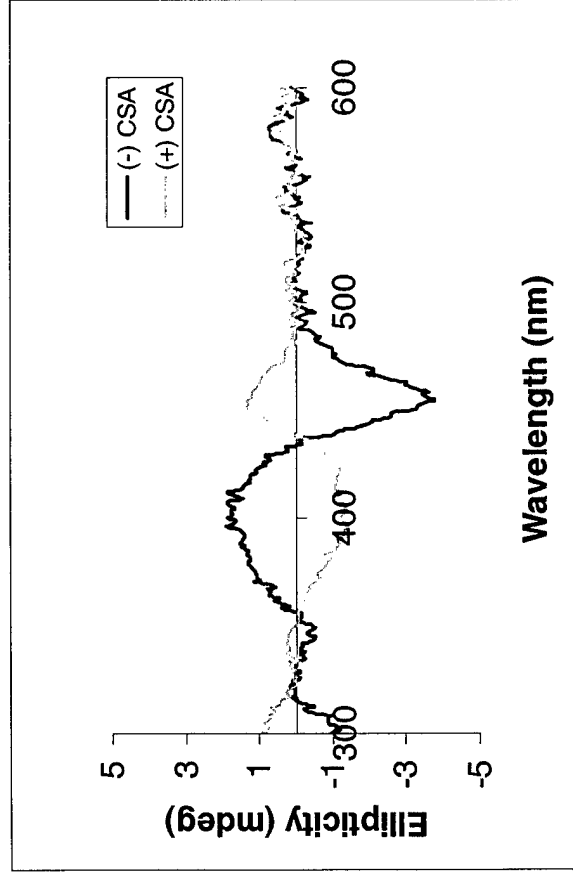
ISI

PHYSICAL SCIENCES INC

Chiral Processing Alters Polyaniline Chirality

VG02-124-30

- Generate mirror-image conformations of polyaniline backbone via incorporation of mirror-image dopants (\pm)CSA
- Initial polymer conformation can be “locked in” by chiral processing
- Coiling also affected by choice of solvent for film fabrication

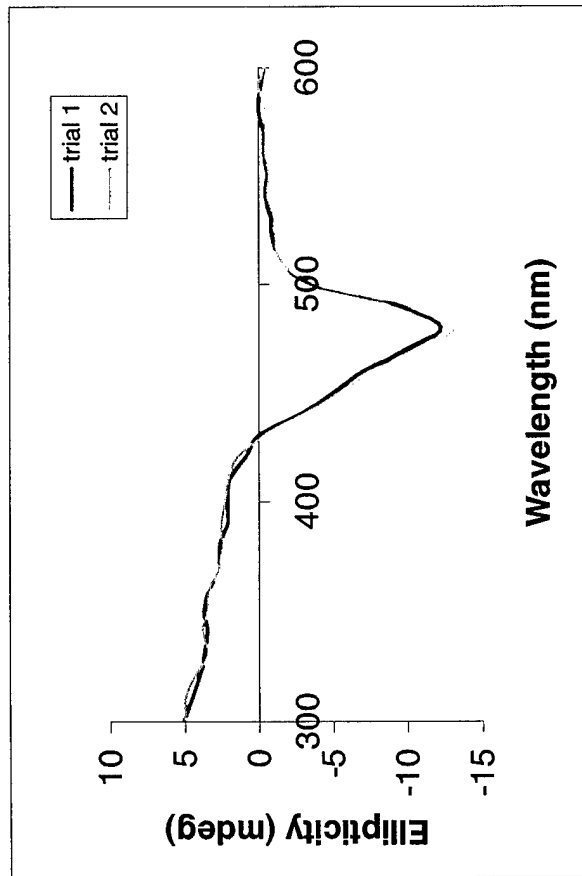


ESI

PHYSICAL SCIENCES INC

Reproducibility of CD Spectral Measurements

VG02-124-31



- ZPani-activated film in oxidized state
- Remove, re-insert film into Jasco J-710 spectropolarimeter

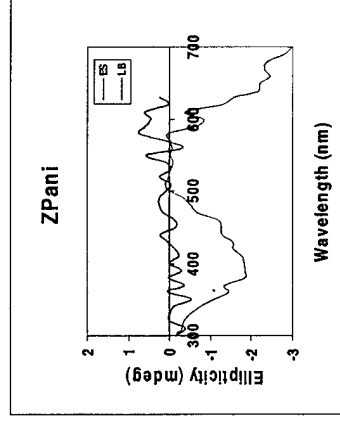
ISI

PHYSICAL SCIENCES INC

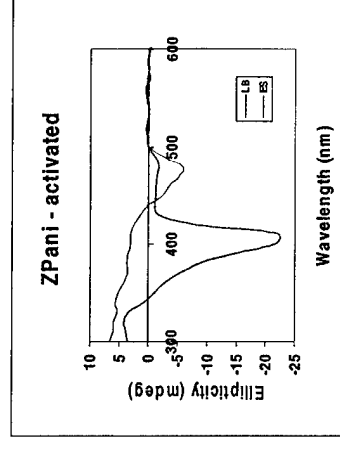
Conformation of Self-Doped Polyanilines Depends on Oxidation State

VG02-124-32

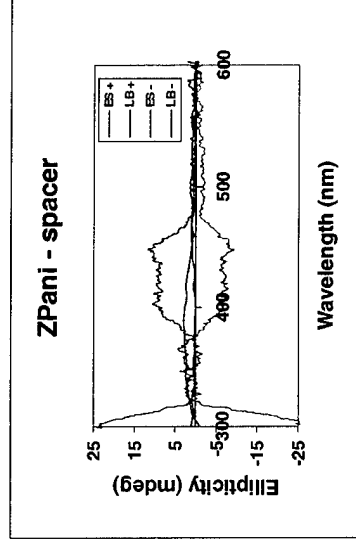
- Self-doped polyanilines exhibit different chiral backbone conformations in the oxidized (ES) and reduced (LB) forms
- Small structural and electronic differences produce striking changes in coiling/uncoiling behavior
- Simple “isolated polymer chain” electrostatics are in general agreement with, but not sufficient to explain, observed results
 - chain-chain electrostatic and steric coupling are key conformational drivers
- Close proximity of acid group to backbone appears to be required for native (intrinsic) asymmetric polymer coiling
- Polymer films craze/delaminate from substrate during redox, thus “actuate”



Native coiling; decreased upon reduction



Native coiling; enhanced upon reduction



Chirally processed coiling; decreased upon reduction

PSI

PHYSICAL SCIENCES INC

Molecular Mechanics of Electroactive Polyanilines

VG02-124-33

- **Performed configurational calculations using HyperChem commercial software package**
 - molecular mechanics with MM+ force field; allows charges
 - reduced and oxidized forms of isolated polymer chains
- **Self-doped polyanilines are more coiled than polyaniline**
- **Investigated effect of spacing between acid group and polymer backbone on conformation**
 - smaller spacing provides greater coiling in oxidized state, greater reduction in coiling in reduced state
 - ZPani exhibits largest coil-uncoil transition upon redox
 - ZPani-spacer exhibits greatest coiling in *half-oxidized* state
- **Calculations generally consistent with CD measurements**

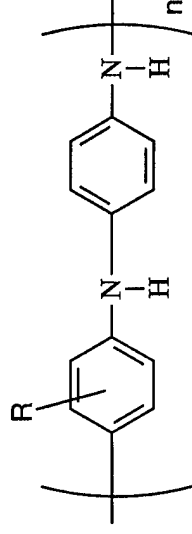
Systems studied:

R = H (n=32) - *polyaniline*

R = SO₃H (n=32) - *ZPani*

R = O(CH₂)₃SO₃H (n=16) – “*ZPani-spacer*”

R = O(CH₂)₆SO₃H (n=16)

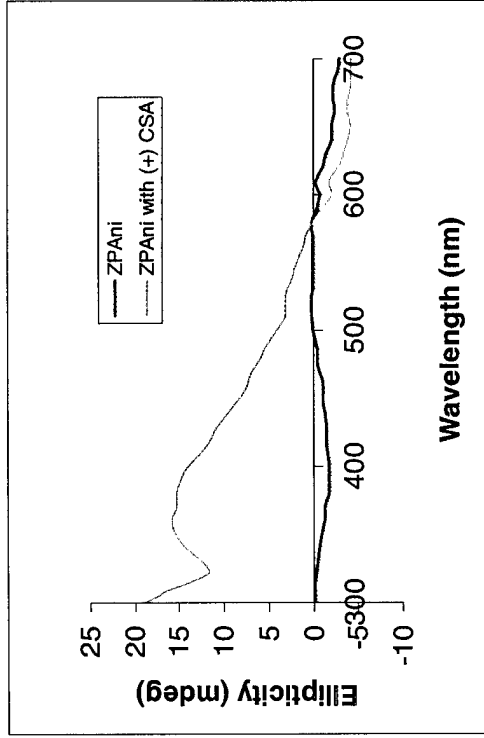


PSI

PHYSICAL SCIENCES INC.

Chiral Processing Alters Self-Doped Polymers

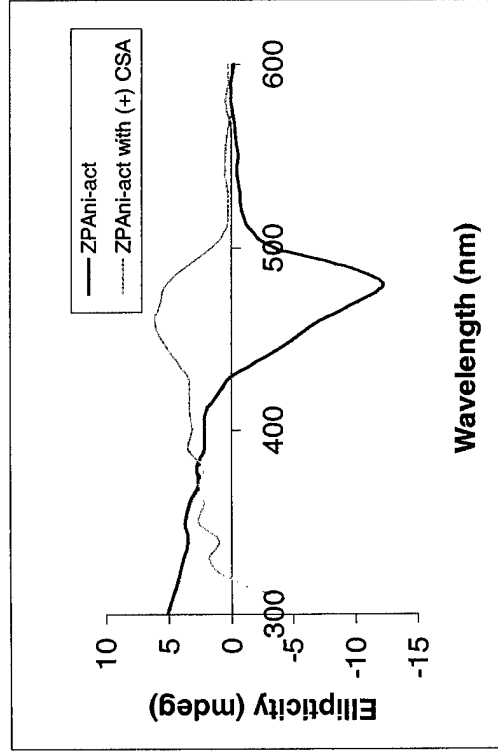
VG02-124-34



- **Add (+) or (-)CSA to self-doped polymer in DMSO solution, cast film**
 - ZPani in oxidized state
 - ZPani-activated in reduced state
 - conductivity affected by CSA treatment?

- **Chiral dopant forces polymer to change conformation of backbone (handedness)**

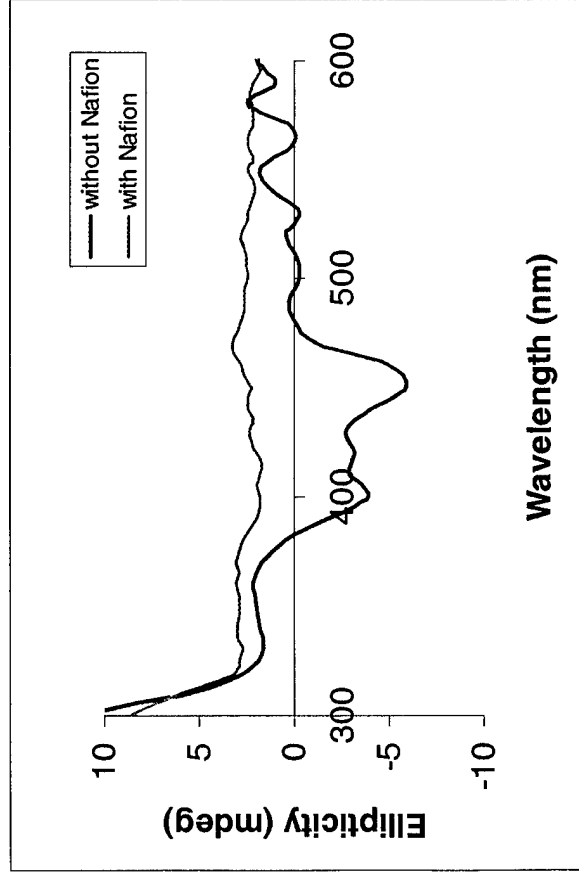
- **Chiral processing alters conformation of both polyaniline and self-doped polyanilines**



PHYSICAL SCIENCES INC

Effect of Nafion Electrolyte on Polymer Coiling

VG02-124-35



Blending of 30% (w/w) Nafion into ZPani-spacer with (+)CSA dopant reduces coiling

- Nafion is an acidic sulfonated fluoropolymer which acts as a large immobile dopant, holding ZPani backbone in place
- similar results observed for other ZPani self-doped polymers

Constrains actuator design to polymer-Nafion-polymer layered configuration

PSI

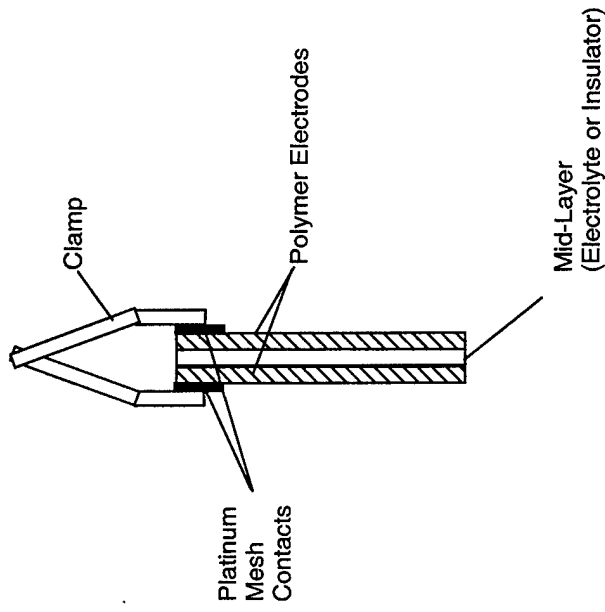
PHYSICAL SCIENCES INC

Construction and Testing of Polymer Actuators

VG02-124-36

- **Constructed simple bender actuators**
 - polymer-insulator and polymer-Nafion sandwich configurations
 - studied polyaniline and ZPani
- **Poor film quality and poor adhesion to Nafion hindered fabrication and characterization of proton-transfer actuators**
- **Actuation observed only for polyaniline in aqueous HCl electrolyte— ZPani did not bend**
 - Polyaniline conductivity 25-40 S/cm
 - ZPani conductivity ~ 0.01 S/cm

Bender Construction



- **Three-layer construction bends due to differential strain in electrodes**

ISI

PHYSICAL SCIENCES INDI

Bender Polymer Properties

VG02-124-37

Polyaniline

- conductivity 25-40 S/cm
- poor solubility in NMP and DMSO, but casts well from DMPU
- strong free-standing films possible
- good films were approximately 13 μm thick

ZPani

- conductivity ~ 0.01 S/cm hydrated
- various solvents and drying processes were tried, but best films were cast from NMP
- films have low tensile strength and are thus very fragile
 - limiting factor in actuator fabrication and testing
- films were approximately 5 μm thick
- material is weakly water-soluble
- bonding to ZPani films is difficult

ISI

PHYSICAL SCIENCES INC

Material Test Matrix and Results

VG02-124-38

#	Electrode	Mid-Layer	Bath	Bending?
1	PANI	Tape	1M HCl	Yes
2	PANI w / Nafion Coat	Tape	1M HCl	No
3	PANI	Nafion	1M HCl	Yes
4	PANI	Nafion	Air	No
5	ZPani	Nafion	Air	No
6	ZPani	Platinized Nafion	DIUF	No
7	ZPani	Tape	1M HCl	No



PHYSICAL SCIENCES INC

Conclusions – Polyaniline Conformational Studies

VG02-124-39

- **The conformation of self-doped polyanilines depends on oxidation state**
- **Polymer coiling decreases as spacing between negatively-charged acid side-chain and positively-charged backbone increases**
- **Electron-donating groups appear to partially screen electrostatic interactions to reduce coiling in oxidized state**
- **Polymer chiral conformation can be altered by material processing**
- **Blending of Nafion into self-doped polyanilines reduces asymmetric coiling**
- **Not able to achieve actuation of self-doped polymers (due to insufficient conductivity)**



PHYSICAL SCIENCES, INC.

Conduction Model for Linear Actuators

VG02-124-40

Redox reactions driven by local overpotential

$$\eta(x) = \eta(0) - V_{iR}(x)$$

$i(x) = i_0 e^{\alpha \eta(x)}$ (Butler-Volmer equation); $\alpha \sim 20 \text{ V}^{-1}$

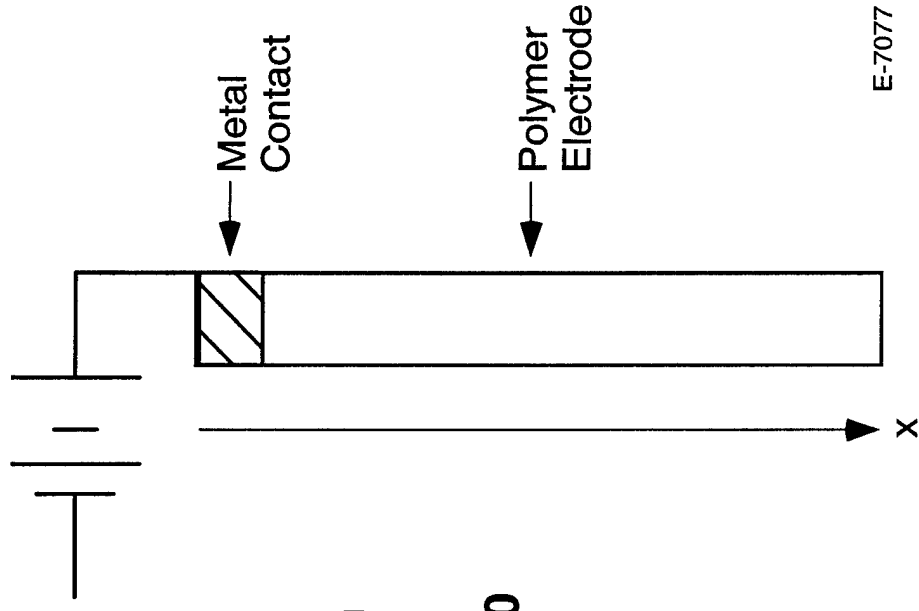
Electrical conductivity must be sufficiently high so that $V_{iR}(x)$ small

$V_{iR}(x) \sim 0.1 \text{ V}$ decreases local rate by factor of 10 relative to $V_{iR}(0)$ (contact point)

Parameters for PANI-type electrodes

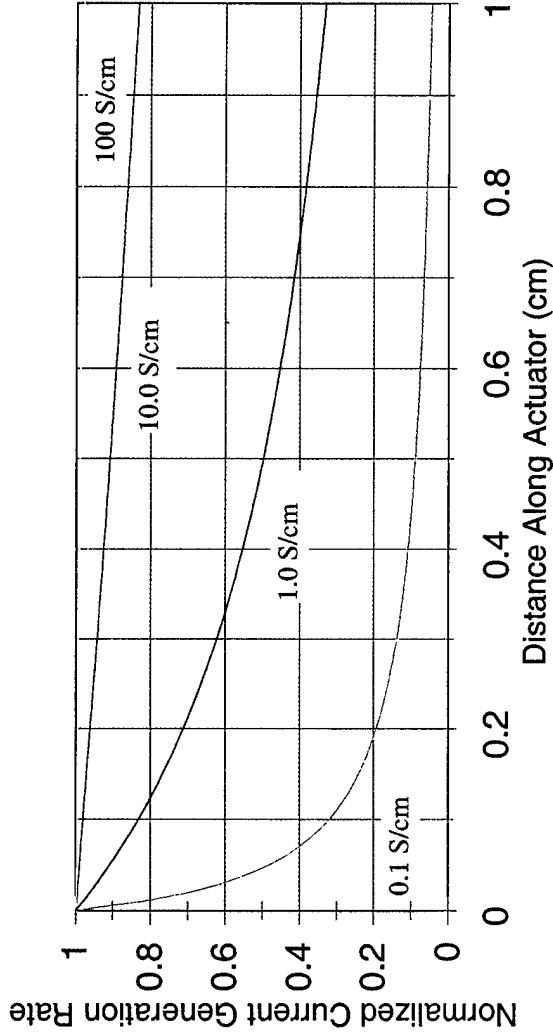
- 20 μm thick
- length = 1 cm, width = 0.1 cm
- $Q = 100 \text{ mC}$
- switching time = 1.0 second
- \therefore total current = 100 mA

Conclusion: high conductivity required



Variation of Current Along Linear Polymeric Actuator

VG02-124-41



Current declines along length of polymer electrode due to resistive (iR) losses

- effect greatest at lowest conductivities
- for modest actuator length (1 cm), effective actuation only achievable for $\sigma \geq 10$ S/cm
- self-doped polyanilines presently have insufficient conductivity (< 0.01 S/cm) to exhibit actuation

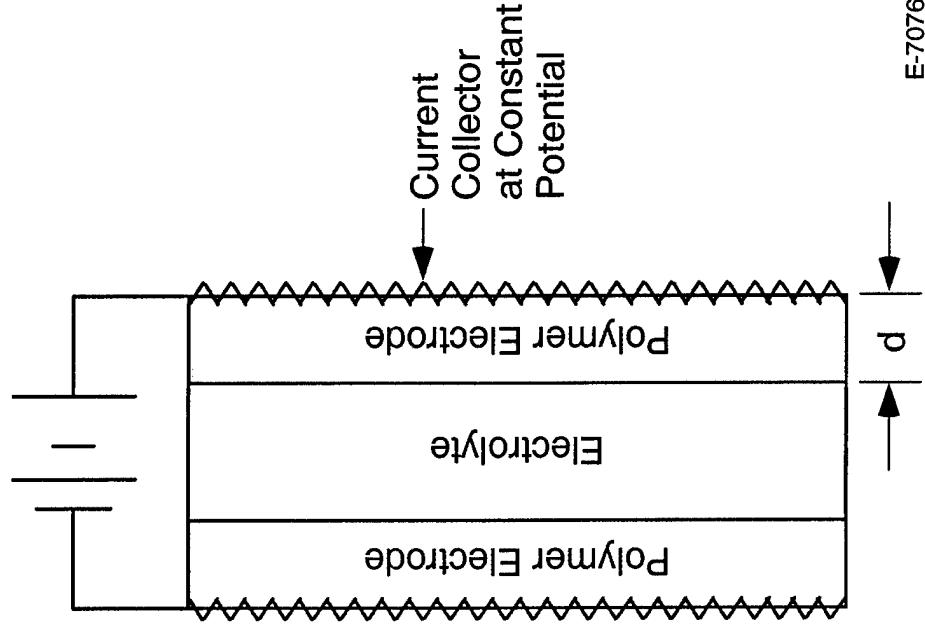
PSI

PHYSICAL SCIENCES INC

Conductivity Model for Cell Actuators

VG02-124-42

- Polymer density $\rho = 1 \text{ g/cc}$
- Electrode thickness d
- Equivalence weight $\omega_e = 200 \text{ amu}$
- Actuation time t
- Current i , current density j
- $j = F (\rho d / \omega_e) / t$ required for actuation
- $j \sim e^{\alpha(\eta - iR)}$ Butler-Volmer equation ($\alpha \sim 20 \text{ V}^{-1}$)
- Want efficient electrode redox:
 - $j_{\min} / j_{\max} \sim 0.5 \Rightarrow \alpha(-iR) \sim 0.4$
- Conclusion: 1 to 10 S/cm required

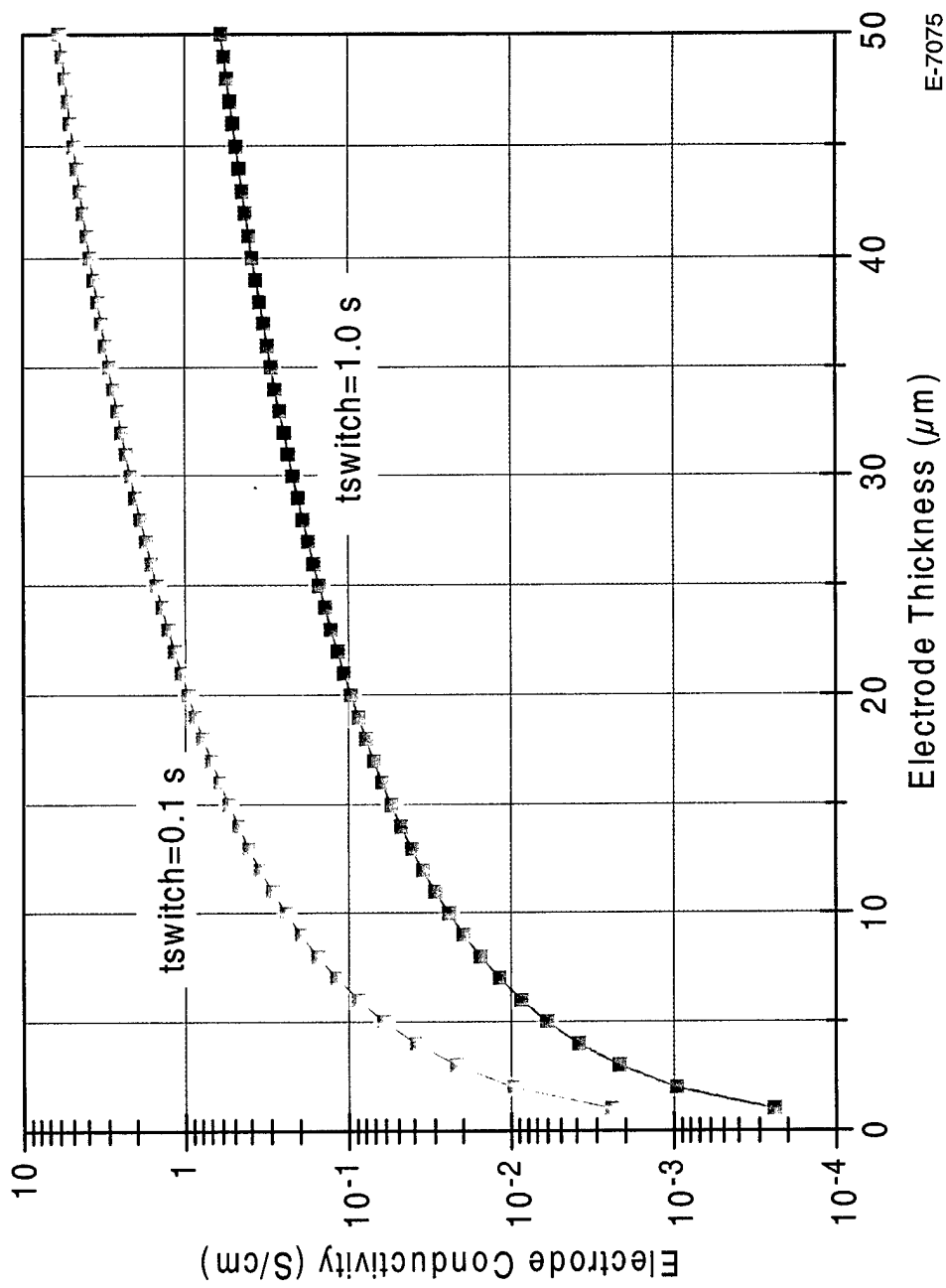


ISI

PHYSICAL SCIENCES INC

Polymer Conductivity Required for Efficient Redox

VG02-124-43



ISI

PHYSICAL SCIENCES INC.

Desired Material Properties for Self-Doped Actuators

VG02-124-44

Based on experiments and modeling, we conclude that the following minimum polymer characteristics are required for actuation:

- **Conductivity ≥ 10 S/cm**
- **MW > 10,000 amu**
- **Insoluble in water**
- **Soluble in organic solvents**
- **Processible from organic solvents**

The logo for Physical Sciences, Inc. (PSI) features the letters 'PSI' in a large, stylized, serif font. The 'P' and 'S' are connected at the top, and the 'I' is separate. The letters are white with a black outline.

PHYSICAL SCIENCES INC

Concept Extension – Polythiophenes as Self-Doped Actuators

VG02-124-45

Polythiophenes have several key advantages:

- **High conductivity (regioregular versions ≤ 1000 S/cm)**
- **Simpler, more rapid polymerization**
 - works for monomers containing bulky side-groups
 - monomers harder to make, but significant literature exists (Reynolds)
- **Exhibit fast redox switching, long cycle lifetime in electrochromic cells (Reynolds)**
- **Strong chiral coiling observed for dibutoxy derivatives (Meijer)**
- **Simple two oxidation state system (unlike polyanilines)**
- **Self-doped versions have conductivities $\sim 5 - 10$ S/cm (LeClerc)**
- **PSI has significant polythiophene experience for sensor applications**

PSI

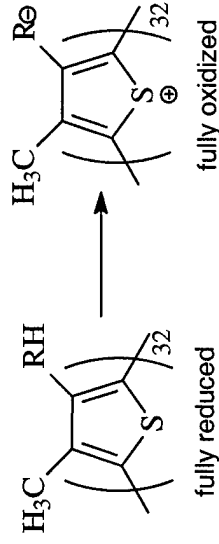
PHYSICAL SCIENCES INC

Molecular Mechanics of Self-Doped Polythiophenes

VG02-124-46

- Performed configurational calculations for representative self-doped polythiophenes as a function of oxidation state

– $R = -O(CH_2)_2SO_3$, $R = -(CH_2)_2SO_3$ (water-soluble)



- Calculations predict reduction of polymer “size” with progressive ionization of acid side-chains (oxidation)

Ionization State	End-to-End Distance (Å)	
	$R = -(CH_2)_2SO_3$	$R = -O(CH_2)_2SO_3$
Fully reduced	77	86
50% oxidized	24(l), 45(w)	24(l), 50(w)
Fully oxidized	20(l), 40(w)	32(l), 37(w)


ISI

PHYSICAL SCIENCES INC

Option Program – Technical Objectives

VG02-124-47

- **Synthesize and characterize self-doped polythiophene and polyaniline copolymers with desired properties**
- **Construct and characterize “dry” self-doped actuators**
 - Nafion or other appropriate electrolyte
 - Measure performance characteristics (speed, cycle operating lifetime, etc.) and compare to polyaniline or polythiophene baseline actuator
- **Perform detailed CD analysis on actuator materials to confirm polymer coiling, relate coiling to actuator performance**
- **(Investigate aqueous-based actuation with H₂O-soluble EA polymers??)**

The logo for ISI (ISI Physical Sciences Inc.) consists of the letters 'ISI' in a large, bold, serif font. The letters are closely spaced and have a slightly distressed or textured appearance.

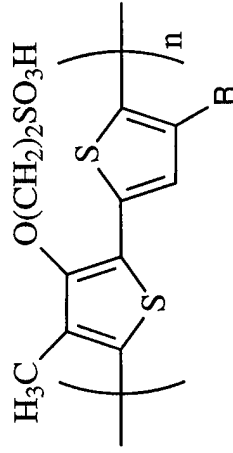
PHYSICAL SCIENCES INC.

Candidate High-Conductivity Self-Doped EAPs

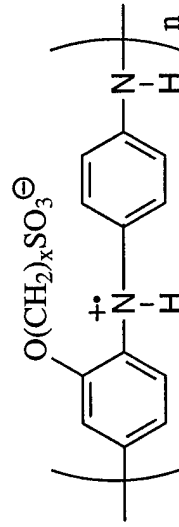
VG02-124-48

Two synthetic strategies:

- Copolymerize self-doped monomer with hydrophobic monomer to achieve water-insolubility
- Synthesize amphiphilic bithiophene or bianiline monomer and polymerize



Bithiophene polymer (5-10 S/cm)



Aniline copolymer (30-40 S/cm)

ISI

PHYSICAL SCIENCES INC