Electroactive polymers

Three main kinds of materials

metals, plastics and ceramics.

Preface

I am inclined to think that the development of polymerization is, perhaps, the biggest thing chemistry has done, where it has had the biggest effect on everyday life. The world would be a totally different place without artificial fibers, plastics, elastomers etc. Even in the field of electronics, what would you do without insulation? And there you come back to polymers again.--- Lord Todd, president of the Royal Society of London, quoted in Chem. Eng. News 58 (40), 29 (1980), in answer to the question, What do you think has being chemistry's biggest contribution to science, to society?

From clothing to the artificial heart, polymers touch our lives as do no other class of materials, with no end in sight for new uses and improved products.

Polymer – Macromolecule

Out line of the science of large molecules



Some linear high polymer, their monomers, and their repeat units

Polymer

- Polyethylene
- Poly(vinyl chloride)
- Polyisobutylene
- Polystyrene
- Polycaprolactam (6nylon)
- Polyisoprene (natural rubber)



Polymerization

- Step-reaction (Condensation) polymerization
- Radical chain (addition) polymerization
- Ionic and coordination chain (addition) polymerization
- Copolymerization

Characterization for Analysis and Testing of Polymers -----Common Methods and Equipments

- Dynamic light scattering spectrometer- thermodynamics properties
- Mass spectrometry- structure of low-molecular- weight species
- Infrared Spectroscopy (IR) structure
- Nuclear Magnetic Resonance Spectroscopy ¹HNMR and ¹³CNMR -chain configuration, sequence distribution, and microstructure
- X-ray diffraction analysis WAXD- the spatial arrangements of the atoms SAXS: larger periodicities
- Light Microscopy (SALS)- spherulites or rod and phase-contrast
- Electron Microscopy and Electron Diffraction
- Scanning Electron Microscopy (SEM) and Transmission Electron Micrograph (TEM)
- Deferential Scanning Calorimetry (DSC)- thermal analysis
- Swr@998strain properties in Tension

States of Polymer





Amorphous rubber Random crystalline plastic

oriented crystalline fiber



X-ray diffraction patterns for unoriented (a) and oriented (b) polyoxymethylene (courtesy of E.S. Clark)



Ringed spherulites of poly(trimethylene glutarate) observed in the optical microscope between crossed polarizers (Keller 1959)



Electro micrograph of a portion of a ringed spherulite in linear polyethylene (photograph by E.W. Fischer, from Geil 1963)



SAXS and WAXD patterns (end view) from polyethylene/carbon blend materials with the indicated compositions





A 4002



YK 3200



KR 1051

(a) H_v SALS photos of low and medium density polyethylene





(c) Surface replica electron microscopy of Polytetrafluoroethylene (Teflon) with different heat treatments (b) and (d) and corresponding with Hv SALS (a), (c)

(b) Hv SALS photos with indicated draw ratios (stretching direction is vertical)

Utilizing plastics for car components



Active materials

sensing and responding to change of environment

Environmental stimuli

- ♦ Temperature
- ♦ Solvent, pH
- ♦ Electric field
- Magnetic field
- ♦ Light or UV

Response

- ♦ Phase
- ♦ Shape
- Optics
- Mechanics
- Permeation rates
- Recognition

Flowers are sensitive to light





Polymers with electrical and electronic properties



Conventional polymers (using their strength, flexibility, elasticity, stability, mould ability, dielectric properties, etc.) **Specialty polymers** (using their electrical conductivity, photoconductivity, nonlinear optical effects, dielectric properties, etc.)

Electroactive Polymer (EAP) Materials

- Electric EAP
- --- PVDF-based Ferroelectric polymers
- Ionic EAP
 ---Electroactive polymer gels
 ---Ionomeric Polymer-Metal Composites
- Non-ionic EAP --- PVA-based
- Carbon nanotube Actuator
- Conductive Polymer
 ---PPy and PANI
 ---PEDOT and PEDOP based

Applications and application potentials

- Antenna and mirror
- Biomimetics and switching technologies
- ---Nafion, Flemion, poly(vinyl alcohol) (PVA) gel, conducting polymer and carbon nanotube actuator
- Switching window, electromagnetic shutter and display technologies
- --Acrylamide and vinyl derivative copolymer, copoly(Aam/vdMG) gel and electrochromic polymer, ProDOT-(CH₃)
- Drug delivery system
- --- Polymer gel and Conducting polymer:
 - e.g. polyacrylamide gel polypyrrole(PPy)
- Sensor

Nafion and polyaniline (PANI)

Dielectric	Dielectric	Applied Electric	Energy	Comments
Material	Constant	Field	Density*	Commonts
		(MV/cm)	(J/cm ³)	
Polyethylene	3.2	4.0	2.3	
Polyester	3.4	4.0	2.5	
PVDF	12.0	2.5	3.3	Ferroelectric
PVDF+BaTiO₃ Composite	40.0	1.6	4.5	40 vol% BaTiO₃ Powder
Al ₂ O ₃	9.0	3.0	3.6	
Ta ₂ O ₃	26.0	2.0	4.6	
Diamond	7.8	7-10	16-24	Unproved
Electrolytic				
Theoretical			20-30	Slow Discharge
Packaged	1000's µFarads	450 Volts max.	1	
Ultracapacitors	1000's Farads	2.5 Volts max.	10-15	Slow Discharge
PbZrO3	>20,000 @ Phase Change	~ 0.5	18	Single Crystal
		(< ½ DBS)		Antiferroelectric
Ceramic	>4000 @ Phase	~ 0.5 - 0.8	12 (material)	
Antilerroelectric		(<¾ DBS)	7-10 (capacitor, projected)	Multilayer Capacitor
PVDF-TrFE Irradiated Copolymer	65	3	12.5	@ Peak Dielectric Temperature
		5 (projected)	> 20 (projected)	

Applications

Comparison of energy storage capabilities of several dielectric materials and capacitors technologies

Space mirror...



(a) Echo 1 passive satellite (courtesy NASA).



(b) Inflatable antenna experiment on orbit. The inflatable antenna was packaged into the reusable Spartan satellite seen on the right (courtesy NASA).





(c) A space shuttle view of the L'Garde's inflatable antenna experiment (IAE). w.wang (d) Dielectric actuator demonstrated to expand and relax (courtesy of R.Kornbluh and R.Pelrine, SRI International). 215

How they work?Antenna



How they work?







voltage off voltage on
(b) Biaxially uniform prestrain and circular electrodes.

voltage off voltage on
(c) Anisotropic prestrain with linear electrodes.

Dielectric actuator







Dielectric Actuator



Dielectric actuator





Dielectric Actuator

W.-C. Wang

Snake-like actuator







Linear actuator



Fish actuator



Walking robot



SRI

Animation





UCSD

How they work?



(a) Bending of a polyacrylic acid gel rod sodium hydroxide. DC applied field, cathode (negative) at a bottom.
Gel swells on the anode side and bends toward the cathode [Shiga, 1997] Without E-fieldWith E-filed(b) Particle suspension forms chains when
electric field is applied







(c) Electrorheological fluid at reference (left) and activated state (right) [courtesy of ER Fluid Developments Ltd, UK]

Applications



(a) Facial muscle that produced sl expression [Netter, 1995] fo



(c) A photographic view of a human hand and skeleton as well as an emulated structure for which EAP actuators are being sought [Courtesy of Garham Whiteley, Sheffield Hallam University, UK]





(b) Smiling robot of Hidetoshi Akasaw w.wang

(d) Dynamic gestural figure with muscles exposed. 227

How they work?

Polymer Gels



Gel structure:

- Solid phase crosslinked polymer matrix
- Liquid phase solvent

Phase transition - discontinuous change of properties, size, shape, etc. under discrete change of environment

Molecular interactions - ionic, hydrophobic, hydrogen bonding, van der Waals



Current applications: Medicine and Biotechnology

1) Drug delivery devices





2) Molecular separations



Study on several EAPs

(1) Poly(vinyl alcohol) (PVA) gel

(2) Nafion and Flemion

(3) Copoly(Aam/vdMG) gel

(4) Electrochromic polymer, ProDOT-(CH₃)

Material development

- Polyvinyl alcohol (PVA) gel:
 - actuation in electric field by contraction and bending
 - influence of structure to deformation:
 - molecular level
 - macroscopic level
 - fastest response (<1s)
 - low strength material
 - high applicable voltage





Influence of structure - molecular level

• Degree of polymerization (DP) - 1400, 2100, 17900





• Tacticity - atactic, syndiotactic



Stress Generation


Mechanism of Electric Actuation

• Dielectric liquid can be ionized upon high E-field

$$j = \rho \cdot b \cdot E = \frac{I}{A}$$
$$E = -grad\phi$$
$$\nabla D = \rho$$

- j current density
- ρ charge density
- b charge mobility
- E electric field strength
- I electric current
- A surface of condenser plates
- ϕ electric potential
- D electric displacement
- Potential and electric field in dielectric material

$$\phi(\mathbf{x}) = \phi(0) - \frac{\varepsilon b A}{3I} \left[\left(\frac{2I}{\varepsilon b A} \mathbf{x} + \mathbf{E}^2(0) \right)^{3/2} - \mathbf{E}^3(0) \right]$$
$$\mathbf{E}(\mathbf{x}) = \left(\mathbf{E}^2(0) + \frac{2I}{\varepsilon b A} \mathbf{x} \right)^{1/2}$$

Mechanism of Electric Actuation

• If the dielectric is liquid, Maxwell stress converts to fluid pressure

$$p(x) \approx \frac{9\varepsilon}{8} \left(\frac{V-V'}{d}\right)^2 \frac{x}{d}$$

d - distance between electrodes $V = \phi(d)$ V' - ionization potential

• Charge injection to the solvent (DMSO) in PVA gel, upon applied



 \bullet For the PVA gel having 96-98% liquid phase, solvent pressure is converted to gel stress, with the efficiency η

w.wang $\sigma(\mathbf{x}) = \eta \cdot p(\mathbf{x})$

E-field

PVA gel actuator as a switch



(a) Schematic diagram

(b) Top view of coated gel

Application potential



Application potential

Carnivorous Plants





2 types of ion flux through membrane



Comparison with Pt electrode





Pt-Cu electrode with copper ion



Pt electrode with Lithium ion $_{240}$

How it works?

Nafion actuator array

Material design: membranes of different thickness and gold electrodes

After 2 plating cycles Nafion 117 7.8 µm 00100 15KY \$1.548'54'4 After 3 and 6 plating cycles Nafion 115 8.2 µm 7.5µm BKU X3.5 Vafion 112 16 um 6.1 µm

The depth of the fractal structure is mostly controlled by the plating conditions not by the amount of gold.

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Nafion loop actuator and performance data





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Parallel device









OFF



Positive (expand)



Negative (Shrink)





• Actuation materials

Material	Advantages	Drawbacks
AAm	Large swelling ratio	Low stiffness
		Slow response
PAN	Faster response	Limited voltage range
	Higher stiffness	
PVA	Fast response	
	Large deformation	Low stiffness
	Large voltage range	
Nafion	Fast response	
	High stiffness	

AAm - acrylamide based PAN - polyacrylnitrile PVA - polyvinylalcohol

Smart system option with PAN fibers concept



positive electrode: H⁺ is created >acid condition, PAN fibers contract

negative electrode: OH⁻ is created >basic condition, PAN fibers expand



Example of possible fin design



<u>Assembly</u> of articulated bones and contractile actuators creates a conformable fin. Many shapes are achievable.

Smart system option with PAN fibers concept: mimic nature!





The Nervous System sends electrical impulses to muscle, telling it to move



The muscle contracts or shortens, pulling the attached bone like a lever.



The bones pivot at the joints

Applications potential

Artificial tactile feel display





Tadokoro et al.

Kobe University, Japan

Applications

Characteristics of IPMC

Low voltage ~1V Bending mode of actuation Large displacement Soft Wet Ionic nature Small scale

Applications

Micropump Catheter Robotfish actuator Gripper



www.eamex.co.jp/index_e.html



www.eamex.co.jp/index_e.html



Fleminon Fish



www.eamex.co.jp/index_e.html

Applications

Actuator arrays



http://voronoi.sbp.ri.cmu.edu/projects/prj_virtu alvehicle.html



http://bifano.bu.edu/tgbifano/Web/ %B5Valve.html



www.sciam.com

Electroactive polymer actuator arrays

Low cost, low power consumption, large displacement, softness Polymer nature, compatible with wet environment

How it works? Flemion actuator array

Actuator design: Flemion beam actuator for microwave switch



Switch design: actuator above board and lifting contact pad in OFF stage. Contact pad resting against the TL in ON stage







3x3 Array from Nafion 112 with gold electrodes and TEA ion: Patterning









How it works?



How they work?

At time = 0sec Voltage goes

Application: Conformable fin for Submarine

Nafion is an Ion Exchange Polymer Membrane. Negative charges are attached to the polymer backbone. Next to each negative charge is a positive Counter ion and some water molecules. If we apply an electric field across Nafion the positive ions move and the whole membrane starts moving. This works best if the membrane is fully hydrated. Therefore Nafion actuators work best in water





Carbon nanotube actuator

4V, strain 0.8%, stress 512GPa Baughman et al. Science 284(5418),1999



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Conducting Polymers

• Insulating polymers: familiar uses include cable sheathings, dielectric layers and films as in capacitors, printed circuit substrates.

Conduction mechanisms



- hole
- electron



Conductivities of various elements, compounds and polymers





Polyacetylene



Difference structure between polyethylene and polyacetylene



(a) Polyactylene thin film



(b) Polyactylene thick film





Polyacetylene after doping



Polyparaphenylenes











Polyphenylene sulfide



Active drug delivery system and actuator





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Clothing technology





Applications of EC Polymer

Present Commercial Products:

 Plastic rechargeable batteries Polyactylenes (PA) and polyanilines (PAn) cell phone, back-up power source for personal computer, solar-powered calculator etc

• Sensors

Polypyrrole (PPy), PA, Polythiophone, Polyparaphenylenes (PPP) and PAn Sensing vapours of nitromathane, toluene, benzene, methanol and water Determining the concentration of ions in solution Electrochemical biosensors

•Shielding PAn etc Electrostatic discharge and electromagnetic interference/ratio-frequency interference applications

Applications of Conductive Polymer

• Printed circuit boards

Flexible insulating substrate with a conducting pattern that could form the basis of printed circuit board Complex multilayer board

- Condenser
- Various semiconductor devices
- Electrochromic displays, smart window
- Solid electrolyte (doped polypyrrole) and etc

Applications of EC Polymer

Present research

- Diode
- Display for mini television

Future

• Electronics

Molecular diode, molecular computer and electroluminescence and etc.

Design of smart window technology

Outline

- 1. Background
- 2. Color changeable gel
- 3. New design of electrochromic color changeable device
- 4. Mechanism for color change
- 5. Preparing three parts for the device
- 6. Assembly
- 7. Testing and analysis of performance
 - Transmittance
 - Optical switching speed
 - Repeatability (Electrochemistry study)
 - Voltage effect on color change speed
 - Voltage effect on color change degree
 - Temperature dependence
- 8. Application potentials

Background

Liquid crystal

Liquid Difficulty in processing Very fast Many colors High cost Small size Narrow angle **Polymer gels**

Electrochromic (EC) polymer Inorganic electrochromic materials e.g. WO₃

Liquid and solid Difficulty in processing Slow Blue Low cost Big size Wide angle

long-term stability rapid switching large changes in transmittance



Machanism for color and volume change of copoly(Aam/vdMG) gel under UVor pH(Electric current) where A and A⁺ represent the neutralized and the ionized vdMG, respectively



Changing concentration of vdMG in the gel to control the degree of color change, color changed under E-current, 1.5A,5V at 20 °C

RESULTS AND DISCUSSION

• Color change speed

stimuli	UV	рН	E-current	UV & E-current	E-current & Na ₂ SO ₄	E-current & AAm gel
light green to dark green dark green to light green	3 min 15 h	1.5 min 2min	40 s 60 s	30 s 60 s	23 s 23 s	19 s 19 s
Previous results, l	frie et	al.→	•		present results	

• Effect of gel thickness on actuation speed under applied E-current Employed the most effective setup given in above

thickness	1.0mm	0.75mm	0.50mm	0.25mm	0.125mm
light green to dark green	25s	19s	15s	11s	9s
dark green to light green	25s	19s	15s	11s	9s

Schematic diagram of device design using color changeable EC polymers

Three-layer scheme:



Transparent

Colored

Two-layer scheme:



Transparent

Colored

Schematic diagram of mechanism for color change of cathodic EC polymer, PProDOT-Me₂



Schematic diagram of device design using color changeable EC polymers

Three-layer scheme:



Transparent

Colored

Two-layer scheme:



Transparent

Colored

Synthetic Route of Monomer, ProDOT -Me 2

for Cathodic EC Polymer





NMR spectra of cathodic monomer, $ProDOT-(CH_3)_2$

The number given over each NMR spectrum peak corresponds to the number given to the proton of $ProDOT-(CH_3)_2$ as shown in the left

Synthetic Route of EC Monomer, XDOP -Benzylation of Dimethyl Iminodiacetate



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Synthetic Route of EC Monomer, EDOP



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Synthetic Route of EC Monomer, $ProDOP-(CH_3)_2$



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Schematic diagram of device design using color changeable EC polymers

Three-layer scheme:



Transparent

Colored

Two-layer scheme:



Transparent

Colored

PMMA based gel electrolyte for EC smart windows

PMMA/LiN(CF ₃ SO ₂) ₂ /PC	PMMA/LiClO ₄ /PC
wt% 20/10/70	wt% 20/10/70
PMMA/LiN(CF ₃ SO ₂) ₂ /PC+EC	PMMA/LiClO ₄ /PC+EC
wt% 20/10/70 (PC:EC=1:1 on volume)	wt% 15/5/80 (PC:EC=1:1 on volume)

Transmittance of Indicated Gel Electrolyte



Schematic diagram of device design using color changeable EC polymers

Three-layer scheme:



Transparent

Colored

Two-layer scheme:



Design of Pattern for Carbon and Gold Based- Counterelectrode



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Transmittance of Indicated Electrode



Assembly of EC polymer device for transmittance control in visible region, carbon-based counterelectrode

Transparent insulating substrate



Assembly of EC polymer device for transmittance control in visible region, Au-based counterelectrode

Transparent insulating substrate



Color Change of EC Polymer Device Using Au Patterned glass as a Counterelectrode



(a) 2.5V, Transparent

(b) - 2.5V, Dark blue



Color Change of EC Polymer Device Using Graphite Patterned ITO glass as a Counterelectrode



(a) 2.5V, Transparent

(b) - 2.5V, Dark blue

Enhanced Contrast Ratio in Cathodic EC Polymer Device Based on Au patterned counterelectrode



Visible spectrum collected in transmittance mode of a cathodic EC polymer device in fully transmitted and fully colored states

Enhanced Contrast Ratio and Rapid Switching in Cathodic EC Polymer Device



Optical switching for the devices based on indicated counterelectrodes monitored at wavelength 580nm

Photographs of potential effect on color changing degree



Blue EC Film Comparison







New Blue



New red color







10c best





A circular smart window with rubber seal







An electrochromic window

A simple electrochromic display

Ishihara et al ,2001 305
Application Potential



Commercial air plane

Special air craft

http://www.boeing.com

Smart window



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http://windows.lbl.gov/materials/chromogenics

Future works

Several new ideas...

- **1.** Carbon nanotube actuator
- **2.** Conducting polymer
 - Bio-related actuator drug delivery system, e.g. polypyrrole
 - Sensing clothing Body stress, signal, e.g. polyaniline(PANI) fiber
- 3. Special fiber

All-solid-state Electrochromic Glazing WO₃, high durability but low contrast ratio (40:1)



Aircraft side window



F. Beteille (France) The SPIE Conference on Switchable Materials and Flat Panel Displays SPIE Vol. 3788 pp.70-73 (July 1999) w.wang

E-ink





How they work?



Flexible active-matrix electric ink display - Electric paper





Nature 136 p.136 (2003)

Shape memory polymer

Camouflage skin of Octopus



Original

Camouflaged in white

Application potential --- Wearable smart sensors/actuator



Day time Land warrior

Day time Taking a break

Night Moving to the position

Conclusions

- From "hard" to "soft" technology
- EAP structure, processing, sensing, actuation... ...all in one
- Advantages for actuator applications:
 - light weight
 - energy storage
 - viscous damping
 - low cost
- Challenges:
 - Materials development

^{w.wang} - Integration into smart devices and structures ³¹⁵