Electronic and Optoelectronic Polymers

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Outlines

- History of Conjugated Polymers
 - **Brief introduction**
 - **Chemistry of Conjugated Polymers**

Doping concepts of Conjugated Polymers (Conducting Polymers)

- <u>Electronic Structures of Conjugated Polymers</u>
- **Polymer Light-emitting Diodes**
- Polymer based Thin Film Transistors
- **Polymer based Photovoltaics**
- Polymer for Memory Device Applications

Scientific Interests in the Polymeric Materials

- Polymeric materials in the form of wood, bone, skin and fibers have been used by man since prehistoric time.
- Hermann Staudinger developed the concept of macromolecules during 1920s. (1953 Nobel Prize in Chemistry)
- Wallace Carothers invented polymer reaction of nylon at the Dupont company in 1935.
- Karl Ziegler and Giulio Natta discovered the polymerization catalyst for the important development of the modern plastic industry. (1963 Noble Prize in Chemistry)
- Paul Flory created the modern polymer science through the experimental and theoretical studies of macromolecules. (1974 Noble Prize in Chemisty)
- Hideki Shirakawa, MacDiarmid and Alan Heeger discovered the chemical and physical properties of conducting polymers. (2000 Noble Prize in Chemistry)

Comparisons Between Conventional and Conjugated Polymers

Conventional Polymers



- Easy Processing/Fabrication Over Large Areas
- Low Cost Materials/Processing
- Excellent Mechanical Properties
- Low Thermal Stability (100~300°C)
- Excellent Insulators
- Lowest Energy Excited States in UV (4~6eV)
 - $\pi\text{-}\mathbf{Conjugated}$ Polymers



- Many of the Conventional Polymer Properties
- Diverse Electronic, Optoelectronic, and Photonic Properties
- <u>Better Thermal Properties (>300°C)</u>
- Lowest Energy Excited States in Visible and Near-IR

Band structures of Polymers

Conventional Polymers



Band structures of Polymers



bond alternation limits the extent of delocalization large gap semiconductor

Band structures of Conjugated Polymers



• The band structure of a conjugated polymer originates from the interaction of the π -orbitals of the repeating units throughout the chain.

Eg: Band gap = IP - EA IP: Ionization potential EA: Electron affinity BW: Bandwidth

LUMO: Lowest Unoccupied Molecular Orbital HOMO: Highest Occupied Molecular Orbital

Electronics/Optoelectronics Materials

Some Clarification of Terms

Electromagnetic phenomena (i.e., the behavior of electronic and magnetic fields) in macroscopic media are described by Maxwell's equation)



Recalls: viscosity, thermal conductivity, diffusion coefficients

basic material constants in transport equations

High Technical Optoelectronic Device

Optical communication, information processing systems, information display systems, optical information storage. (originally from inorganic materials)

Rationale for Polymer Electronics/Optoelectronics

Compare to conventional inorganic semiconductors: Why Polymers?

• Easier Processing/Fabrication

Spin coating or ink jet printing

- <u>Low-Cost Materials and Processing</u> No multiple etching and lithographic process
- Low Capital Investment

Contrast: \$1 Billion Si chip fab line

• Large Area Devices Systems

Displays, photo-detectors, solar cells

• Novel Properties or Features

Flexible in modifying materials, LEDs with tunable colors, polymer optical fibers

<u>Adequate Performance</u>

Amorphos-Si $\mu \sim 1 \text{ cm}^2/\text{VS}$ VS P3HT $\mu \sim 0.1 \text{ cm}^2/\text{VS}$

• Market Trend

Potential commercial product

Trend on the Applications of Conjugated Polymers



Part of the figure from Prof. C. S. Liao of Yuan-Zu

2000 Noble Prize in Chemistry

- for the Discovery and Development of Conductive Polymers



Alan G. MacDiarmid University of Pennsylvania, Philadelphia, USA Hideki Shirakawa Emeritus, University of Tsukuba, Japan Alan J. Heeger University of California at Santa Barbara, USA The initial discovery of conducting polymers in 1977 was made by team led by polymer chemists (Shirakawa), an organometallic chemist (MacDiarmid) and a physicist (Heeger)

MacDiarmid died on Feb 7, 2007.



Opportunities of Conductive Polymers

New Field of Research on the Boundary between chemistry and condensed matter physics

- Conducting polymers open the way to progress in understanding the fundamental chemistry and physics of π -bonding macromolecules.
- Conducting polymers provide an opportunity to address questions that had been of fundamental interest to quantum chemistry for decades. (e.g. Bond length alternation, electron packing)
- Conducting polymers provide an opportunity to address fundamental issues of importance to condense-matter physics as well, for example, the metal-insulator transition and Peierls instability.
- Conducting polymers offer the promise of achieving a new generation of polymers: materials which exhibit the electrical and optical properties of metals or semiconductors and which retain the attractive mechanical properties and processing advantages of polymers.

Noble Lecture by A. J. Heeger

Chemical Structures of Conjugated Polymers



Polyacetylene (PA)



Polythiophene (PT)



Polyethylenedioxythiophene (PEDOT)



Polypyrrole (PPy)

Polyaniline (PANI)



Polyisothianaphthene (PITN)



Polyparaphenylene vinylene(PPV)

Synthesis Route of Conjugated Polymers



(b) Direct Route chain growth (addition) polymerization step growth (condensation)

Advantages:

- Soluble or fusible conjugated polymers can be readily processed into films and other form.
- Allow tuning of conjugation length and physical properties such as morphology, crystallinity, electronic& optical properties.

Challenges: impurity, precise control of structure/property

Precursor Routes to PPV



Scheme 1. Synthesis of PPV (6): a) tetrahydrothiophene. MeOH. 65°C; b) NaOH. MeOH/H₂O or Bu₄NOH. MeOH. 0°C; c) neutralization (HCl): d) dialysis (water): e) MeOH. 50°C; f) 220°C. HCl(g)/Ar, 22 h; g) 180-300°C, vacuum, 12 h.

Wesssing and Zimmerman (1985) J Polym Sci Polym Symp. 72, 55

McCullough Route





Development of Various Conjugated Polymers





Part of the figure from Prof. C. S. Liao of Yuan-Zu

Multi-component Conjugated Polymers

Conjugated Homopolymer



Conjugated Copolymers

- Random Copolymers
- Alternating Copolymers $(-AB)_{n}$
- Block Copolymers

Diblock Copolymers

triblock Copolymers $(A)_{I}(B)_{m}(C)_{n}$

Blends of Conjugated Polymers

Blends mean physical mixtures of two or more polymers

Binary Blends

A + B = A:B

• Ternary Blends

Characterization on Chemical and Physical Properties of Conjugated Polymers

- Molecular Structure (NMR, IR, other spectroscopies)
- Molecular weight (GPC, Light Scattering)
 - Mw, Mn, polydipersity
- Viscosity
 - $\eta \sim [\rm molecular \ weight]^a$ (chain rigidity)
- Optical absorption spectra (solution, solid state)
 - Ground state electronic structure
- Photoluminescene spectra (solution, solid state)
 - **Excited state electronic structure**
- Thermal transition (TGA, DSC)
 - **Glass transition temperature or melting temperature**
- Morphology (electron microscopy, AFM, XRD)

Methods on Processing of Conjugated Polymers

Solution casting

Simple, cannot control thickness

• Spin coating

Film uniformity, thin film thickness (~nm)

• Langmuir-Blodgett (LB) technique

Amphiphilic polymers, monolayer to multiplayer

- Dip coating
- Electrochemical polymerization
- Ink jet Printing
- Layer-by-Layer Self-Assembly

- Electrospinning
 - **Fiber-like**
- Lamination
- Chemical Vapor Deposition

Thermal evaporation of low molecular weight polymers

Electrically Conducting Polymers

The intrinsic conductivity of conjugated polymers, including polyacetylene polypyrrole and polythiophene is rather low: typically about 10⁻¹² to 10⁻⁵ S/cm

The low intrinsic conductivity must be due to the small concentration of charge carriers and perhaps also small mobility.

Discovery of doping phenomena and resulting 10 order of magnitude increase in the conductivity of polyacetylene.

Discovery of conducting polymers and the ability to dope these polymers over the full range from insulator to metal.

 $\sigma = \mathbf{e} \mathbf{n} \mu$

σ : conductivity (S/cm n: carrier (e or h) density (cm⁻³) μ : mobility (cm2/VS) e=1.6×10⁻¹⁹ C



Doping or Redox Phenomena in Conjugated Polymers

Doped conjugated polymers are good conductors for two reasons:

- Doping introduces carriers into the electronic structures. Since every repeat unit is a potential redox site, conjugated polymers can be doped n-type (reduced) or p-type (oxidized) to a relatively high density of charge carriers.
- The attraction of an electron in one repeat unit to the nuclei in the neighboring units leads to carrier delocalization along the polymer chain and to charge carrier mobility, which is extended into three dimensions through interchain electron transfer.

Disorder limits the carrier mobility and in the metallic state, limits the electrical conductivity. Research directed toward conjugated polymers with improved structural order and higher mobility is a focus of current activity in the field.

Concepts of Doping and Redox Phenomena

The term doping as used in the filed of conducting polymers was borrowed from analogous term and phenomena in <u>inorganic semiconductors</u> such as Si or GaAs.



These doping processes in inorganic semiconductor are achieved by thermal diffusion or ion implantation.

Conjugated Polymers with Doping

Doping in conjugated polymers is a redox process, i.e. oxidation (p-type) or reduction (n-type)

• P-type, hole transport conjugated polymer

 $P \longrightarrow P+ \cdot + e^{-}$

Radical cation (positive polaron)

• N-type, electron transport conjugated polymer

 $P + e^- \longrightarrow P^- \bullet$

Radical anion (negative polaron)

 $[P^{y+}(A^{-})_{y}]_{n}$ $[P^{y-}(D^{+})_{y}]_{n}$ A⁻ and D⁺ are counterions

(A⁻ = counter anion, D⁺ = counter cation) which are required to neutrality of the doped conducting polymers.

Band Structures of Conjugated Polymers with Doping



spinless & charge (2e)

Band Structures & Optical Properties of Conjugated Polymers with Doping



Concepts of Doping of Conjugated Polymers

Chemical Doping by charge transfer

• P-type doping (electron acceptor oxidizing agents)

• N-type doping (electron donor, reducting agents)

Polymer Counterions

PEDOT:PSS (Baytron P from H. C. Starck)

Commercial conducting polymer available as aqueous solution

 σ ~10 S/cm

Concepts of Doping of Conjugated Polymers

Electrochemical Doping

• P-type doping

 $(\pi\text{-polymer})_n + [\text{Li}^+(\text{BF}_4^-)]_{\text{soln}} \longrightarrow [(\pi\text{-polymer})^{+y}(\text{BF}_4^-)_y]_n + \text{Li}_{\text{electrode}}$

• N-type doping

$$(\pi ext{-polymer})_n + \operatorname{Li}_{\operatorname{electrode}} \longrightarrow [(\operatorname{Li}^+)_y(\pi ext{-polymer})^{-y}]_n + [\operatorname{Li}^+(\operatorname{BF}_4^-)]_{\operatorname{soln}}$$

The electrode supplies the redox charge to the conducting polymer, while the ions diffuse into (or out of) the polymer structure from the nearby electrolyte to compensate the electronic charge.

Advantages :

Easy reversibility

Many dopant counterions can be readily introduced

The necessary redox potential is supplied electrically

Concepts of Doping Conjugated Polymers

Doping of polyaniline by acid-base chemistry

Conductivity Measurements of Doping Conjugated Polymers

To measure the effect of the dopant on conductivity, four point probe is generally used.

Acceptor doping of a polymer film and reversal to the neutral state by compensation with a donor

Conductivity of Doping Conjugated Polymers

Conductivity of trans-polyacetylene versus AsF₅ dopant concentration

Conductivity of Doping Conjugated Polymers

Polymer	Abbreviation	Dopant ion		
		Species	Concentration*	Conductivity, S/em
polyacetylene	· PA	I.	0.10	550
A-65		AsFé	0.10	1100
		BF. *	0.09	100
		K **	0.16	50*
poly(<i>p</i> -phenylene)	PPP	15		<10-4
		AsF.	0.4	500
		BF.*	0.2	70
		K-*	0.6	20
poly(<i>p</i> -phenylene sulfide)	PPS	Iī		<10-5
		AsF.	0.7	5'
		BF.*		<10-8
		K.		<10-8
polypyrrole	PPY	15	•	600
		AsFe	0.3	100
		BF7'	0.3	100
		к-		<10-4
polythiophene	PTh	I ₁		0.1
		AsFa	0,24	10
		BF;"	0.42	100

Conductivity of Conjugated Polymers with Selected Dopants

Conductivity network of Conducting Polymers

- A: single chain or intramolecular transport
- **B: intechain transport**
- **C: interparticle contact**

Effect of Chain Conformation on the Conductivity

R. McCullough Adv. Mater. 1998

in regioregular HT-coupled 3-dodecylthiophene/3-methylthiophene copolymers increases, the conjugation length increases, the oxidation potential decreases, and the conductivity increases

DD

Fields of Doping of Conjugated Polymers

Doping Mechanisms and Related Application

Electrical conductivity Conductivity approaching that of copper Chemical doping induces solubility Transparent electrodes, antistatics EMI shielding, conducting fibers

High-performance optical materials

1D Nonlinear optical phenomena Photoinduced electron transfer Photovoltaic devices Tunable NLO properties Charge injection without counterions Organic FET circuits Tunneling injection in LEDs

Dream of Conducting Polymers

Polymer	Maximum conductivity, Ω ⁻¹ cm ⁻¹	Reference no
Polyacetylene	10 ³ -10 ⁵	1, 2
Poly(<i>p</i> -phenylene) Poly(<i>p</i> -ohenylene	10 ³	3
vinylene) Poly(<i>p</i> -obenylene	10 ³	46
sulfide	102	7, 8
Polypyrrole	102-103	9
Polythiophene	10 ²	10
Polyfuran	102	11
Polyazulene	10 ⁰	12
Polyaniline	100	13

J. R. Reynolds, CHEMTECH 1988

Conducting Polymers-based Rechargeable Batteries (M. G. Kanatzidis, C&EN 1990)

Rechargeable batteries are among the first commercial products based on conducting polymers. They utilize either polypyrrole, polythiophene, or polyaniline (or their derivatives) as cathodes. The anodes are usually lithium or some lithium alloy, such as lithium-aluminum. During cell discharge, electrons flow from the anode to the cathode, through an external load, to reduce the p-doped polymer to the neutral (undoped) state. The dopant anions are ejected from the polymer into the ejectrolyte phase. At the same time, lithium at the anode dissolves into the electrolyte as lithium ion.

When all of the polymer is converted from the p-doped to the neutral state, the cell is fully discharged. To recharge it, an opposite potential is applied to the electrodes. During recharging, the neutral polymer at the cathode is oxidized to the p-doped state by taking up dopant anions from the electrolyte, while lithium ion deposits at the anode as lithium metal. However, poor performance of the lithium anode during the recharge cycle has decreased the potential lifetime of the batteries developed thus far. The chemical processes occurring at the electrodes of a polythiophene battery are:

The electrolyte can be a solution (usually in propylene carbonate) of an appropriate salt or a solid polymer electrolyte, such as lithium salt/polyethylene oxide, in which case an allsolid-state cell results. Such all-solid-state batteries, which have not yet been commercialized, would be safer, flexible, and could be made in many shapes and sizes. Conductive polymer rechargeable batteries are usually made as flat buttons or laminated rolled films.

Researchers at Allied-Signal have recently demonstrated functioning rechargeable batteries in a reverse configuration using n-doped polyphenylene at the anode and cobalt dioxide at the cathode.

Cathode (positive electrode):

Electrochromic Devices Made of Conducting Polymers Operate Like Rechargeable

An electrochromic device of the type diagramed above is not very different from a rechargeable battery. It has a conducting polymer cathode, an electrolyte, and a metal such as lithium as the anode. Electrical potential is applied to cause doping and undoping of the conductive polymer and thus to induce controlled color changes. For these changes to be visible, one of the electrodes must be optically transparent. Indium-doped tin oxide glass is commonly used for this purpose.

In a "smart window," which changes color in response to sunlight or temperature changes, both electrodes must be transparent. In the transparent (bleached) state of the device, the polymer is in the undoped form. To block sunlight, a positive potential is applied, causing oxidative doping of the polymer, which results in intense coloration with good optical contrast. Dopants from the electrolyte enter the polymer structure. To bleach the color, a negative potential is applied to undope the polymer. With polyisothianaphthene, which is transparent in the doped state, the opposite process occurs. The table below shows the particular color changes for different polymers.

Polymer	Color, undoped	Color, doped	
Polythiophene	red	blue	
Polypyrrole	yellow-green	blue-black	
Polyaniline	yellow	green or blue	
Polyisothlanaphthene	blue	light yellow	

Difficulties on Commercial Applications of Conducting Polymers

- Processibility: Highly π -conjugated polymers result in poor solubility.
- Stability: Highly doping levels induces instability toward oxygen or moisture.

Light Emitting Diode Based on Conjugated Polymers

Solution-processible Conjugated Polymers (PPV)

Green yellow Light

Nature 1990, 347, 539

Electron Transport Materials (ETM) in PLEDs

EL mechanism

Energy level diagram

Control charge injection, transport, and recombination by ETM

- ♦ lower barrier for electron injection
- $\mu_{e} > \mu_{h}$ in ETM
- Larger \triangle IP to block hole

Jenekhe et al, Chem Mater 2004, 16, 4556

Conjugated Polymers Photovoltailc Cells

Enhanced Efficiency via Network of Donor-Acceptor Heterojunction

Fig. 3. $\eta_{\rm c}$ (A) and $\eta_{\rm e}$ (B) of Ca/MEH-PPV: [6,6]PCBM(1:4)/ITO (solid squares); Ca/MEH-PPV:[6,6]PCBM(1:1)/ITO (open squares); Al/MEH-PPV:[6,6]PCBM(1:1)/ITO (diamonds); Ca/MEH-PPV:[5,6]PCBM(1:1)/ITO (open circles); Ca/MEH-PPV:C_{60}(3:1)/ITO (triangles); and Ca/MEH-PPV/ITO (solid circles).

Heeger et al., Science 1995, 270, 1789

Thin Film Transistors Based on Conjugated Polymers <u>Regioregular Poly 3-hexylthiophene (P3HT)</u>

Mobility ~ 0.1 cm²/VS

Subjects of the Polymer Optoelectronic Device

Integrated Optoelectronic Devices Based on Conjugated Polymers

An all-polymer semiconductor integrated device is demonstrated with a high-mobility conjugated polymer field-effect transistor (FET) driving a polymer light-emitting diode (LED) of similar size. The FET uses regioregular poly(hexylthiophene). Its performance approaches that of inorganic amorphous silicon FETs, with field-effect mobilities of 0.05 to 0.1 square centimeters per volt second and ON-OFF current ratios of >10⁶. The high mobility is attributed to the formation of extended polaron states as a result of local self-organization, in contrast to the variable-range hopping of self-localized polarons found in more disordered polymers. The FET-LED device represents a step toward all-polymer optoelectronic integrated circuits such as active-matrix polymer LED displays.

Sirringhaus H., Tessler N., Friend RH, Science 1998

Progress on Flexible Organic Display Devices

In an active Matrix each pixel contains a light-emitting diodes (LED) driven by a Field-effect transistor (FET). The FET performs signal processing while the LED converts the electrical signal processing into optical output.

Conjugated Polymer Based Photovoltaic Devices

*Efficiency η(%)值為太陽能電池元件關鍵參數。單晶矽:25%;多晶矽:15%;非晶矽:12%。有機 半導體:共軛高分子 heterojunction:1.9% (Cambridge Univ.); Dye-sensitized heterojunction (Hoechst): 0.74%。

Fig. 1. Power conversion efficiencies of solar cells. E: single crystalline silicon; P: polycrystalline silicon; A: amorphous silicon; O: organic solar cell. In each case both the laboratory (left) and commercial status (right) are shown.

Figure 1 Prototype of a flexible organic solar cell that uses a liquid electrolyte. An amorphous conducting material has now been used as an alternative to the electrolyte in an otherwise comparable device.

Cited from Prof. C. S. Liao

Conjugated Polymer Based Photovoltaic Devices

Measured Solar Cell Efficiency from 1975 to the present

From NREL, USA

Commercial Products of Organic Optoelectronic Devices

40 inch full color display (Sekio Epson)

Organic thin film transistors (Lucent Technologies)

Flexible solar cell (NREL USA)

Sheets of paper-thin lighting (GE)

Commercial Products of Organic Optoelectronic Devices

Flexible clock (Citizen)

PLED display (Philips) Organic solar cell

PLED MP3display (Delta Electronic)

Polymers for Memory Device Applications

Non-Volatile Memory (e.g., Flash, WORM...) Volatile memory (e.g., DRAM)

Engineering Polymers for Electronic, Optoelectronics and Photonic Applications

Property

- High dc Conductivity
- Intrinsic Semiconductivity (high charge mobility)
- Large Photoconductivity
- Efficient Luminescene
- High Contrast Electrochromism/
 Photochromism
- High Refractive Index
- •Large, Ultrafast NLO Properties

Application

- Conductors, Electrodes
- Thin Film Transistors
 - Photodetectors, Photovoltaic
 Cells
- ← → ●LEDs, Lasers
 - Information Storage, Display, Windows
 - → •Waveguides
 - → Ultrafast Optical Switching, Sensor Protection

Nature of The Field of Electronic & Optoelectronic Polymers

To make, understand and use conjugated polymers, the prototype electronic and optoelectronic polymers, require concepts and ideas from three main fields

Physics

- Nature of Charge Transport
- Nature of NLO Response
- <u>Complex Photophyscis</u>

Chemistry

- Synthetic Methodologies and Molecular Design
- Quantum Chemistry
- <u>Characterization of Chemical Structures</u> <u>Engineering</u>
- <u>Novel Processing Methods</u>
- <u>Morphology/Property Relationships</u>
- Device Engineering towards Nono-/Molecular Electronics
- <u>Manufacture of Small Volume/High Value Materials</u>

Design of Conjugated Polymers for Optoelectronic Applications

Figure from Prof. C. S. Liao

Applications of Conjugated Polymer Systems

Part of the figure from Prof. C. S. Liao of Yuan-Zu

Properties and Applications of Organic Optoelectronic Devices

Skeleton of Conjugated Polymers

