Polymer Conductivities

Polyacetylene
Poly (p-phenylene)
Doped germanium
Silicon
Polyethylene
Nylon
Polystyrene

$\sigma$(S/cm)

$10^{-18}$  $10^{-16}$  $10^{-14}$  $10^{-12}$  $10^{-10}$  $10^{-8}$  $10^{-6}$  $10^{-4}$  $10^{-2}$  $10^{-1}$  $10^0$  $10^2$  $10^4$  $10^6$

Copper
Iron
Mercury

Poly (p-phenylene sulfide)
PA
PPP
PPS

Figure by MIT OCW.
Polypyrrole Actuator

- Low voltage required to operate (< 2 V)
- High power density (150 W/kg)
- High active stress (10 - 40 MPa)
- Moderate active strain (2 - 10%)
- Light and Flexible

**Deposition Solution Components:**

- **Monomer:** Pyrrole
- **Solvent:** Propylene Carbonate
- **Counterions:** Tetraethylammonium Hexafluorophosphate (TEA-PF6)

**Polypyrrole Chemical Structure**
Polypyrrole Microstructure

- Bundles do not give rise to crystalline peaks in x-ray, but do cause certain characteristic reflections.
- Bundles consist of $\pi$-stacked segments and serve as pseudo-crosslinks, keeping the material insoluble and unmeltable.
- Bundles allow percolative path of rigid, electronically conductive chains through bulk sample.
- Solvent and counterions are randomly distributed outside of bundles. They act as plasticizers for the film.
- Actuation occurs when polymer conducts charges/discharges and counterions enter and leave the disordered regions between bundles.

Polypyrrole has disordered rigid chains held together by small, $\pi$-stacked bundles.

Figure by MIT OCW.
As polymerized film has polypyrrole chains positively charged, $\text{PF}_6^-$ anions are present at a ratio of about 1 anion per 3 monomeric repeats of the pyrrole chain.

- Solvent and counter anions are homogeneously distributed outside of pyrrole bundles.
- Actuation (expansion) occurs when more electrons are removed (oxidation) from pyrrole backbone and more anions enter to maintain charge neutrality.
- Actuation (contraction) occurs when more electrons are added (reduction) to the pyrrole backbone and some anions leave to maintain charge neutrality.
Mechanism of Actuation in Oriented Pyrrole Films

Propylene carbonate

Polypyrrole chain

BMIM $^+\quad$ (Big change)

Figure by MIT OCW.
Actuation of Different Recipes

One has to find a balance between fast and large active strains.

<table>
<thead>
<tr>
<th>Recipe</th>
<th>Contraction (%) at +0.8V in:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 sec</td>
</tr>
<tr>
<td>TBA-TFSI/MB on GC</td>
<td>2.05</td>
</tr>
<tr>
<td>TBA-TFSI/MB on Ni</td>
<td>2.75</td>
</tr>
</tbody>
</table>

Potential (V) or Strain (%)

Images of polypyrrole morphology and voltage-strain curves removed due to copyright restrictions.

TBA-TFSI/MB on Ni
\[\sigma = 3.6 \times 10^3 \text{ S/m} \]
\[E = 40 \text{ MPa} \]

TBA-TFSI/MB on GC
\[\sigma = 2.5 \times 10^4 \text{ S/m} \]
\[E = 240 \text{ MPa} \]
Polypyrrole Actuation

Isometric Testing

• Apply constant strain to polymer strip, measure active stress

Isometric: $\varepsilon_0 = 1\%$

Applied Potential (V)

Measured Current (mA)

Calculated Charge (mC)

$\sigma(t)$

$\varepsilon_0$

$\varepsilon_0$

Actuation Solution: 0.1M LiTFSI in PC

Images of polypyrrole actuation and various data removed due to copyright restrictions.
1. Linear, homogeneous, isotropic, nondispersive media
   \[ P(r,t) = \varepsilon_0 \chi \vec{E}(r,t) \]
   \[ n = \left( \frac{\varepsilon}{\varepsilon_0} \right)^{1/2} = (1 + \chi)^{1/2} \]

2. Inhomogeneous medium
   \[ n = n(r) \quad \chi = \chi(r) \quad \varepsilon = \varepsilon(r) \]
   position dependent, due to variation of material properties
   (e.g. oriented glassy polymer via injection molding, photonic crystal, etc.)

3. Anisotropic medium: the electric susceptibility is a 2\textsuperscript{nd} rank tensor
   \[ P_i = \sum_j \varepsilon_0 \chi_{ij} E_j \]
   By a suitable choice of coordinate system, \( \chi_{ij} \) can be made so that off-diagonal elements are zero. \( \chi_{11}, \chi_{22}, \chi_{33} \) define the principal susceptibilities along the principal axes.

4. Absorption
   \[ \chi = \chi' + i\chi'' \]
   complex susceptibility
Optical Properties
Interaction of E-M Radiation with Polymers

Possible Interactions:
1. reflection
2. refraction
3. absorption
4. polarization change

\[ n = n_R - in_i \]
\[ \text{Re}(n) = n_R \]
\[ \text{Im}(n) = n_i \equiv \text{absorption} \]
Materials Interaction with E-M Radiation

1. Reflection
   • **Law of Reflection:** the incident and reflected wave are in the same plane (of incidence) and they make an angle $\theta_i$ with the normal on the interface between the 2 materials.

2. Refraction
   • **Snell’s Law of Refraction:** \( n_1 \sin(\theta_i) = n_2 \sin(\theta_r) \)
     - it is possible to determine \( n_2 \) if \( n_1 \) known (for air \( n = 1 \)), by measuring \( \theta_i, \theta_r \).
   • **Origin of Refractive Index:** given by the polarizability of the material, interaction of incident light with rapid oscillating electrons in the material (especially valence electrons).

\[ \frac{n^2 - 1}{n^2 + 2} = \frac{1}{3 \varepsilon_0} \sum_i N_i \alpha_i \]  
(Lorenz - Lorentz equation)

- \( n = \) refractive index, \( \alpha_i = \) polarizability of the \( i^{th} \) chemical bond
- \( N_i = \) number of \( i^{th} \) type chemical bond

3. Absorption
   - when the frequency of the incident wave is close to the frequency of a certain oscillations in the material:

   e.g. IR – vibrations of atoms / chemical bonds (basis for IR spectroscopy which identifies atomic groups based on characteristic vibrations)
   UV – electronic transitions between different energy levels (in quantum mechanics see electrons as waves, different energies, different frequencies)

Absorption is maximum at resonance (when the frequency of the incident wave equals the frequency of a particular oscillation in the material) and when the direction of polarization is along the direction of vibration
Absorption of Polymers in IR and UV

IR:

UV:

Figure by MIT OCW.
4. Polarization Change
Methods of Producing Polarized Light

1. Selective Dichroism—oriented polymer matrix with aligned guest dye molecules (Edwin Land)

2. Birefringence
   - orientational birefringence: alignment of optically anisotropic molecules
     \[ \Delta = n_\parallel - n_\perp \]
   - strain birefringence: applied stress alters bond distances which alters polarizability along stress direction. Can occur in an isotropic medium subject to stress.
   - form birefringence: material comprised of two or more components with different indices of refraction with shape anisotropy of at least one of the components (e.g. cylindrical microdomains in roll cast BCP). Domains must be on the scale of the wavelength or larger

Q: how does a LCD pixel work?
Nonlinear Optical Materials

\[ \mathbf{P}_i = \chi_{ij}^{(1)} \mathbf{E}_j + \chi_{ijk}^{(2)} \mathbf{E}_j \mathbf{E}_k + \chi_{ijkl}^{(3)} \mathbf{E}_j \mathbf{E}_k \mathbf{E}_l \]

alternatively can write in terms of molecular susceptibility per unit volume

\[ \mu_i = \alpha_{ij} \mathbf{E}_j + \beta_{ijk} \mathbf{E}_j \mathbf{E}_k + \gamma_{ijkl} \mathbf{E}_j \mathbf{E}_k \mathbf{E}_l \]

\( \alpha_{ij} \) = molecular susceptibility
\( \beta_{ijk} \) = nonlinear molecular susceptibility of order 2 (3rd rank tensor)
\( \gamma_{ijkl} \) = nonlinear molecular susceptibility of order 3 (4th rank tensor)

the \( \beta \) and \( \gamma \) terms depend on the number of molecules per unit volume and their orientation.

\[ \chi^{(2)} \sim \beta \langle \cos^3 \theta \rangle \]
\[ \chi^{(3)} \sim \gamma \langle \cos^4 \theta \rangle \]

\( \chi^{(2)} \) is zero for centrosymmetric orientation of an array of dipoles since \( \cos^3 0^\circ = 1 \)
but \( \cos^3 180^\circ = -1 \) so averages to zero
\( \chi^{(3)} \) can be nonzero for centrosymmetric systems
Influence of Different Orientational States on NLO Parameters

Dipolar orientation
- High $x^2$
- High $x^3$

Quadrupolar orientation
- Zero $x^2$
- High $x^3$

Random orientation
- Zero $x^2$
- Low $x^3$

Figure by MIT OCW.
Frequency Doubling

\[ \overrightarrow{P}_i = \chi^{(1)}_{ij} \overrightarrow{E}_j + \chi^{(2)}_{ijk} \overrightarrow{E}_j \overrightarrow{E}_k + \chi^{(3)}_{ijkl} \overrightarrow{E}_j \overrightarrow{E}_k \overrightarrow{E}_l \]

Second-Order NLO Materials

\[ |\overrightarrow{P}_{NL}| = \varepsilon_o \chi^{(2)} |E|^2 \]

where \( |\overrightarrow{P}_{NL}| \) is the magnitude of the 2\(^{nd}\) order nonlinearity

assume \( E(z,t) = E_o \cos(2\pi v t - k z) \)

then \( |\overrightarrow{P}_{NL}| = \frac{\varepsilon_o}{2} \chi^{(2)} E_o^2 (1 + \cos(4\pi v t - 2 k z)) = P_{NL}(0) + P_{NL}(2\nu) \)

The term \( P_{NL}(2\nu) \) is the source for radiation @ twice the input frequency. This is called second harmonic generation (SHG).

Note that \( \chi^{(2)} \) is zero for all centrosymmetric structures. This means SHG samples need to be strongly poled to align the dipoles.
Frequency Tripling

Third-Order NLO Materials
Centrosymmetric materials at very high applied fields, $\chi^{(2)} = 0$, but $\chi^{(3)} \neq 0$

\[
|\vec{P}_{NL}| = \varepsilon_0 \chi^{(3)} |E|^3
\]

Intensity modulation of incident $\nu$

\[
|\vec{P}_{NL}| = \frac{\varepsilon_0}{4} \chi^{(3)} E_0^3 \left(3 \cos(2\pi \nu t - 2kz) + \cos(6\pi \nu t - 3kz)\right)
\]

Frequency tripled (THG)

The polarization component at incident frequency $\nu$, $\vec{P}_{NL}(2\nu)$ has changed due to interaction of the light with the NLO material.
This corresponds to an incremental change in susceptibility: $\Delta \chi$

\[
\Delta \chi = \frac{P_{NL}(\nu)}{E(\nu)} = \frac{3}{4} \varepsilon_0 \chi^{(3)} E_0^3 \cos(2\pi \nu t - k z) \cos(2\pi \nu t - k z)
\]

\[
= \frac{3}{4} \varepsilon_0 \chi^{(3)} E_0^2
\]
### NLO Chromophores Values, $\beta$

<table>
<thead>
<tr>
<th>STRUCTURE</th>
<th>$\beta$ at 1.9 $\mu$m $\times 10^{-30}$ esu</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NH}_2$-$\text{NO}_2$</td>
<td>5.7</td>
</tr>
<tr>
<td>$\text{N(CH}_3)_2$-$\text{CN}$-$\text{CN}$-$\text{CN}$</td>
<td>21.4</td>
</tr>
<tr>
<td>$\text{N(CH}_3)_2$-$\text{CN}$-$\text{C}$-$\text{CN}$</td>
<td>41.8</td>
</tr>
<tr>
<td>$\text{N(CH}_3)_2$-$\text{CH}=$-$\text{N}$-$\text{NO}_2$</td>
<td>23.4</td>
</tr>
<tr>
<td>$\text{N(CH}_3)_2$-$\text{C}$-$\text{CH}$-$\text{NO}_2$</td>
<td>60.0</td>
</tr>
<tr>
<td>$\text{NH}_2$-$\text{NO}_2$</td>
<td>20.1</td>
</tr>
<tr>
<td>$\text{NH}_2$-$\text{NO}_2$</td>
<td>50.7</td>
</tr>
<tr>
<td>$\text{N(CH}_3)_2$-$\text{C}$-$\text{CH}$-$\text{CH}$-$\text{CH}$-$\text{CN}$</td>
<td>111.2</td>
</tr>
</tbody>
</table>

Figure by MIT OCW.
“All-Optical Switching”

“Use light to switch light”

• Employ optical materials with intensity dependent properties:

\[ n(I) = n_0 + n_2 I \]

\[ n(I) = n_0 + n_2 I \]

Q: sensor protection?

• Nonlinear phase shift:

\[ \phi_{NL} = (2\pi/\lambda)(n_2 I)L \]

• Fast: light switching light illuminate

Figure by MIT OCW.