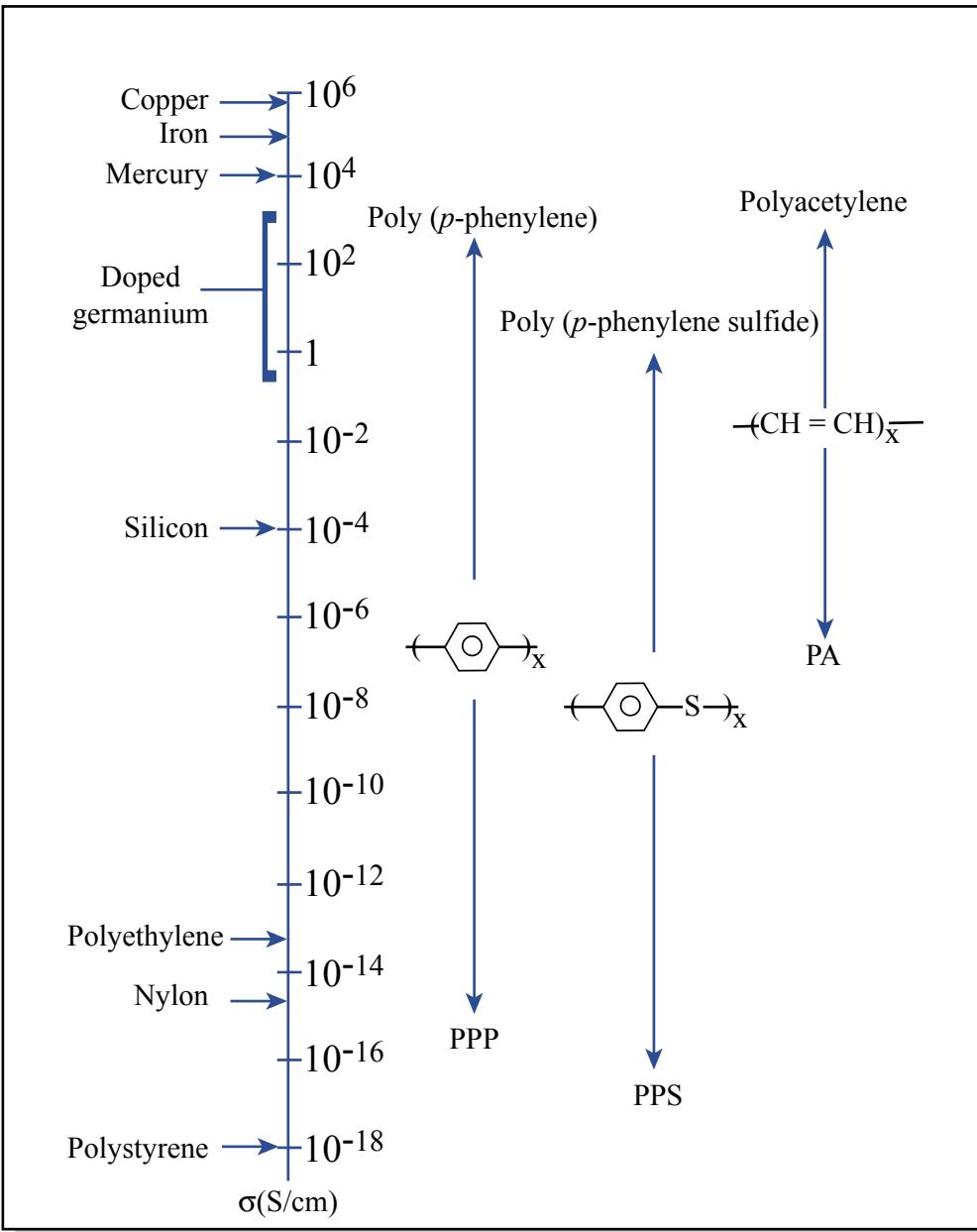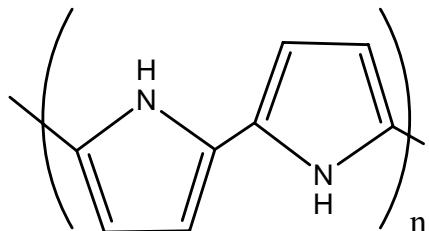# Polymer Conductivities

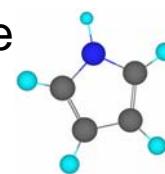Figure by MIT OCW.

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%)
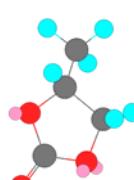
- Light and Flexible

Polypyrrole
Chemical Structure

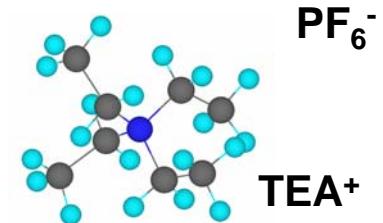Deposition Solution Components:

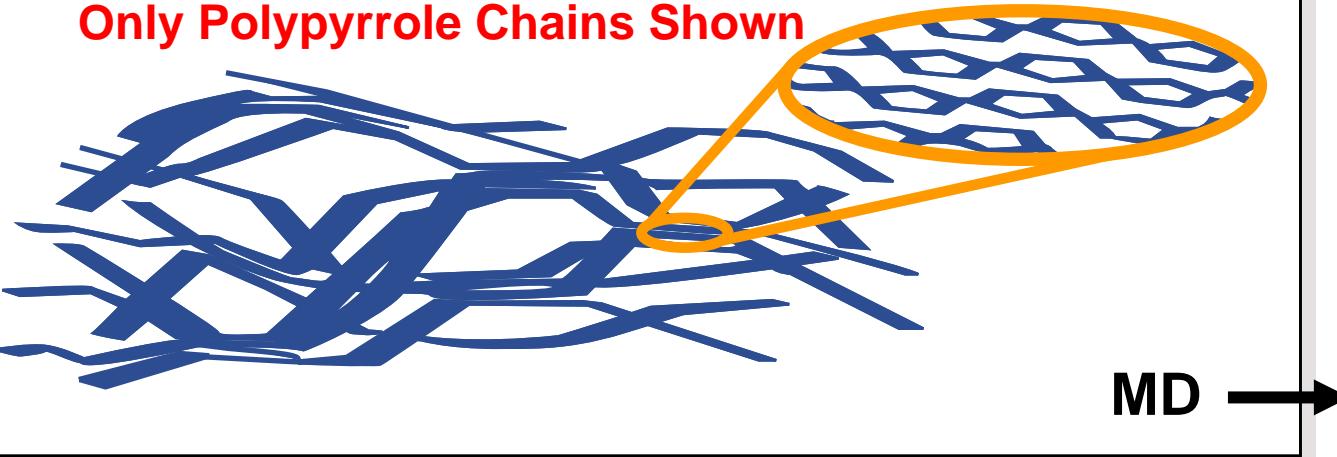Monomer:
Pyrrole

Solvent:
Propylene Carbonate

Counterions:
Tetraethylammonium
Hexafluorophosphate
(TEA-PF6)

PF_6^-

TEA^+

Polypyrrole Microstructure

Only Polypyrrole Chains Shown

MD →

Polypyrrole has disordered rigid chains held together by small, π-stacked bundles.

Figure by MIT OCW.

- Bundles do not give rise to crystalline peaks in x-ray, but do cause certain characteristic reflections

- Bundles consist of π-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 Microstructure

Stretched Film Components

MD ⟶

As-deposited film is ~40% polypyrrole, 30% propylene carbonate and 30% PF$_6^-$
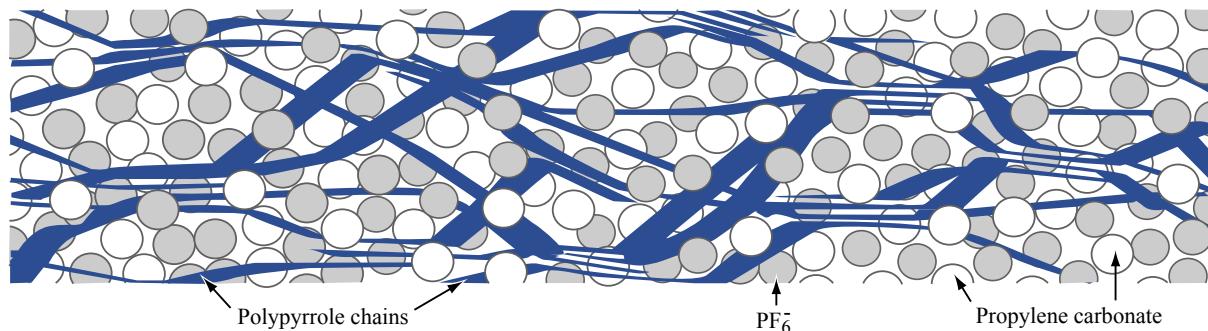
Polypyrrole chains

PF$_6^-$

Propylene carbonate

Figure by MIT OCW.

- As polymerized film has polypyrrole chains positively charged, **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.

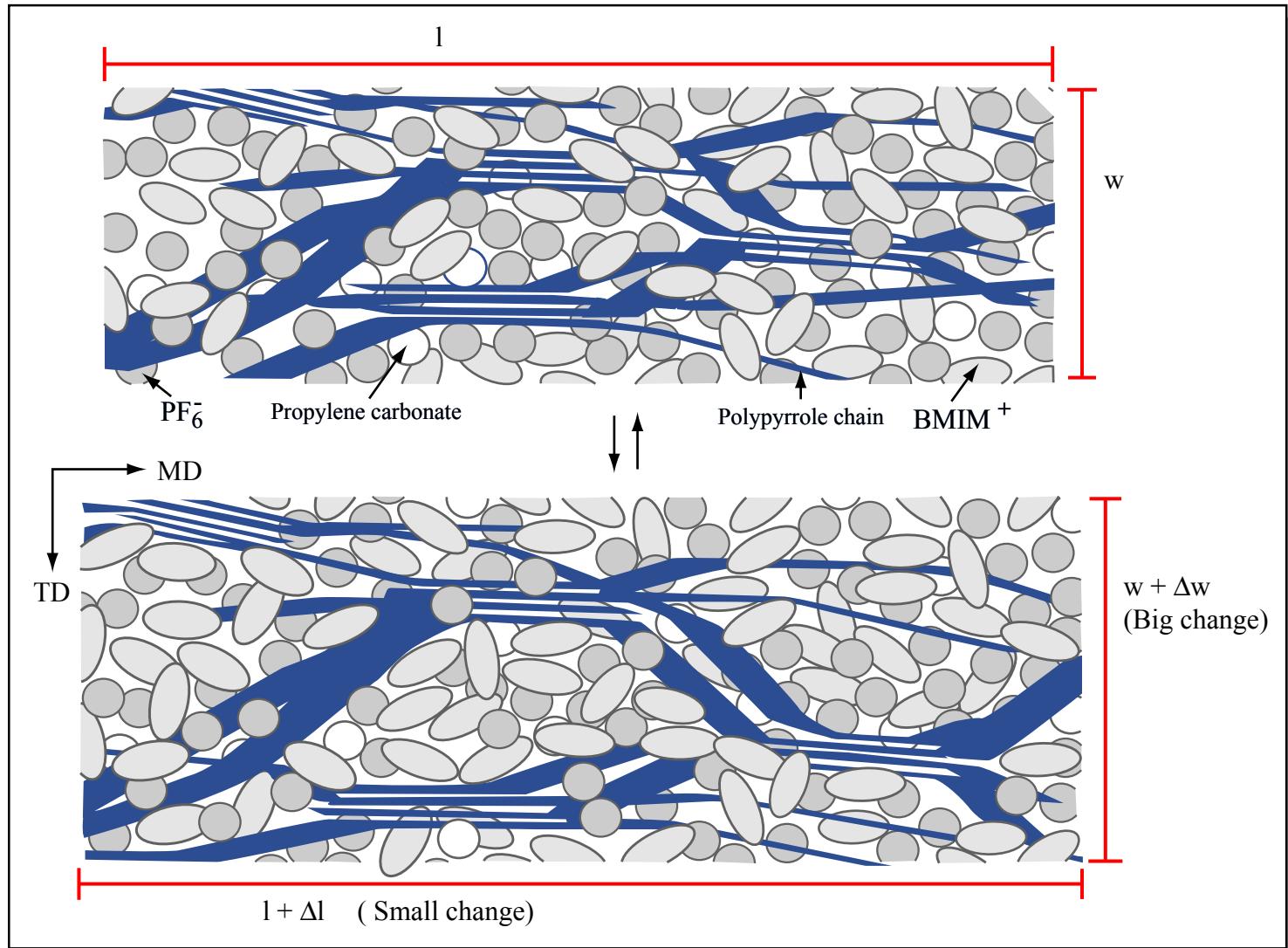# Mechanism of Actuation in Oriented Pyrrole Films

l

w

PF_6^- Propylene carbonate   Polypyrrole chain   BMIM$^+$

MD

TD

$w + \Delta w$
(Big change)

$l + \Delta l$ (Small change)

Figure by MIT OCW.

Actuation of Different Recipes

Potential (V) or Strain (%)

TBA-TFSI/MB on Ni

$\sigma = 3.6 \times 10^3$ S/m
E = 40 MPa
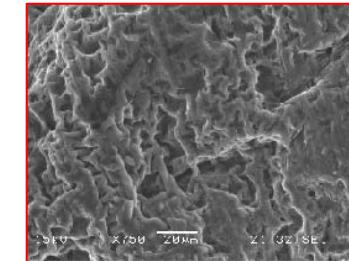
TBA-TFSI/MB on GC

$\sigma = 2.5 \times 10^4$ S/m
E = 240 MPa

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

Surface morphology

Potential

One has to find a balance between fast and large active strains
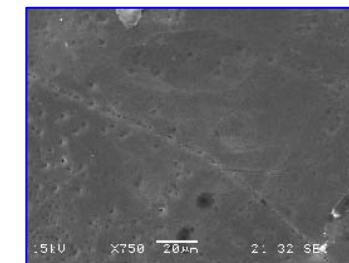
Recipe	Contraction (%) at ±0.8V in:	
	10 sec	60 sec
TBA-TFSI/MB on GC	2.05	5.22
TBA-TFSI/MB on Ni	2.75	4.27

Polypyrrole Actuation

Isometric Testing

- Apply constant strain to polymer strip, measure active stress

Isometric: ε_o **= 1%**

Applied Potential (V)

Measured Current (mA)

Images of polypyrrole actuation and various data removed due to copyright restrictions.

Calculated Charge (mC)

$q(t)$

Measured Stress (MPa)

$\sigma(t)$

Actuation Solution: 0.1M LiTFSI in PC

PC

TSFI⁻

Optical Properties of Materials

1. Linear, homogeneous, isotropic, nondispersive media

P = polarization density

E = electric field

ε_0 = dielectric permittivity

χ = scalar constant $\equiv$ electric susceptibility

n = index of refraction = c/v

$$\vec{P}(\vec{r},t) = \varepsilon_0 \, \chi \, \vec{E}(\vec{r},t)$$

c = speed of light in vacuum,
v = speed of light in material

$$n = \left(\frac{\varepsilon}{\varepsilon_0}\right)^{1/2} = (1+\chi)^{1/2}$$

2. Inhomogeneous medium

$$n = n(\vec{r}) \quad \chi = \chi(\vec{r}) \quad \varepsilon = \varepsilon(\vec{r})$$

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 2nd rank tensor

$$P_i = \sum_j \varepsilon_0 \, \chi_{ij} \, E_j$$

By a suitable choice of coordinate system, χ_{ij} can be made so that off-diagonal elements are zero. χ_{11}, χ_{22}, χ_{33} define the principal susceptibilities along the principal axes.
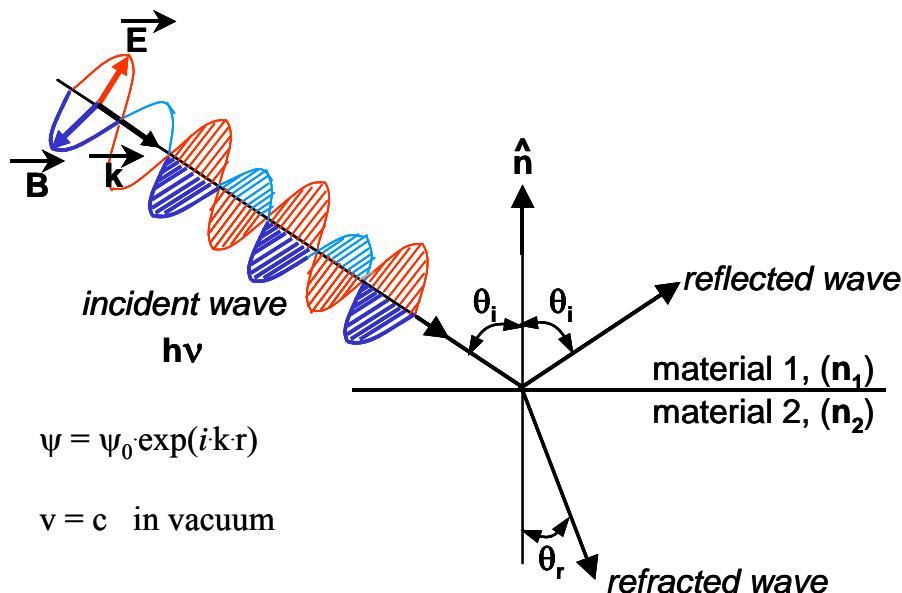
4. Absorption $\qquad \chi = \chi' + i\chi''$ $\qquad\qquad$ complex susceptibility

Optical Properties
Interaction of E-M Radiation with Polymers

$$\psi = \psi_0 \cdot \exp(i \cdot k \cdot r)$$

$$v = c \quad \text{in vacuum}$$

Possible Interactions:

1. reflection
2. refraction
3. absorption
4. polarization change

$$n = n_R - i n_i$$

$$\text{Re}(n) = n_R$$

$$\text{Im}(n) = n_i \equiv \text{absorption}$$

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 θ_i with the normal on the interface between the 2 materials.

2. **Refraction**
   - **Snell's Law of Refraction:** $\quad\quad\quad\quad\quad\quad n_1\sin(\theta_i) = n_2\sin(\theta_r)$
     - it is possible to determine n_2 if n_1 known (for air $n = 1$), by measuring θ_i, θ_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).

   For neutral molecules: $\quad \dfrac{n^2 - 1}{n^2 + 2} = \dfrac{1}{3\varepsilon_o} \sum_i N_i \alpha_i \quad$ (Lorenz - Lorentz equation)

   n = refractive index, $\quad\quad\quad\quad\quad \alpha_i$ = polarizability of the ith chemical bond
   $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad N_i$ = number of ith type chemical bond

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

   e.g. $\quad$ IR $\quad\quad\quad\quad$ – vibrations of atoms / chemical bonds (basis for IR spectroscopy which identifies atomic groups based on characteristic vibrations)
   $\quad\quad\quad$ UV $\quad\quad\quad\quad$ – 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
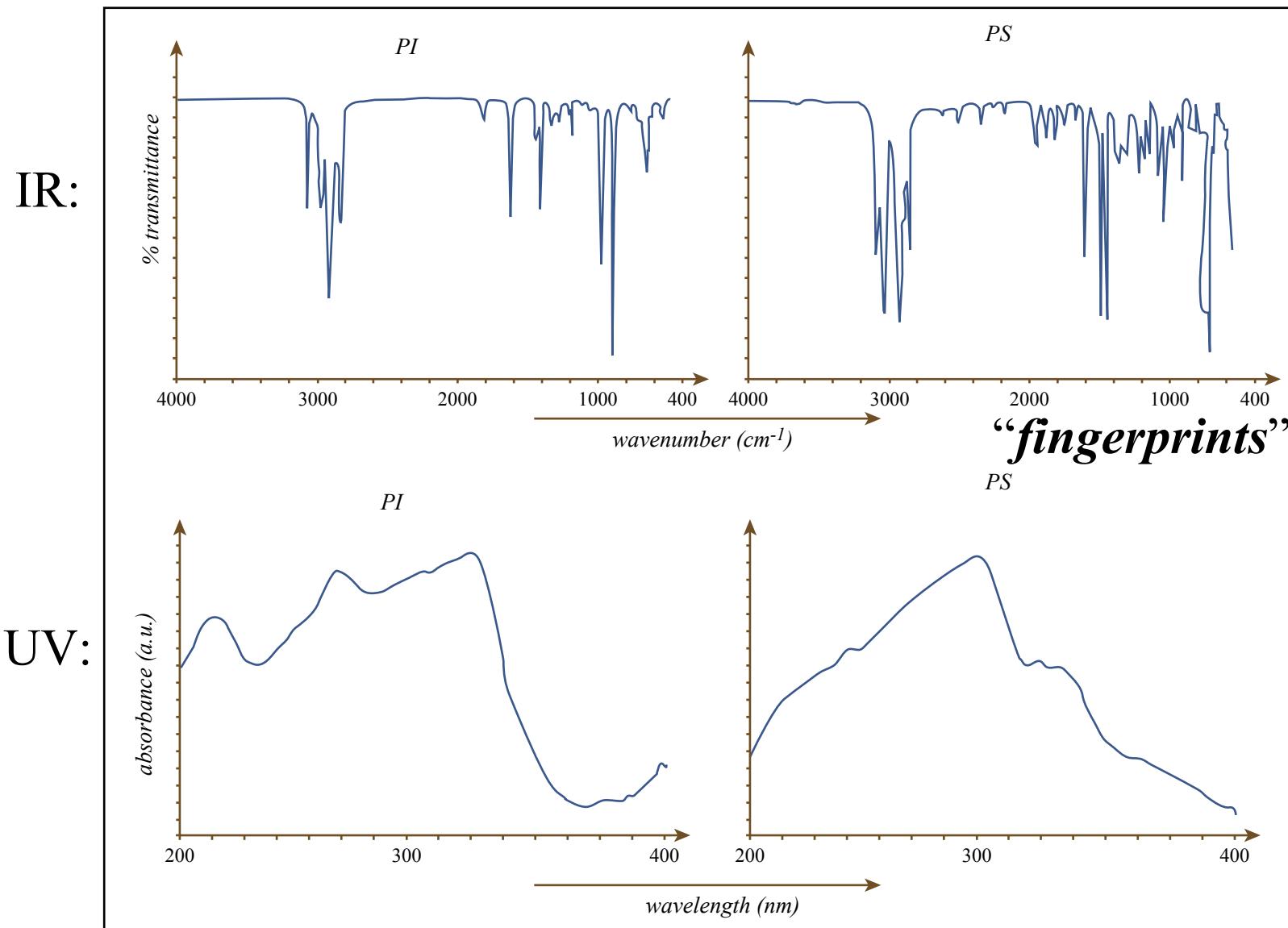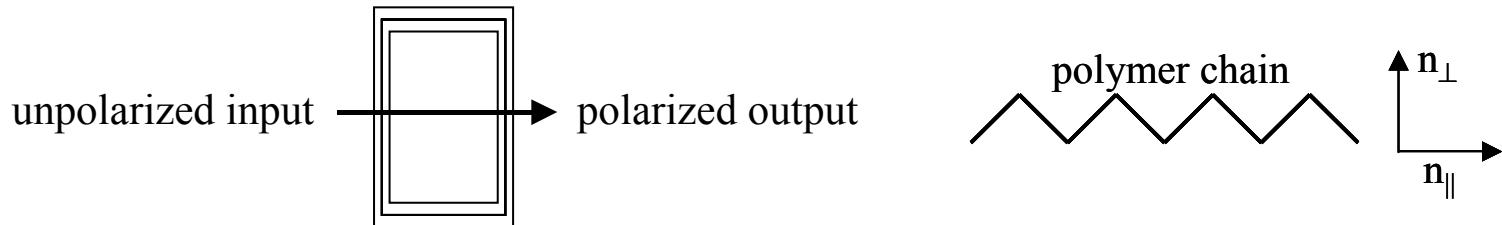
Absorption of Polymers in IR and UV

Figure by MIT OCW.

4. Polarization Change

Methods of Producing Polarized Light

unpolarized input → polarized output

polymer chain $n_\perp$ $n_\parallel$

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

2. Birefringence

    Q: how does a LCD pixel work?

    - 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

Nonlinear Optical Materials

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

alternatively can write in terms of molecular susceptibility per unit volume

$$\mu_i = \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l$$

α_{ij} = molecular susceptibility

β_{ijk} = nonlinear molecular susceptibility of order 2   (3rd rank tensor)

γ_{ijkl} = nonlinear molecular susceptibility of order 3   (4th rank tensor)

the β and γ terms depend on the number of molecules per unit volume and their orientation.

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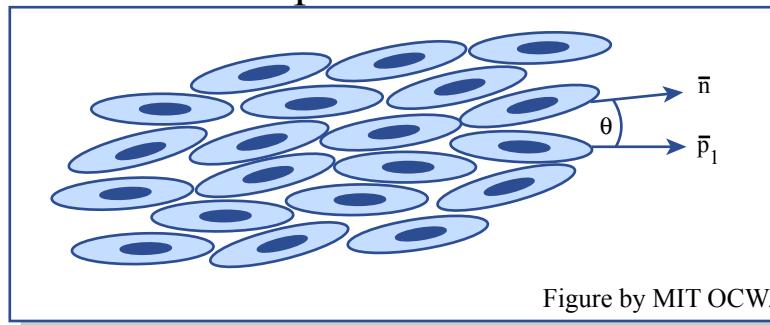$$\chi^{(3)} \sim \gamma\langle\cos^4\theta\rangle$$

Figure by MIT OCW.

$\chi^{(2)}$ is zero for centrosymmetric orientation of an array of dipoles since $\cos^3 0^\circ = 1$
        but $\cos^3 180^0 = -1$ 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

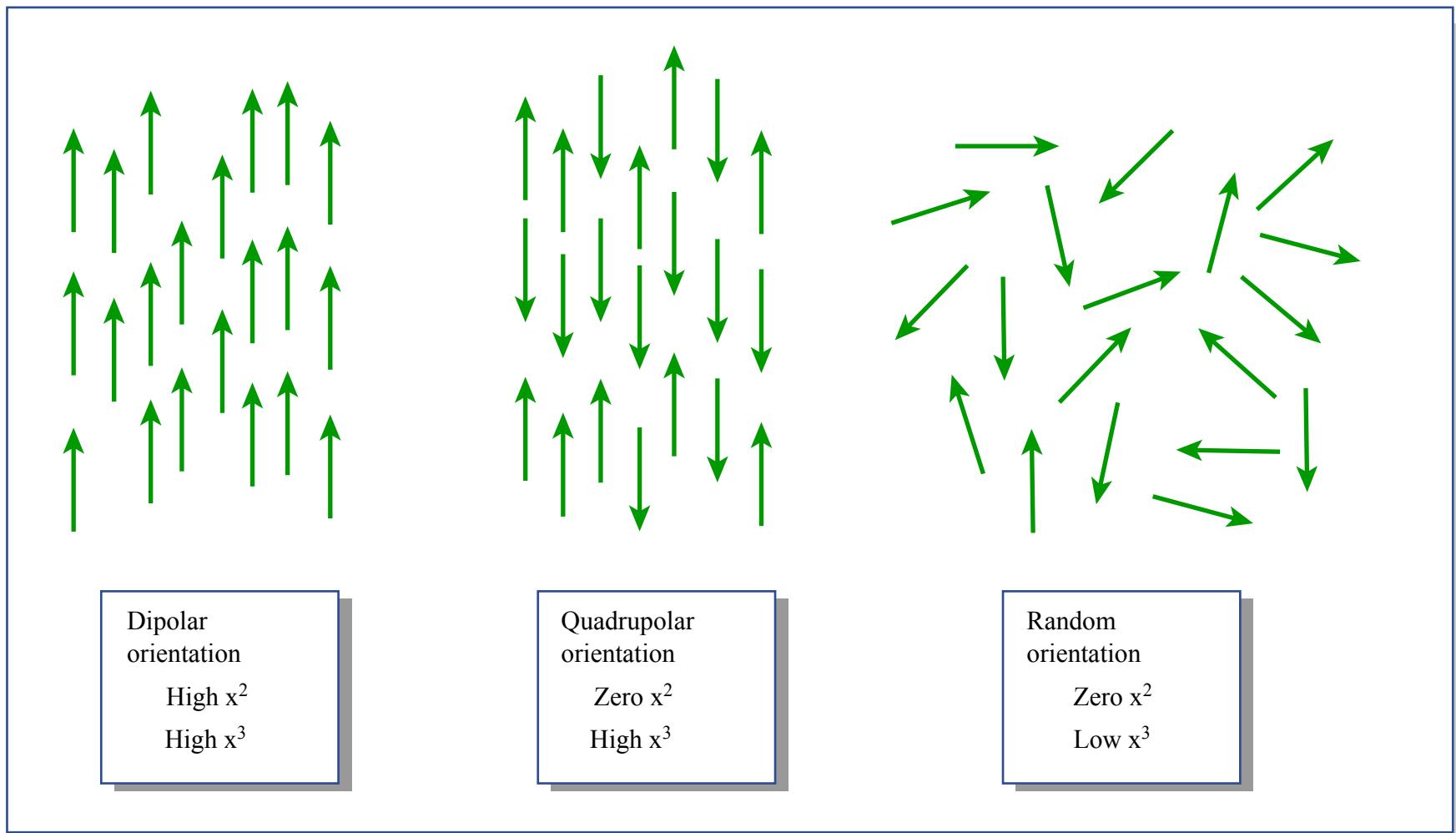Random orientation

Zero x^2

Low x^3

Figure by MIT OCW.

Frequency Doubling

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

Second-Order NLO Materials

$$\left|\vec{P}_{NL}\right| = \varepsilon_o \chi^{(2)} |E|^2 \qquad \text{where } \left|\vec{P}_{NL}\right| \text{ is the magnitude of the 2}^{nd} \text{ order nonlinearity}$$

assume $\qquad E(z,t) = E_o \cos(2\pi\nu t - k z)$ $\qquad$ DC $\qquad$ frequency doubled

then $\qquad \left|\vec{P}_{NL}\right| = \dfrac{\varepsilon_o}{2} \chi^{(2)} E_0^{\,2} \left(1 + \cos(4\pi\nu t - 2k z)\right) = P_{NL}(0) + P_{NL}(2\nu)$

The term $\vec{P}_{NL}(2\nu)$ 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 $\chi^{(3)} \neq 0$

intensity modulation
of incident ν

frequency tripled
(THG)

$$\left|\vec{P}_{NL}\right| = \varepsilon_o \, \chi^{(3)} \left|E\right|^3$$

$$\left|\vec{P}_{NL}\right| = \frac{\varepsilon_o}{4} \chi^{(3)} E_0{}^3 \left(3\cos(2\pi\nu t - 2kz) + \cos(6\pi\nu t - 3kz)\right)$$
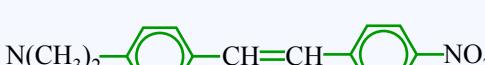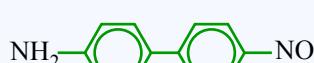
The polarization component at incident frequency ν, $\vec{P}_{NL}(2\nu)$ has changed due to interaction of the light with the NLO material.

This corresponds to an incremental change in susceptibility: $\Delta\chi$

$$\Delta\chi = \frac{P_{NL}(\nu)}{E(\nu)} = \frac{\frac{3}{4}\varepsilon_0 \chi^{(3)} E_0{}^3 \cos(2\pi\nu t - kz)}{E_0 \cos(2\pi\nu t - kz)}$$

$$= \frac{3}{4}\varepsilon_0 \chi^{(3)} E_0{}^2$$

NLO Chromophores Values, β
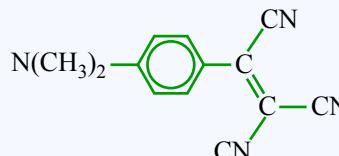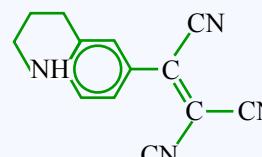
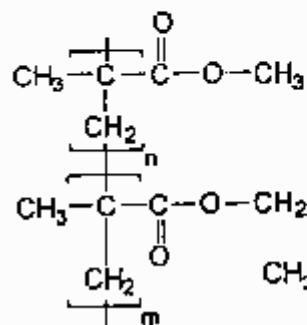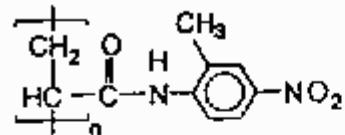| STRUCTURE	β at 1.9 μm ×10⁻³⁰ esu
NH_2—⬡—NO_2	5.7
$N(CH_3)_2$—⬡—C=C(CN)(CN) with CN	21.4
(ring)NH—⬡—C=C(CN)(CN) with CN	41.8
$N(CH_3)_2$—⬡—CH=N—⬡—NO_2	23.4
$N(CH_3)_2$—⬡—CH=CH—⬡—NO_2	60.0
NH_2—⬡—⬡—NO_2	20.1
NH_2—⬡—⬡—⬡—NO_2	50.7
$N(CH_3)_2$—⬡—CH=CH—CH=CH—⬡—NO_2	111.2

Pendant Chromophores

Figure by MIT OCW.

"All-Optical Switching"

"Use light to switch light"

- Employ optical materials with intensity dependent properties:

$$n(I) = n_0 + n_2 I$$

Q: sensor protection?

- Nonlinear phase shift: $\phi_{NL} = (2\pi/\lambda)(n_2 I)L$

- Fast: light switching light illuminate

Figure by MIT OCW.