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Order and Charge Collection Correlations in Organic Materials for Neutron Detection

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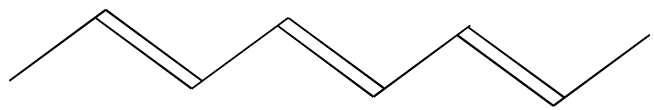
Overview

- Polymers for Radiation Detection
  - Advantages over current methods
  - Electrical/material property considerations
- Processing Effects
  - Order
  - Preliminary Electrical

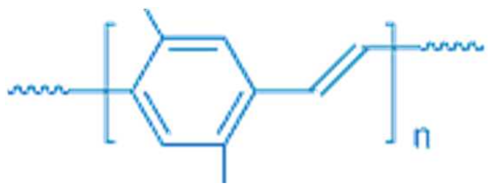
Polymer Radiation Detection - Why?

- Direct detection of fast neutrons (2 MeV), with no moderator
- Semiconducting radiation detectors allow direct detection with no photomultiplier, as required with scintillators
- Room temperature operation improves cost, size and convenience
- Low Z polymer provides natural gamma discrimination
- High H/C ratio for neutron sensitivity

Conjugated Polymer Properties



- Conductivity from insulator to metallic (after doping)
- PPVs have mobilities typically from ~10^{-5} to $1x10^{-2}$ cm^2/Vs



- Workable air stability
- Properties depend on side chain symmetry – higher symmetry leads to more extended conformation*
- Very dependant on processing!
  - Solvent, concentration
  - Additives – nanoparticles and plasticizers
  - Deposition method and conditions
  - Post-Deposition processing – vapor, anneal, stretch

*Geens, *Synthetic Metals* **2001**; Tanase, *Journal of Applied Physics* **2005**; van Breemen, *Advanced Functional Materials* **2005**

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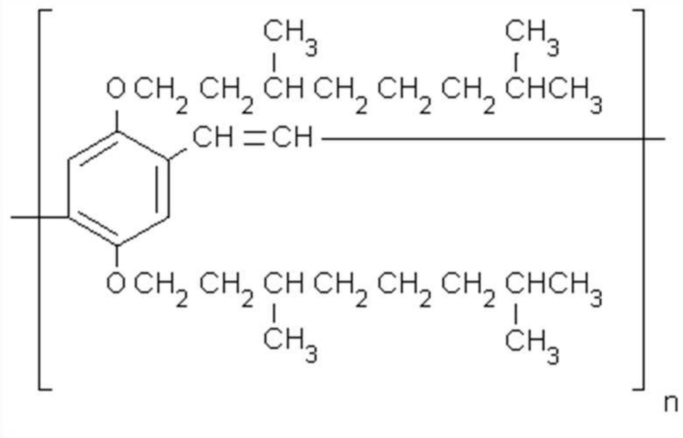
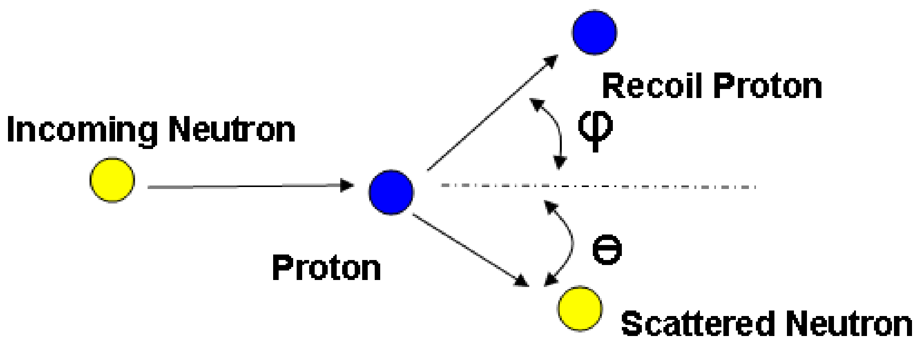
Focus Polymer - $OC_{10}PPV$

- Commercially available
- Symmetric PPV with Hydrogenous side chains
- poly[2,5-bis(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene]
- H/C = 1.7



Polymer Radiation Sensors – How?



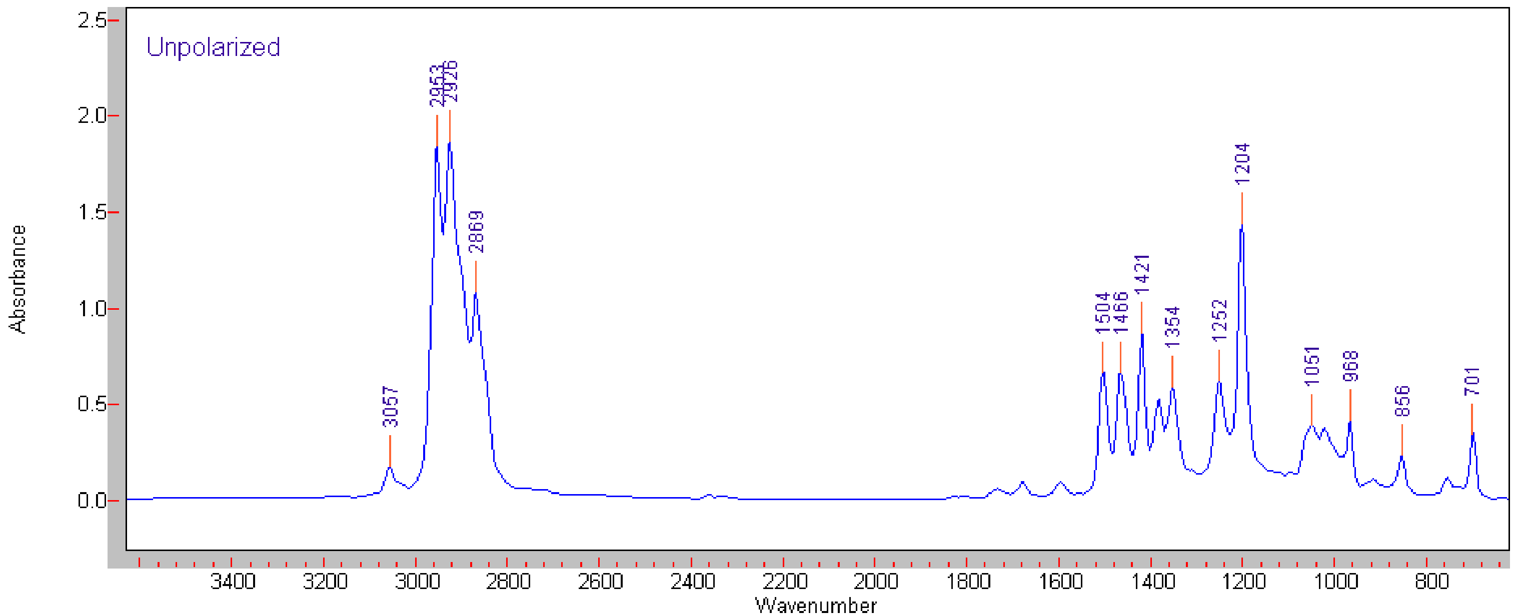
- Proton recoil reaction
- Proton excites mobile charged particles → detection

- We Need
  - High mobility
  - High resistivity
  - Thickness (high H density per unit area)
  - Low trapping
- Controlled by
  - Chemistry
  - Environment
  - Processing!!
  - Additives

Processing/ Orientation

- Drop cast onto glass/electrodes
- Drop cast onto unoriented PTFE surface, remove and test
- Drop cast onto skived PTFE substrate, dry, remove and test
- Drop cast onto skived PTFE substrate, dry and stretch, then remove and test
- Additional variables
  - Vapor environment
  - Anneal after stretching

Infrared Spectroscopy



Wavenumber (1/cm)	Absorbance	Likely Origin
2955	2.06	Aromatic C-H Stretch
2926	2.05	Vinylene C-H Stretch
1469	0.78	C-C ring stretch
1256	0.75	C-H in-plane bend
1206	1.74	C-H bend
966	0.58	C-H out of plane wagging vinylene
856	0.35	C-H out of plane wagging phenylene

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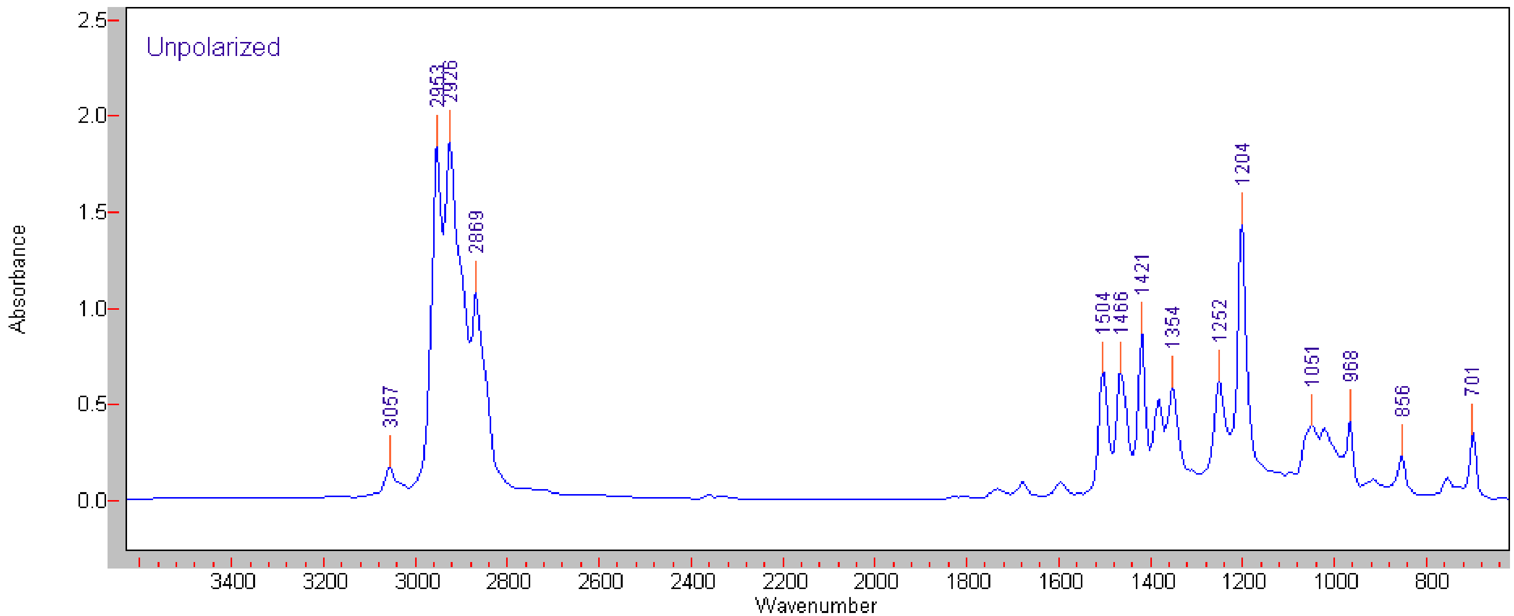

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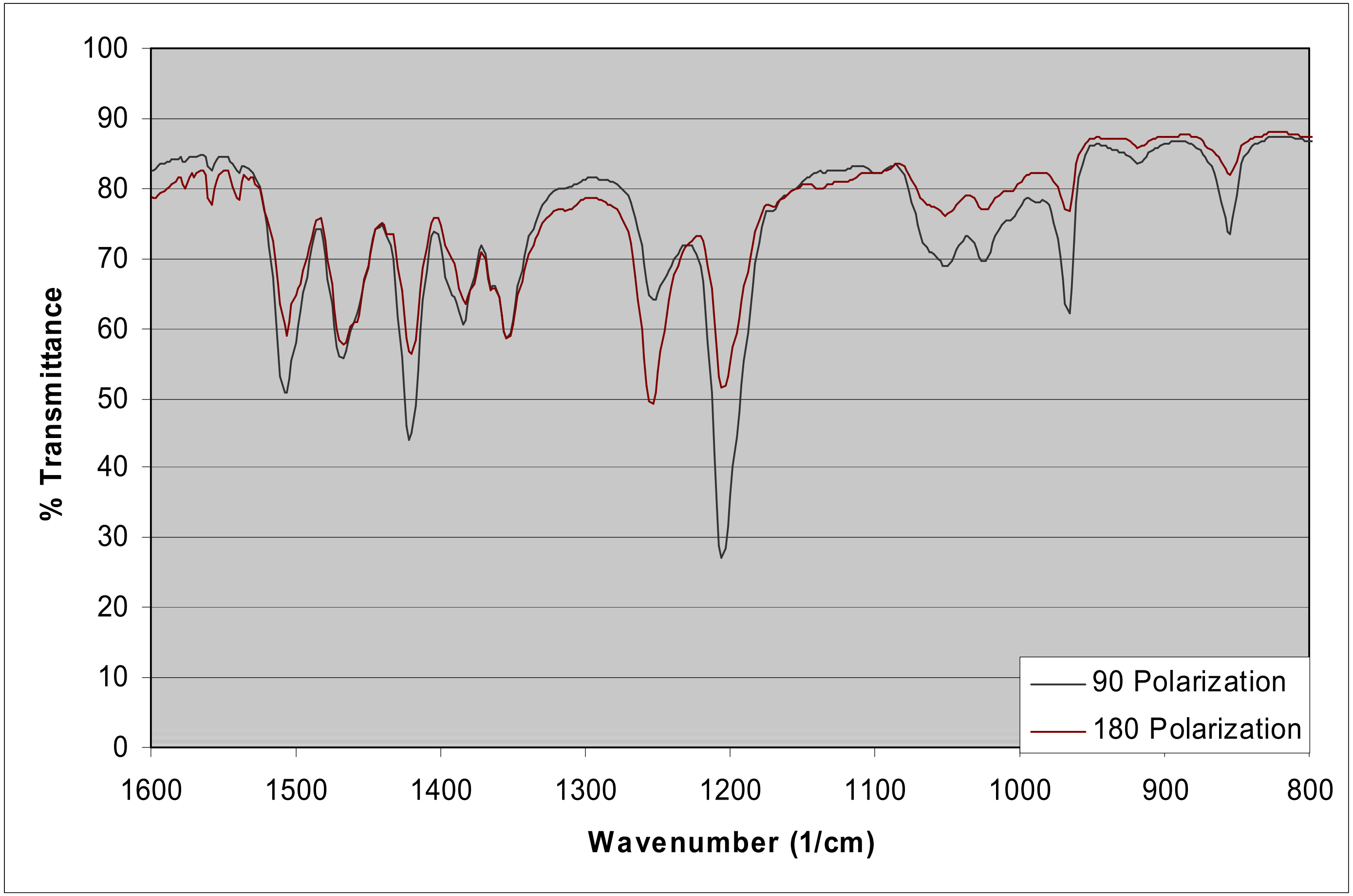
Infrared Dichroism

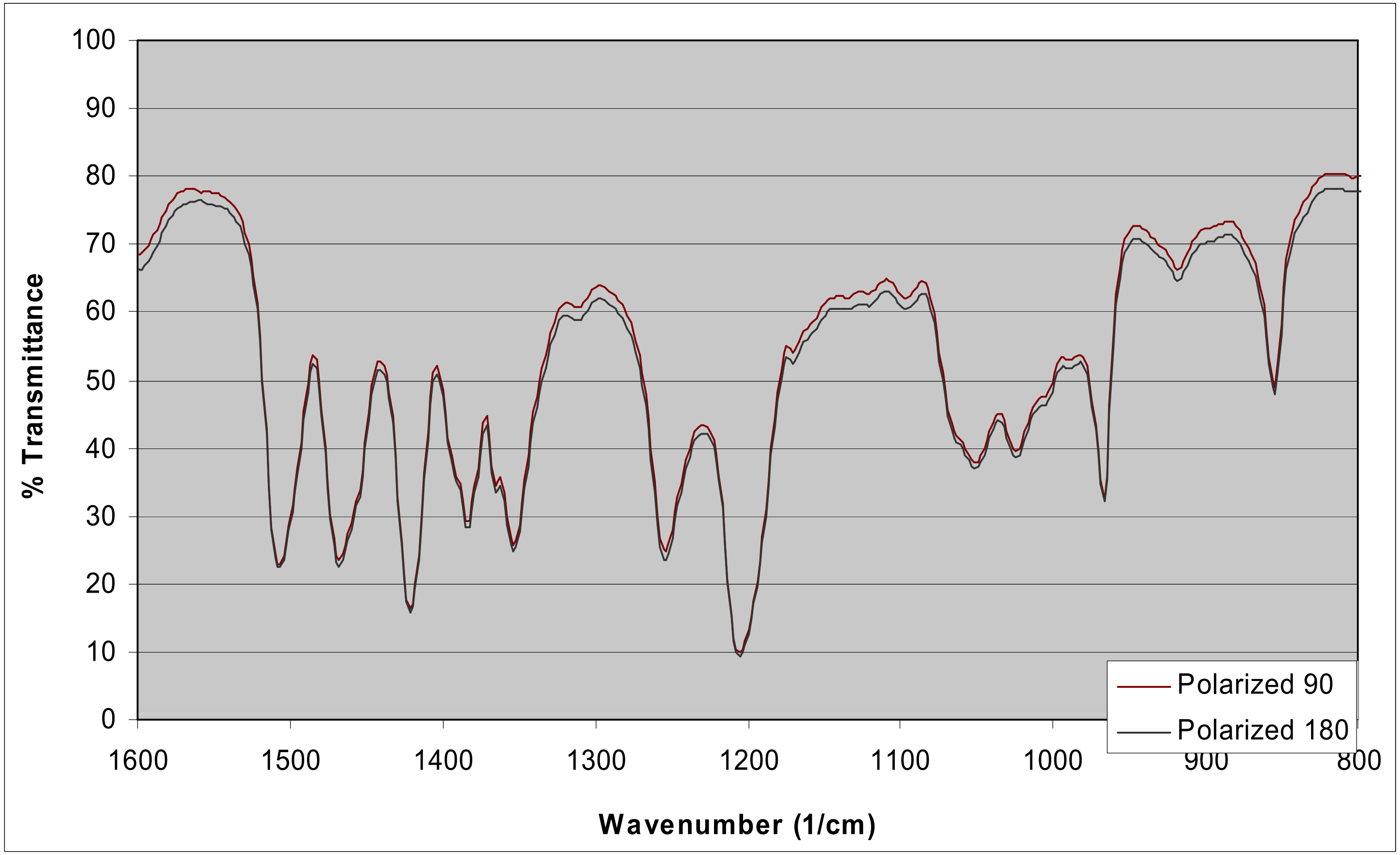
- Experimental method to determine order in amorphous or crystalline samples
- Yields Hermans orientation function, f
- Equivalent, for appropriate samples, to X-Ray Diffraction and birefringence
- Use two orthogonal angles of polarization
- Vibrational excitations respond differently based on angle relative to polarization angle
- Dichroic ratio is ratio of absorbance in one orientation relative to that in orthogonal orientation
- Dichroic ratio of 1 is perfectly amorphous and tends toward 0 or ∞ with increasing order

FTIR Results



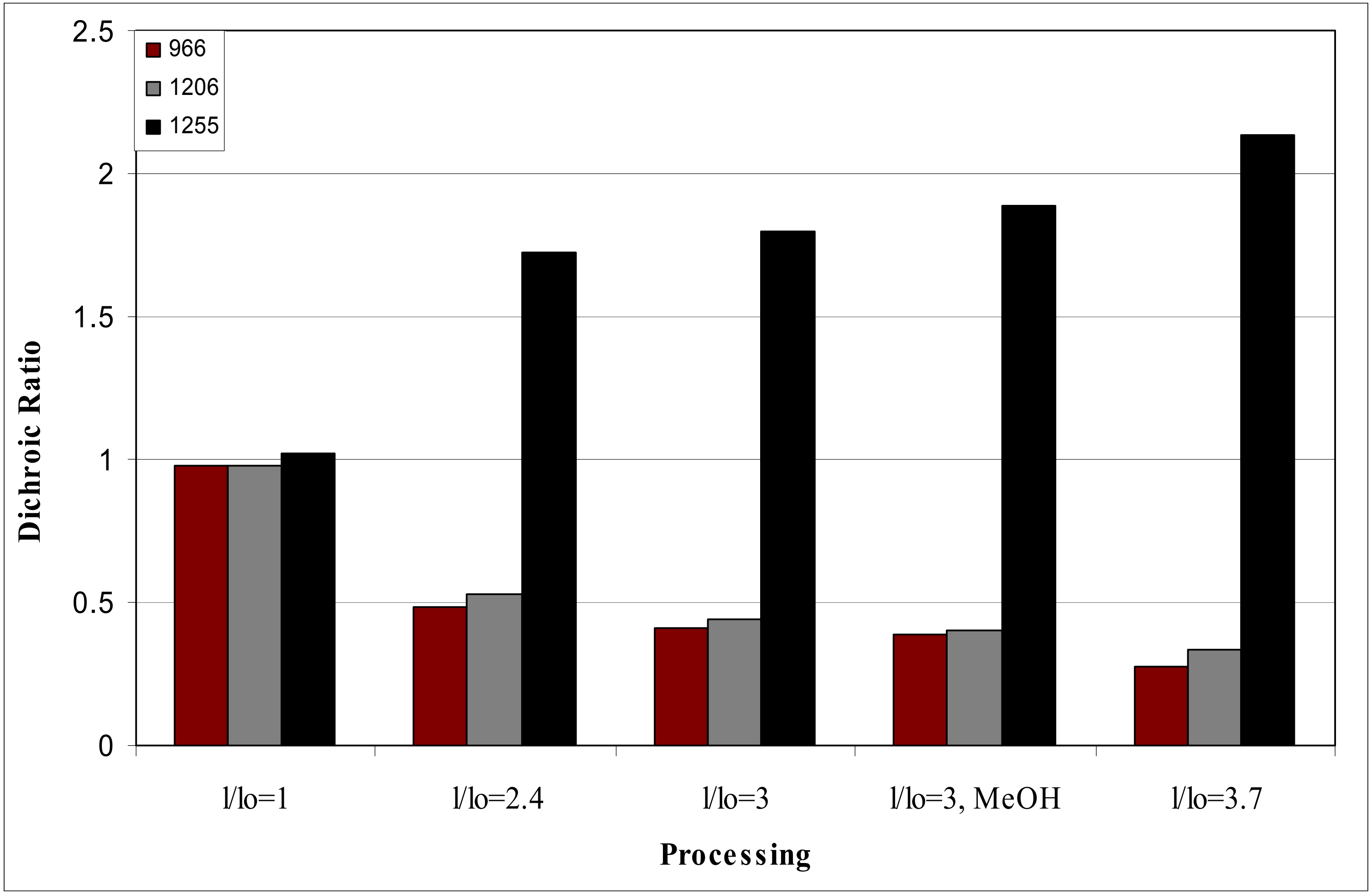
Sample stretched 3x shows significant dichroism, ratios of 1.8 and .44 for peaks at 1254 and 1205 cm^{-1}

As cast film



Unstretched sample shows negligible dichroism, .97 and .96 for peaks at 1254 and 1205 wavenumber

IR Dichroism



Polarized FTIR

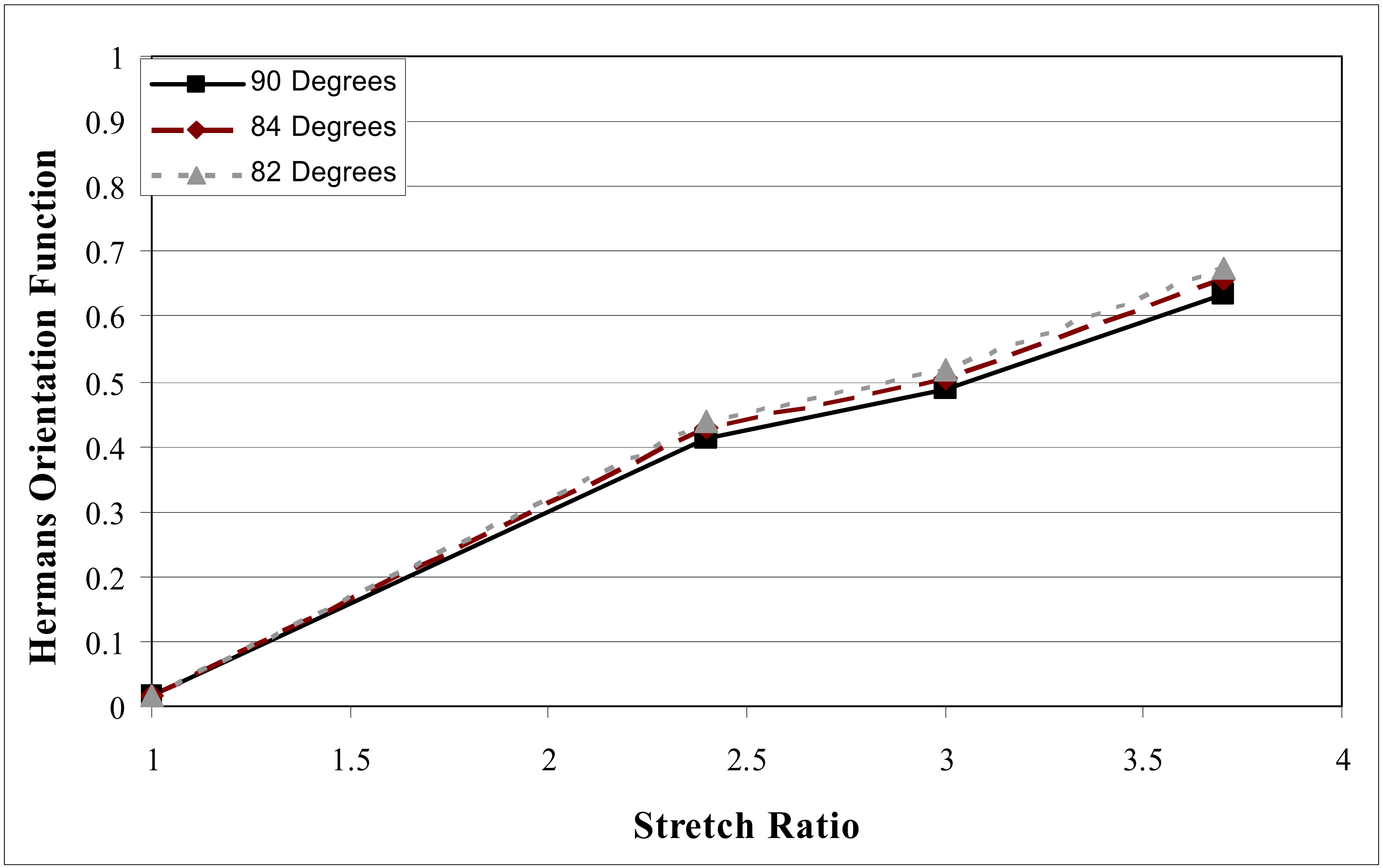
- Dichroic Ratio, R, is a measured figure of merit used to determine an order parameter, s, used to calculate Hermans orientation function, *f*
- Function of α, the angle between the transition dipole and the chain axis

$$R = \frac{A_{\parallel}}{A_{\perp}} = \frac{2\cos^2\alpha + s}{\sin^2\alpha + s}$$

$$f = \frac{2}{3s+2}$$

Dermaut, et.al. *Macromolecules* **2000**

Hermans Orientation Function, *f*



- **Based on absorbance at 966 cm^{-1}**
- **Shown as a function of α and stretch ratio**
- **90 degrees is theoretical and provides lower limit of *f***
- **82 and 84 are experimental values from literature**

Bradley, *Journal of Physics D – Applied Physics* **1987**
Dermaut, et al. *Macromolecules* **2000**

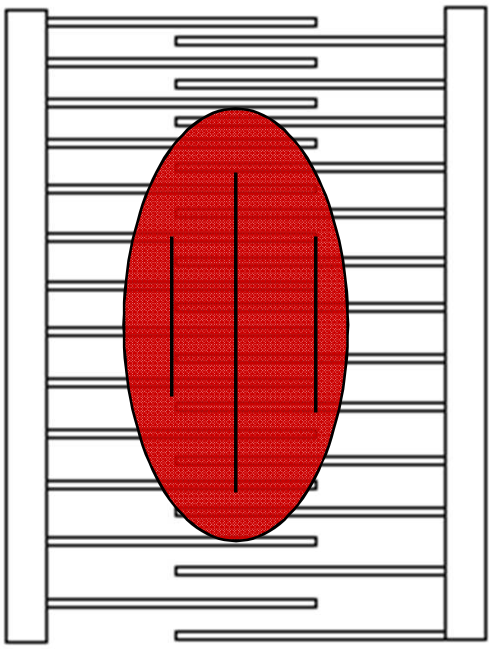
Alpha Calculations

- **Use s from 966 wavenumber to determine alpha for other absorbance peaks**
- **Alpha values are agreeing well**
- **Additional data points will improve reliability of value, and enable use of additional peaks for *f* calculation**

	Calculated orientation parameter, s	Observed Dichroic Ratio at 1205 cm^{-1}	Calculated α at 1205 cm^{-1}	Observed Dichroic Ratio at 1254 cm^{-1}	Calculated α at 1254 cm^{-1}
l/lo=2.4	0.893	0.526	78.3°	1.714	37.2°
l/lo=3	0.656	0.441	80.0°	1.972	38.6°
l/lo=3.7	0.349	0.334	77.9	2.135	38.5

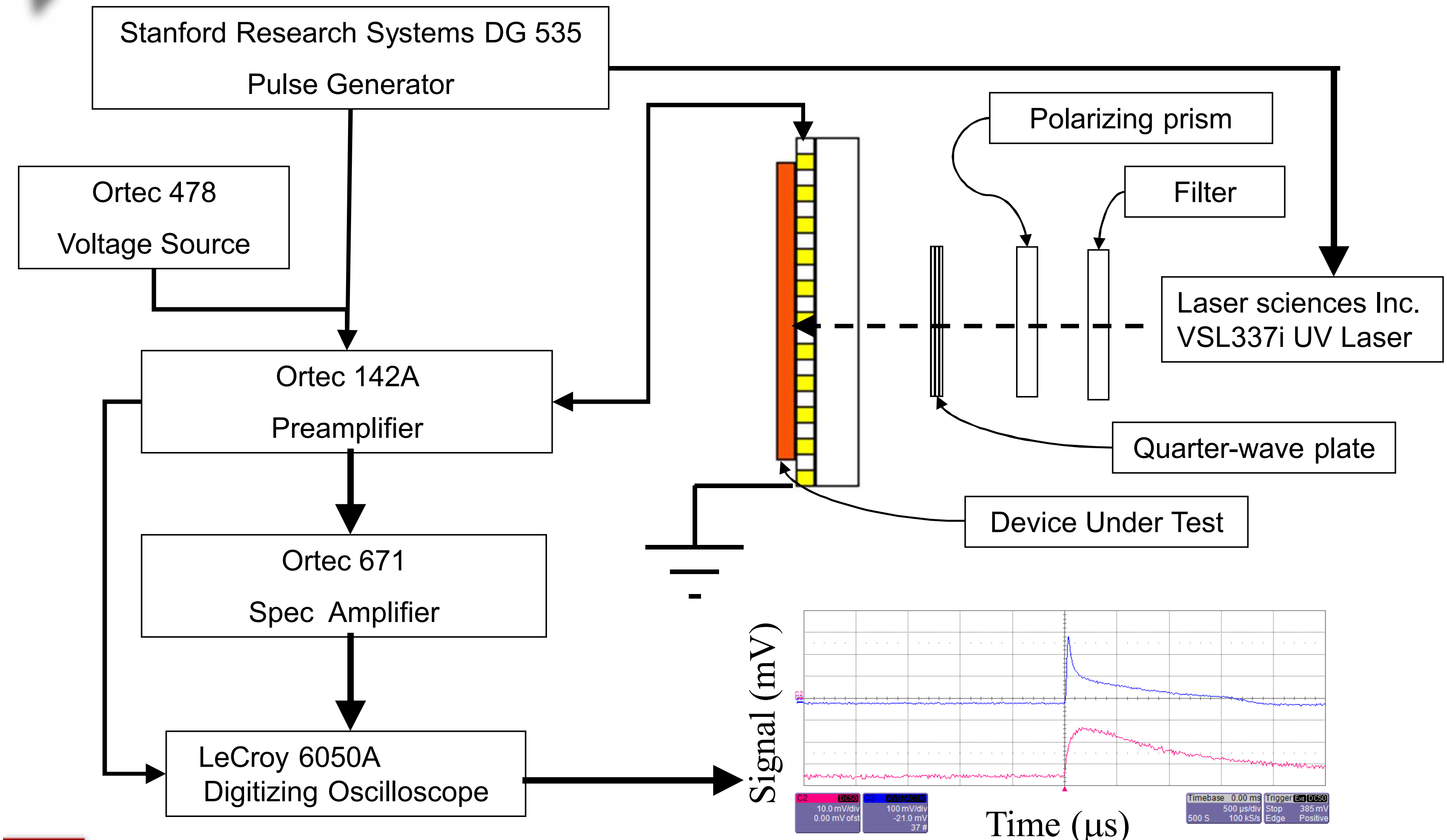
Electrical Testing

- Interdigitated electrodes (IDEs)
- Pitch of 32 μm
- Bias between electrodes
- Can orient film for bias to be parallel or perpendicular to the orientation direction
- Can also directly apply solution with no orientation



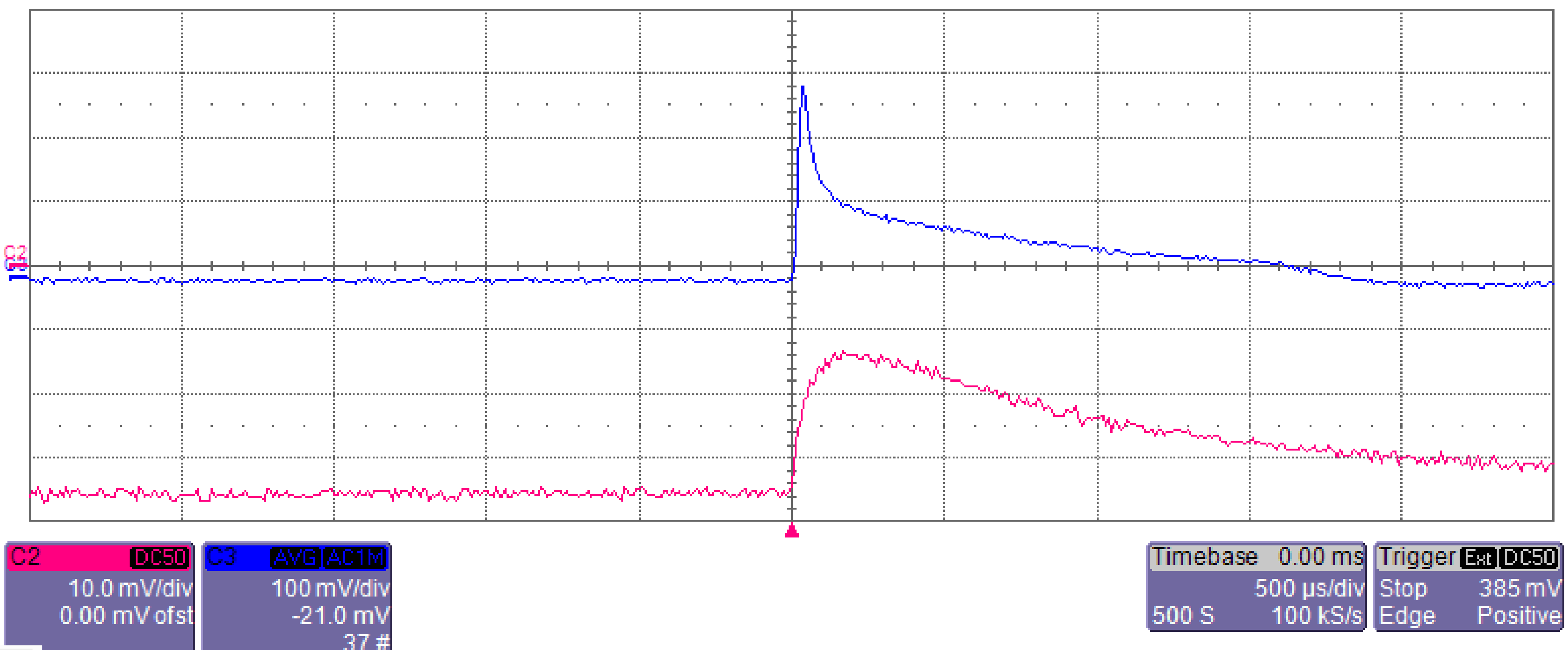
Parallel Orientation

Pulsed Photoconductivity setup

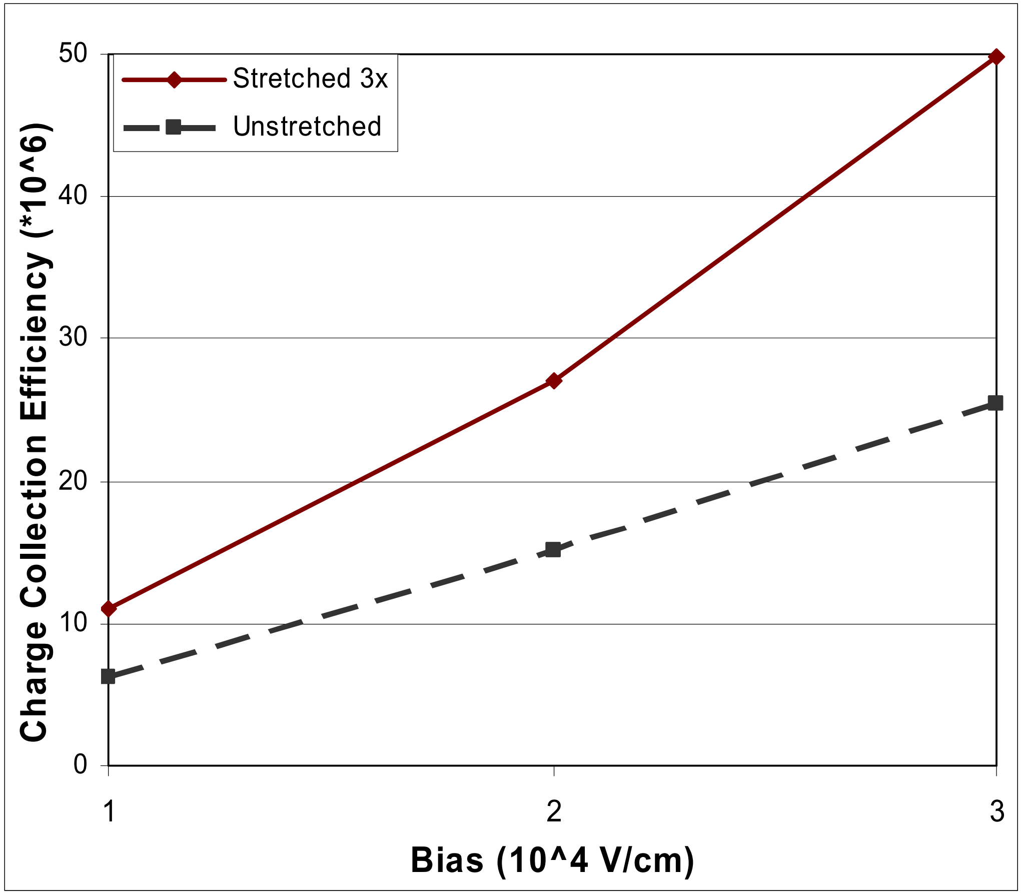


Pulse Length

- Shaping time up to 10μs on amplifier
- Signal length of closer to 1 ms



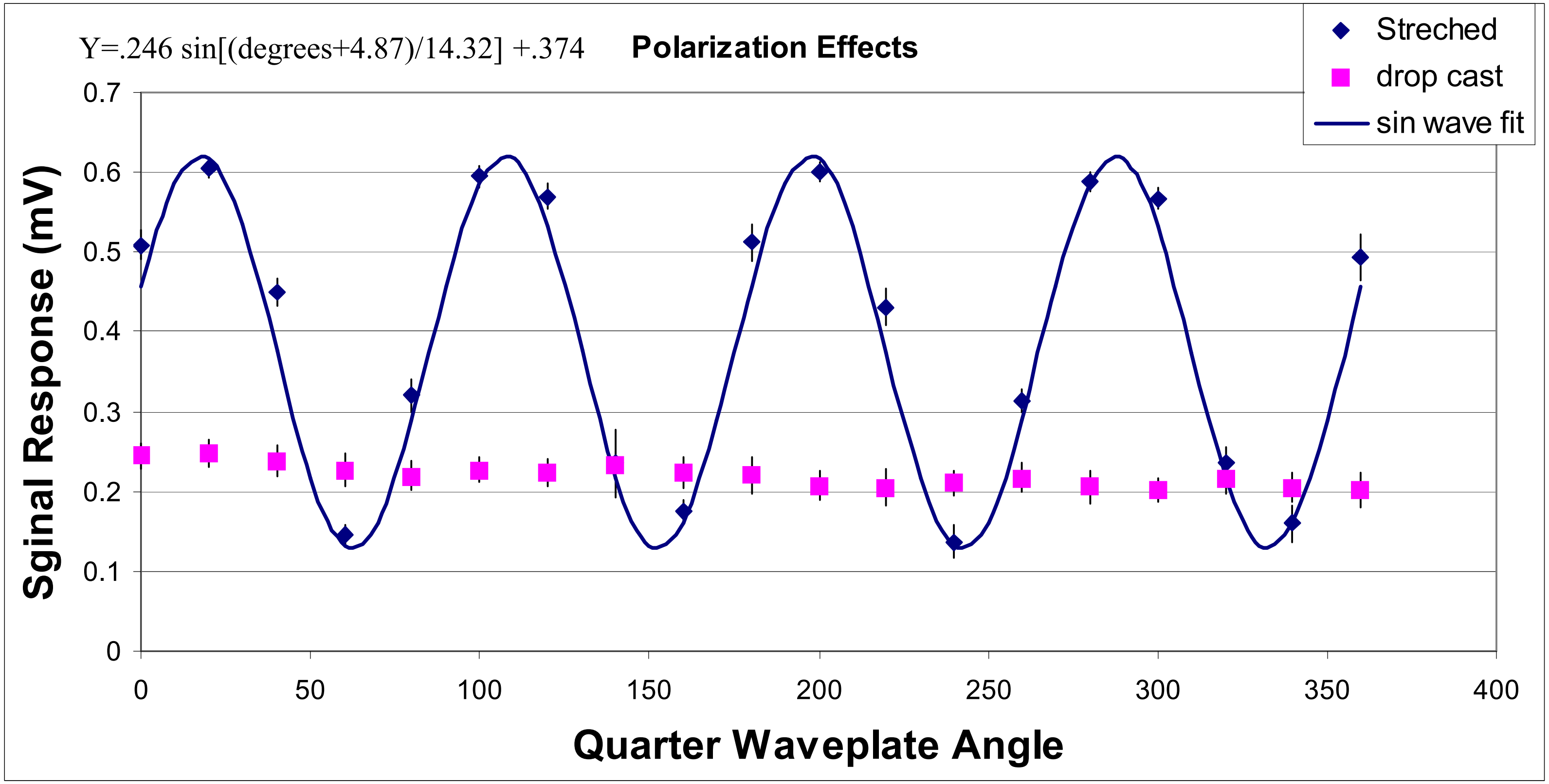
Charge Collection Efficiency



- **32 μm IDTs**
- **590nm pulsed laser**
- **6 μs shaping time**
- **Based on 10% Quantum Efficiency***
- **Stretched sample shows increased charge collection**

*Moses, D.; Dogariu, A.; Heeger, A. J., *Synthetic Metals* **2001.**

Polarization Response



- Effect of stretching on polarization response
- 590 nm stimulus with polarizing filter
- Values shown are for comparison only, not absolute
- Response fits well to a sin wave

Conclusions

- Stretch alignment of polymers can improve order in a film
- Order changes affect electrical response
- Much more improvement should be possible, particularly combined with other variables of additives, plasticizers, and secondary dopants
- Improved knowledge of structure/property relations will greatly improve device performance
- Preliminary data looks promising for a semiconducting polymer neutron detector

Future Work

- Improve processing for higher mobility
- Testing over larger parameter space for
  - orientation parameter (dichroic ratio)
  - electrical properties
  - photoresponse
- Repeatability testing
- Test other variables
  - plasticizers
  - stretch rate
  - secondary solvent
  - anneal
- Test with nanoparticle additives
- Optimization of variables for neutron detection

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