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Nonlinear charge transport in semiconducting polythiophene

I&EC 168 http://oasys2.confex.com/acs/231nm/techprogram/P946482.HTM

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We measured the complex impedance and nonlinear conductivity for regioregular poly(3-hexylthiophene) (P3HT) by recording and analyzing AC waveforms at their fundamental frequency and at higher order harmonic frequencies. We used 50 µm thick films of P3HT with head-to-tail regioregularity of more than 99 %. Gold electrodes were prepared by evaporation. The complex impedance of the semiconducting P3HT decreases exponentially with increasing electric field strength. Furthermore, our broadband dielectric measurements indicate that the apparent semiconducting character of P3HT ceases above a critical frequency, above which the material becomes a dielectric. At room temperature the semiconducting to dielectric transition takes place at about 5 kHz. At frequencies below 5 kHz, P3HT shows a semiconducting character, and the overall response is dominated by conductivity. At low electric fields, the combined temperature and field dependent conductivity of P3HT obeys the bulk-limited Poole-Frankel (PF) model. At higher electric fields, above 10^4 V/cm, the electric field affects the rate of carrier generation or injection, and a bulk limited charge transport undergoes a transition to the electrode limited conduction, which can be expressed as a Richardson-Schottky effect. The non-linear charge transport in P3HT is dominated by the third-order conductivity, which originates from extended p-type electronic states in P3HT. The presented waveform technique is a novel method, which can be used to determine complex impedance and conductivity of semiconducting polymers at high AC electric fields. Our results demonstrate that the third order conductivity can be used to quantify the effect of electric field on conduction mechanism in organic semiconductors and to correlate the intrinsic charge carriers mobility with molecular structure.

Advanced Materials for Microelectronic Packaging (Sponsored by Advanced Materials and Nanotechnology Sub-Division)
8:30 AM-12:00 PM, Monday, 27 March 2006 Georgia World Congress Center -- B313B, Oral

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ACS National Meeting, Atlanta, GA 2006

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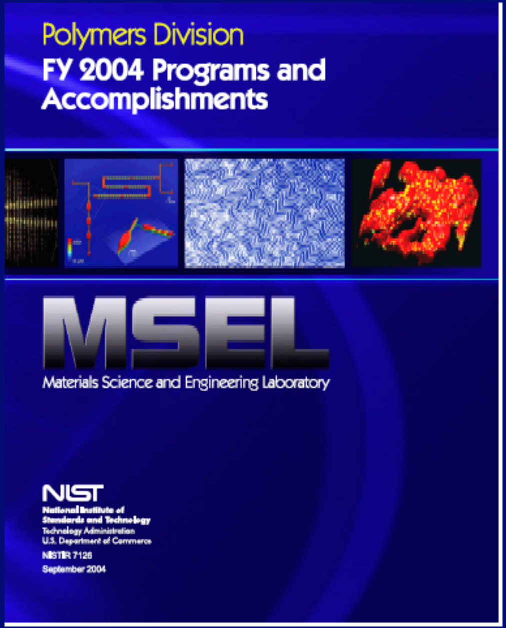

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MSEL
Materials Science and Engineering Laboratory

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September 2004

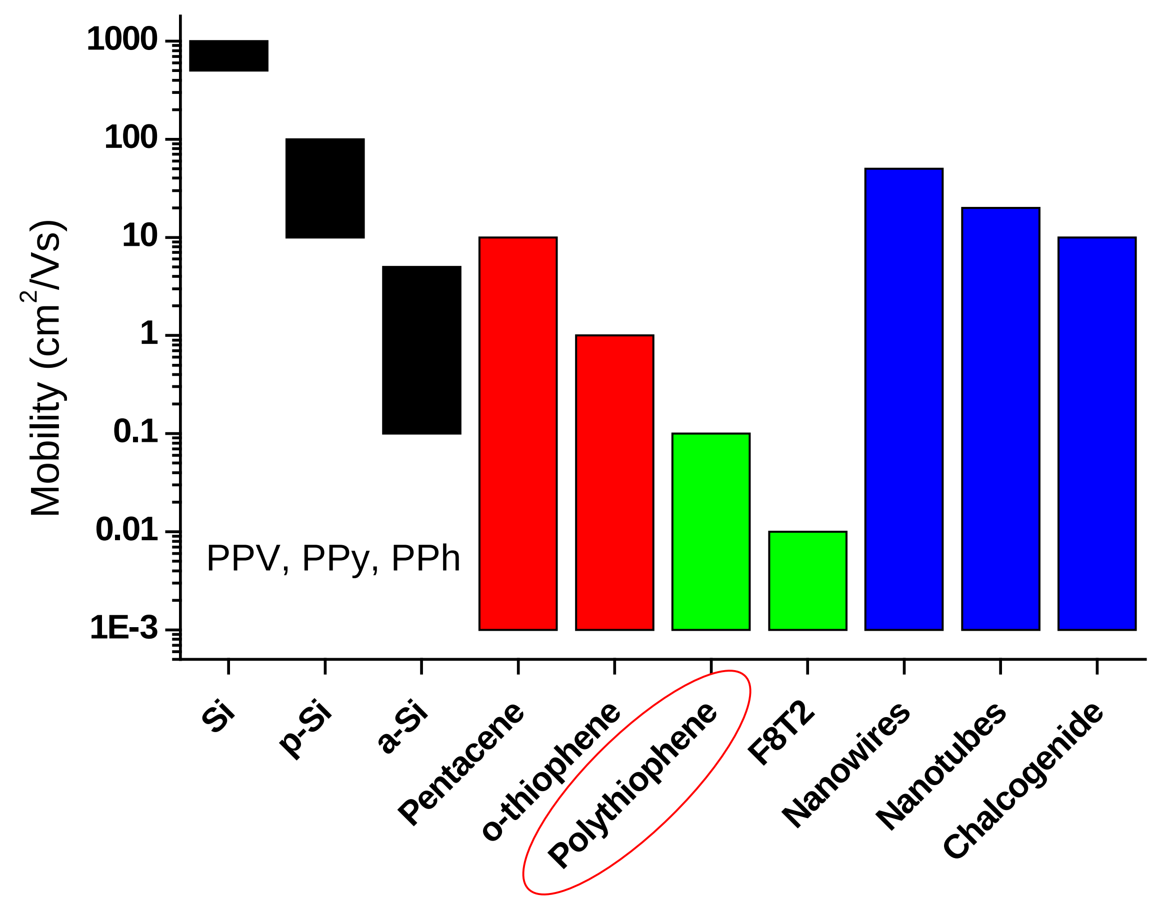
NIST CENTENNIAL 1901-2001

- Established 1901
- 3300 employees

http://polymers.msel.nist.gov

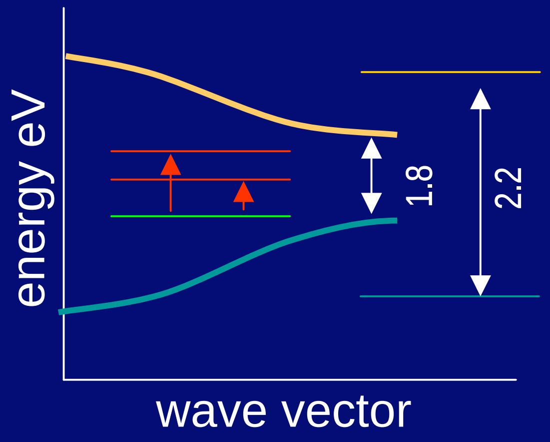
- Combinatorial Methods
- Polymer Processing
- Biomaterials
- Polymer Characterization
- Electronic Materials

Materials considered for Organic Electronics



poly(3-hexyl-tiophene), P3HT

Electrical properties of poly(3-hexyl-tiophene) (P3HT)



field effect mobility

$\mu_h \approx 10^{-5}$ cm^2/Vs to 10^{-2} cm^2/Vs

conductivity - 10^{-8} S/cm^2 to 10^{-6} S/cm^2

F. Grainier in *Intrinsically Conducting Polymers,* edited by M. Aldissi, NATO ASI, vol. 246 (1989), p. 107

Desirable functional properties:

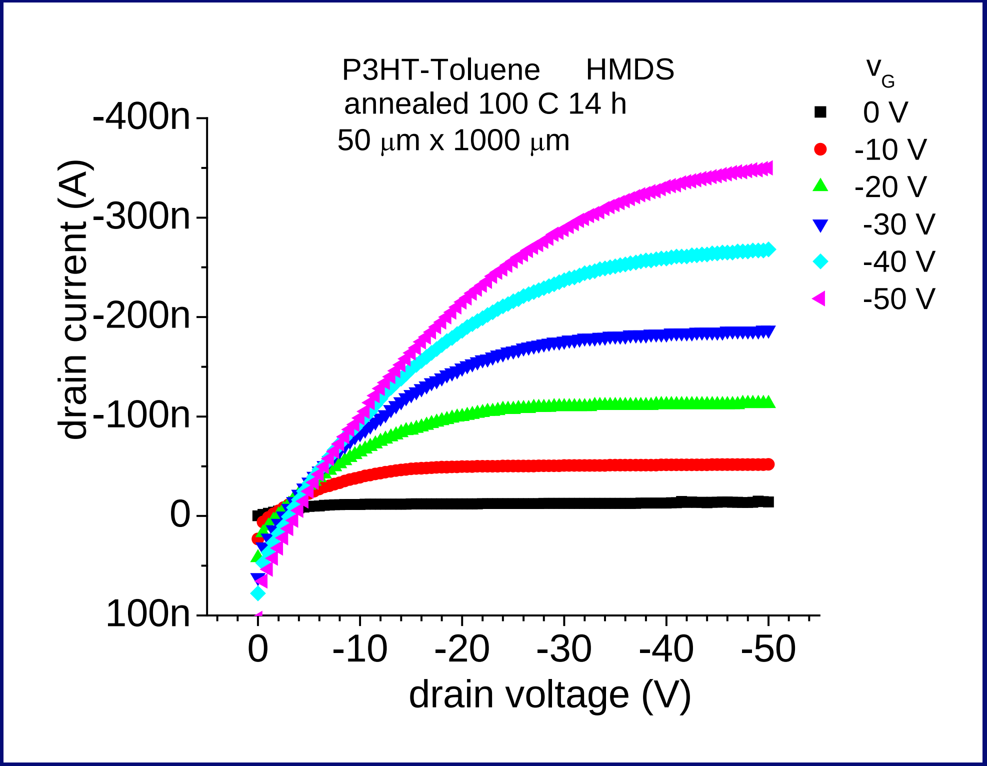
Operating voltage < 5V

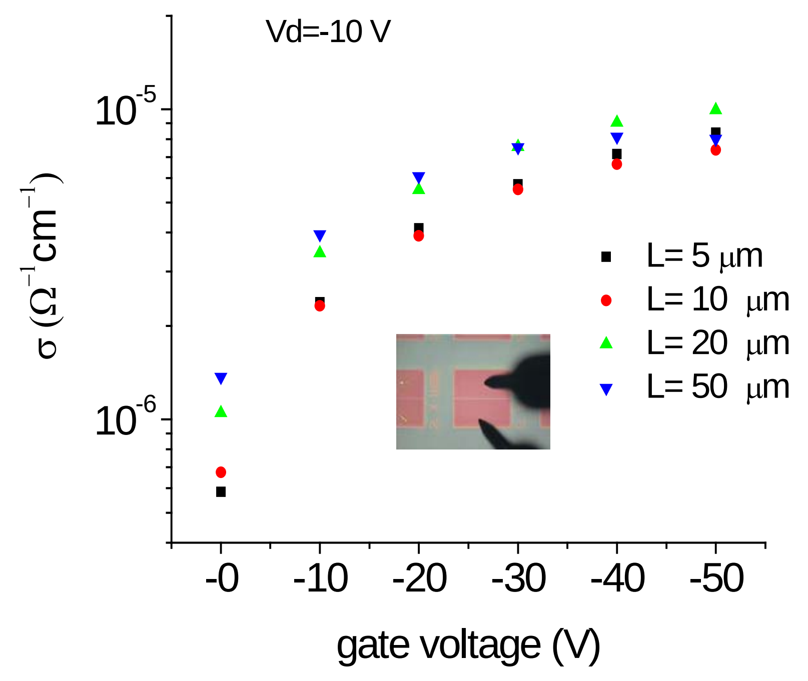
$\mu_h \approx 1$ cm^2/Vs

P3HT – a molecular solid with hopping conduction

Our objective is to asses the molecular relaxation and nonlinear dielectric effects in this semiconducting polymer

P3HT(solvent) typical output characteristics from the FET configuration





field effect mobility $\mu_h \approx 10^{-3}$ cm^2/Vs
conductivity $\sigma \approx 10^{-6}$ S/cm

Technology needs:
ON/OFF ratio > 10 dB

Operating voltage < 5V

Intrinsic electrical properties of poly(3hexyl-tiophene) (P3HT)

- Dielectric permittivity 40 Hz - 12 GHz
  - separate conductivity from dielectric relaxation
- AC Impedance
  - semiconducting to dielectric transition
    mobility, effective mass,
- Conductivity / Impedance Measurement under high AC electric fields
  - Waveforms in Time Domain and Frequency Domain
  - bulk-limited and electrode limited charge transport
- Nonlinear conductivity
  - fundamental, and 3rd harmonic current
  - effect of processing

Dielectric permittivity

$\varepsilon^* = \varepsilon' - j\varepsilon''$

$\tan(\delta) = \varepsilon''/\varepsilon'$

measurement method for high frequency range (GHz)

separate dielectric relaxation and conductivity

effect of temperature

activation energy

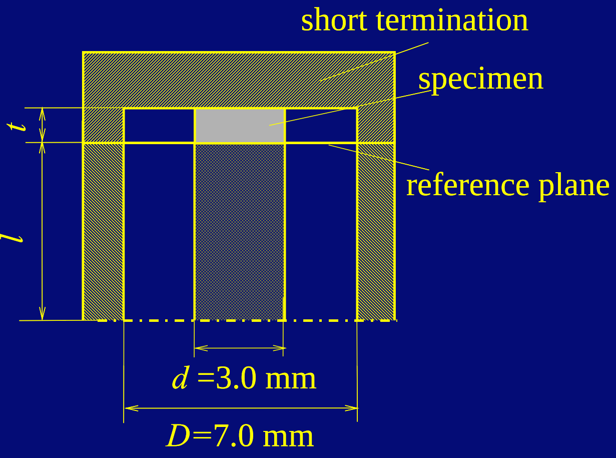
Broadband dielectric permittivity measurements (to 12 GHz)

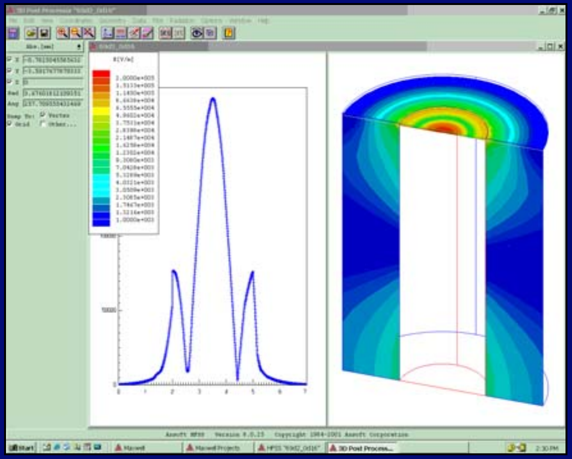
measure scattering wave parameter $S_{1,1}$ → impedance Z_{in}

At higher frequencies the specimenc represents a network of a transmission line with capacitance and inductance (wave propagation)

IPC Standard TM650-2.5.5.10

$\varepsilon' < 100$, t - 1 μm to 100 μm , f to 12 GHz (18 GHz)





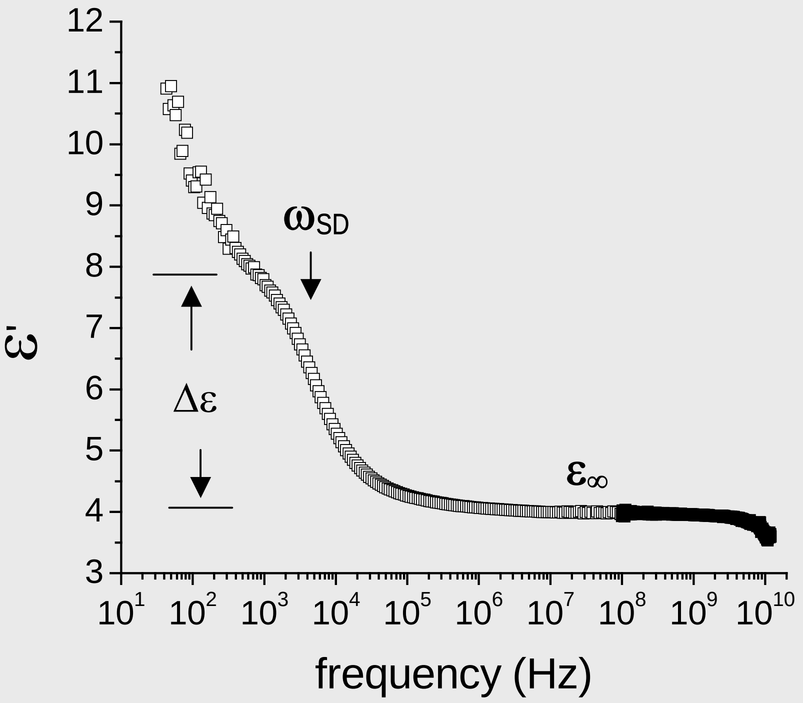
$$Z_{in} = Z_0\,(1+S_{11})/(1-S_{11})$$

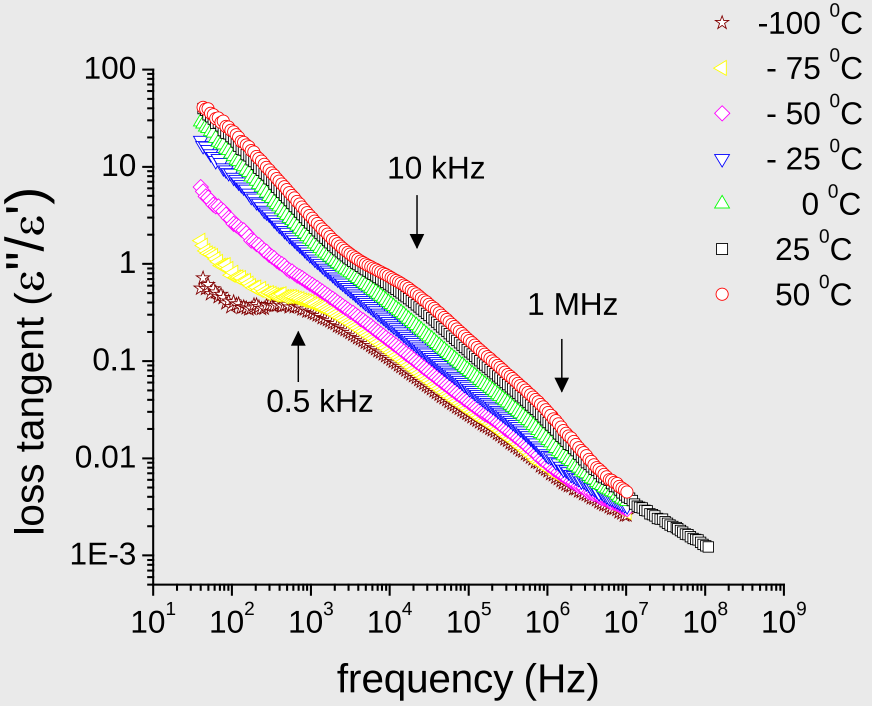
$$\varepsilon_r^* = \frac{x\cot(x)}{j\omega C_p\left(Z_0(1+\mathbf{S}_{11})/(1-\mathbf{S}_{11}) - j\omega L_s\right)}$$

$$x = \omega a\sqrt{\varepsilon_r^*}\,/2c$$

J. Obrzut and A. Anopchenko, IEEE Trans. Instr. Meas. 53 1197 (2004)
IPC Std http://www.ipc.org/4.0_Knowledge/4.1_Standards/test/2-5-5-10.pdf

Dielectric properties of P3HT(pristine)



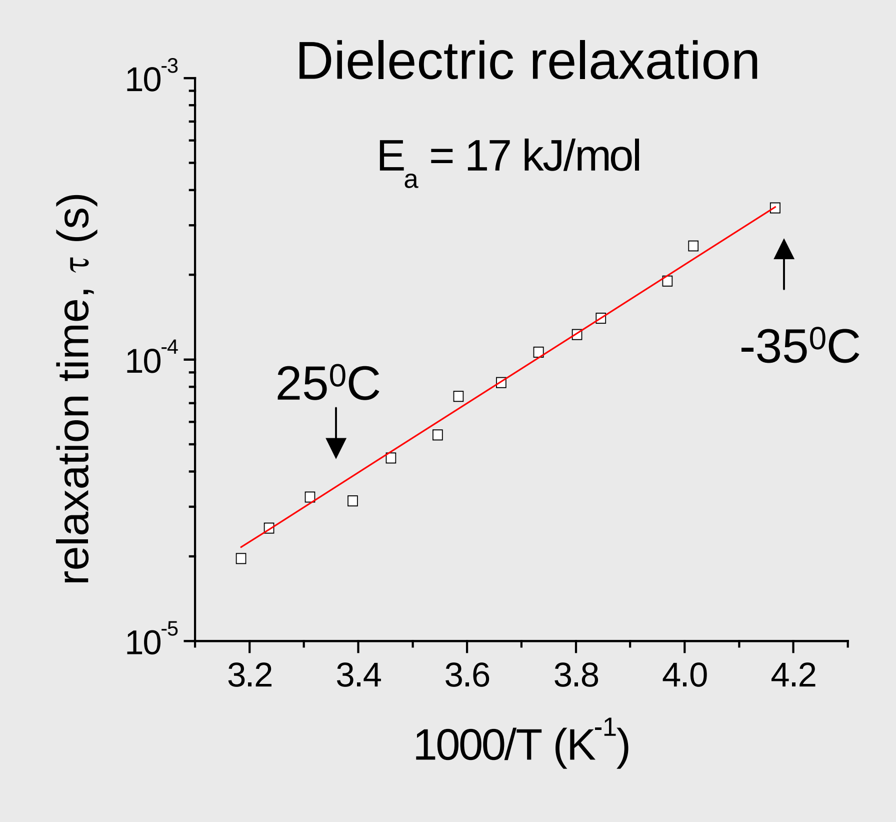


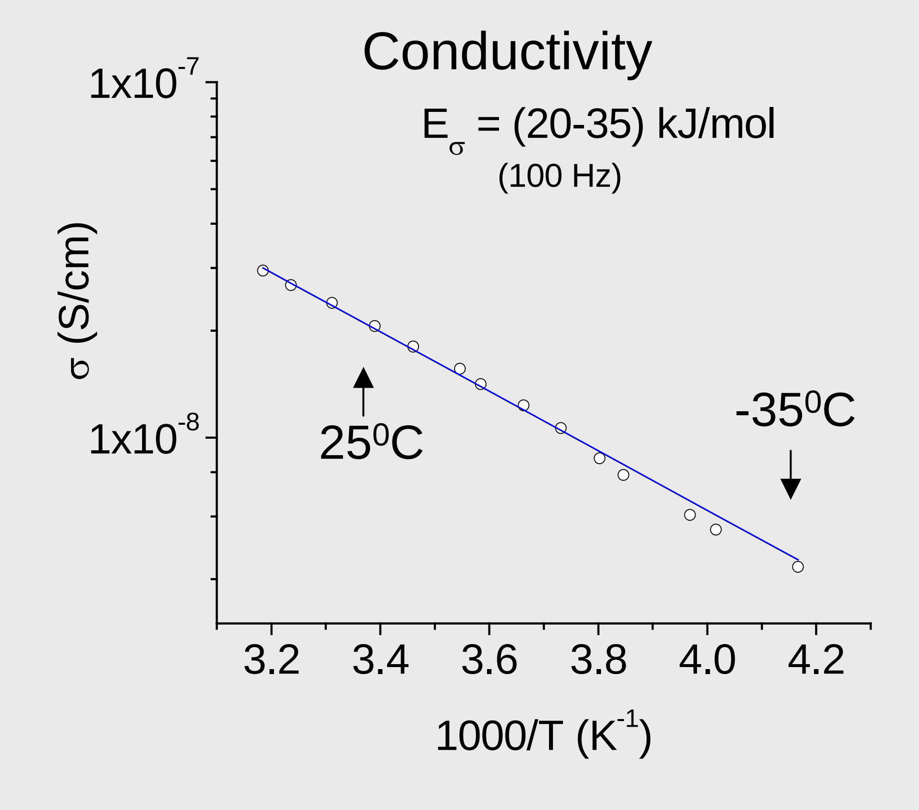
conductivity dominates < 5 kHz
dielectric relaxation at higher frequencies

$$\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\Delta\varepsilon}=\frac{1}{\left(1+(i\omega\tau)^\alpha\right)^\beta}+\frac{4\pi\sigma}{\omega}$$

Havriliak-Negami model
σ - conductivity
τ - dielectric relaxation time

P3HT conductivity & dielectric relaxation





relaxation time $\tau_{20} = 2.4 \times 10^{-4}$ s

$\Delta\varepsilon = 1.9$

$\varepsilon_\infty = 3.9$

E_{diel} = 17 kJ/mol

(β relaxation local molecular motions)

conductivity $\sigma_{20} = 2 * 10^{-8}$ S/cm

E_σ = (20 to 35) kJ/mol

Electrical modulus – representation for conductivity

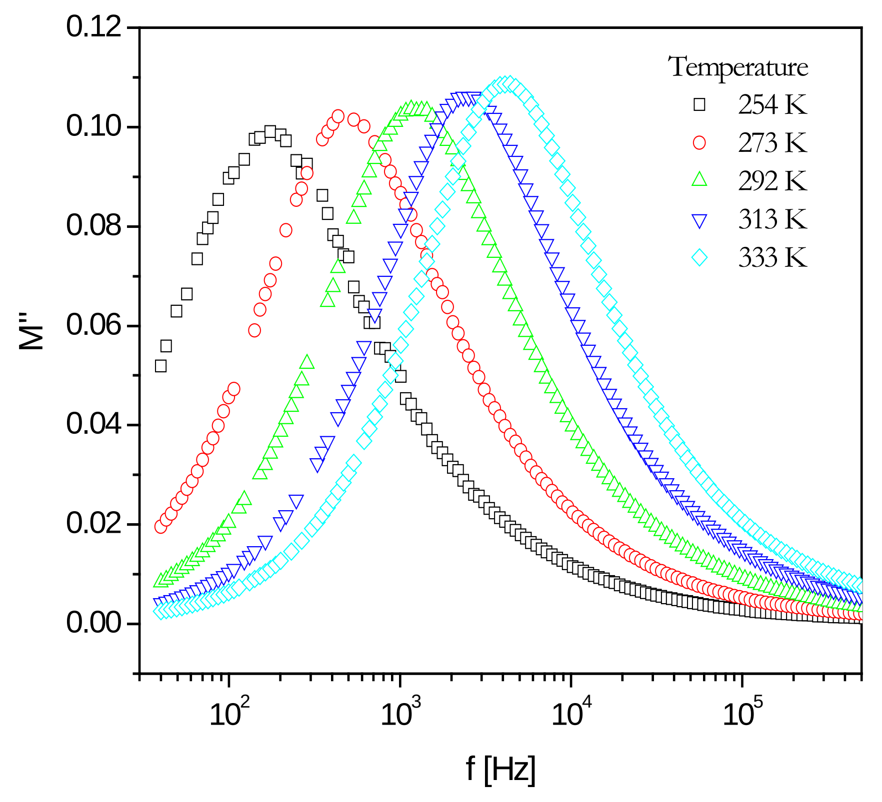
- Electrical modulus *($M^* = 1 / \varepsilon^*$):*

$$M'' = M_\infty + \frac{\omega\tau_{cond}}{1+(\omega\tau_{cond})^2}$$

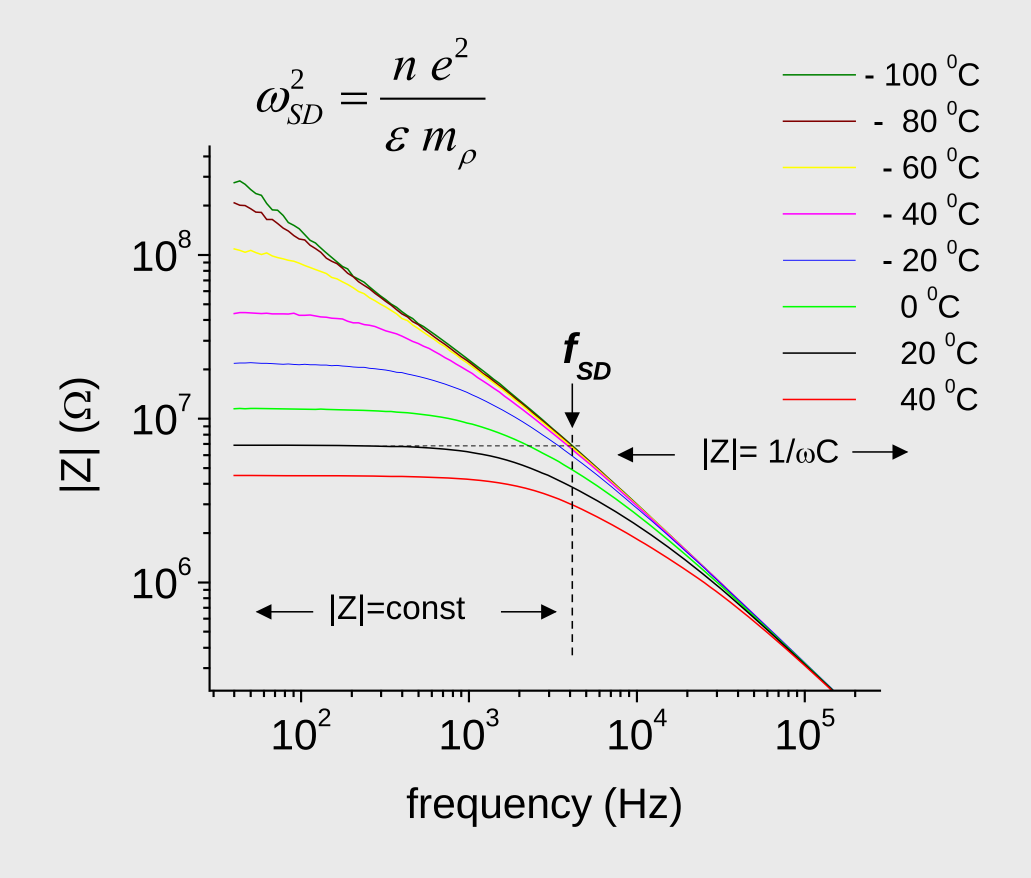
  - conductivity is represented in terms of its 'relaxation time' (τ_{cond}) – gives opportunity to compare it with dipole relaxation time (τ_{diel})

$$\sigma = \frac{\varepsilon_0\varepsilon_\infty}{\tau_{cond}}$$

  - conductivity appears as a peak on the frequency scan rather than slop of a line, which allows to separate conductivity and relaxation with higher confidence
  - conductivity increases with increasing temperature – peaks move to higher frequencies

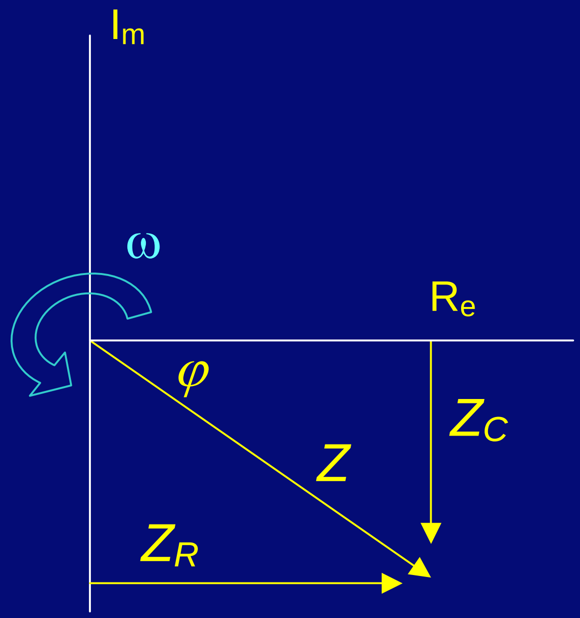


Impedance spectra of P3HT
semiconducting to dielectric transition



$$\omega_{SD}^2 = \frac{n\,e^2}{\varepsilon\, m_\rho}$$

impedance on the complex plane



$Z_R = R = |Z| \cos(\varphi)$

$Z_C = - i\, 1/\omega C$

$Z_L = i\, \omega L$

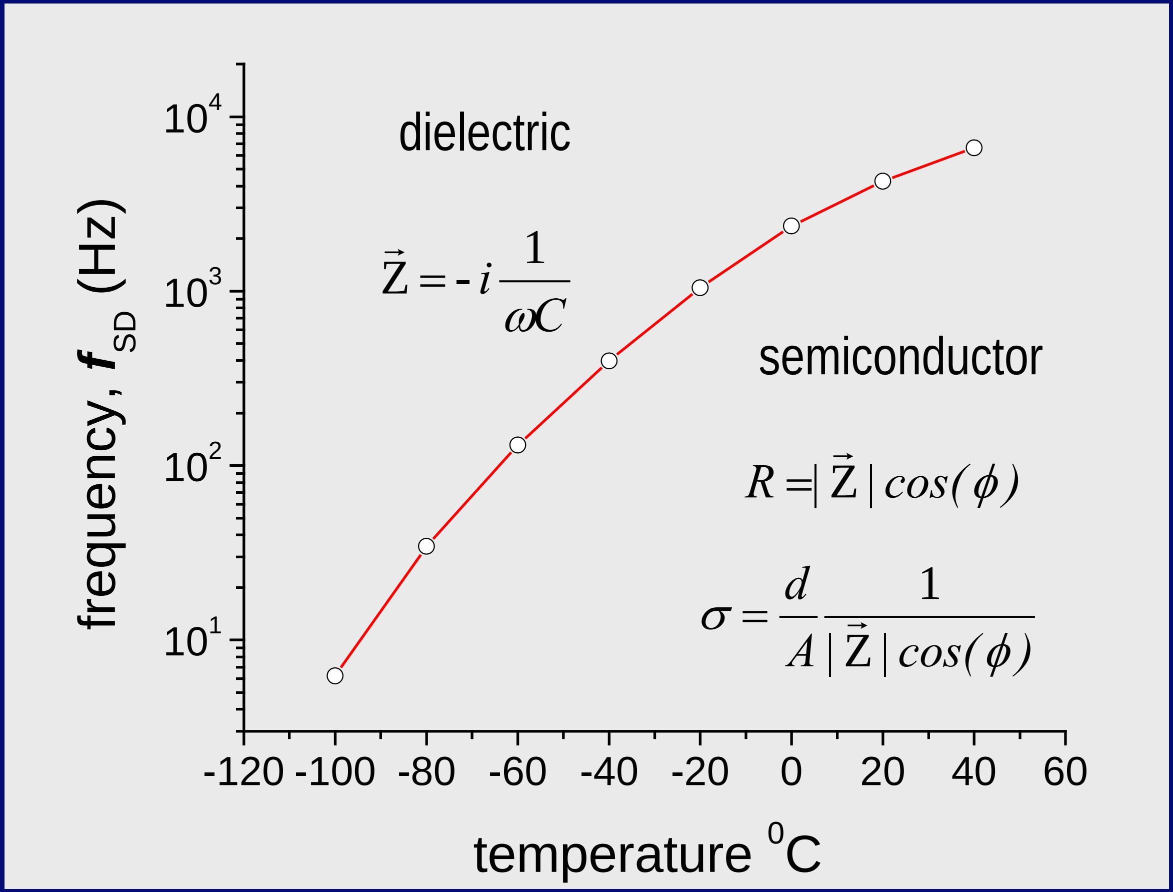
$|Z| = \mathrm{Sqrt}\,(R^2 + (Z_L - Z_C)^2)$

$f < f_{SD}$ $|Z|$= const = R semiconductor, $\varphi=0$

$f >\ f_{SD}$ $|Z|= 1/\omega C$ dielectric, $\varphi=-\ 90^0$

f_{SD} depends on temperature

semiconducting to dielectric transition



There is a definite frequency at a fixed temperature at which semiconducting to dielectric transition first occurs and we denote this frequency f_{SD}.

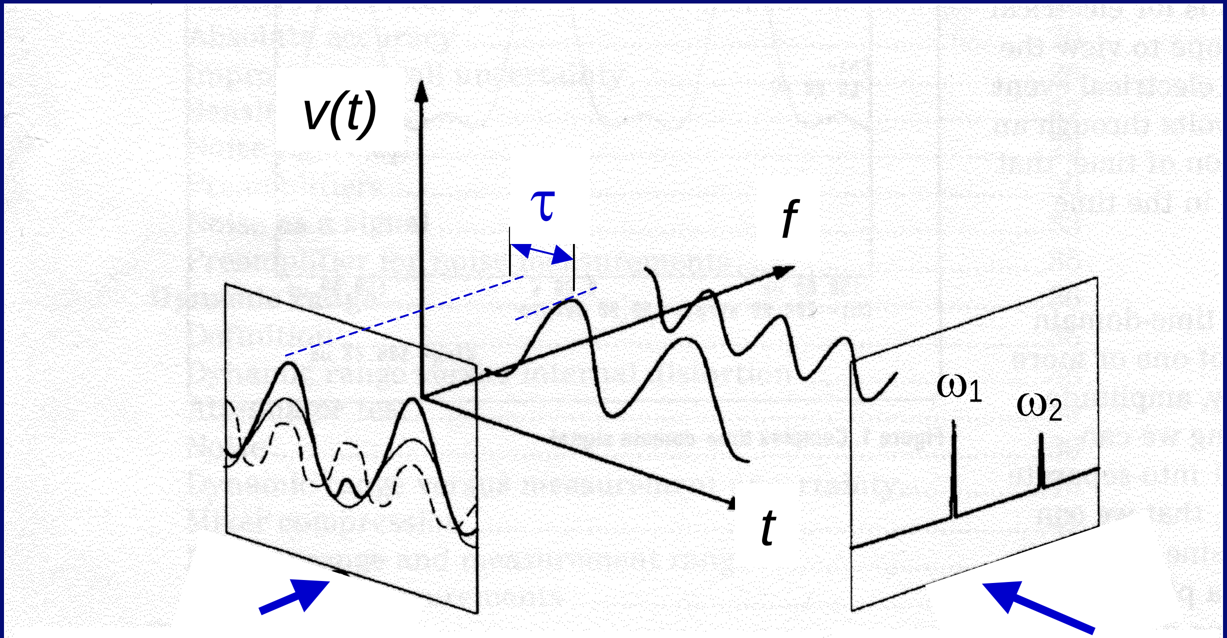
This characteristic frequency is determined by the point at which impedance |Z| = R intersects impedance of a capacitance, Z = 1/ωC .

In the semiconducting range the conductivity σ can be determined from Z

- permittivity, dielectric relaxation time, local motions of the P3HT backbone
- conductivity, (merges with relaxation 55 ^{0}C)
- semiconducting to dielectric transition f_{SD}
- no electric field effect

- impedance measurements under high AC voltages
- waveforms technique
- effect of electric field on conductivity
- charge transport mechanism
- nonlinear conductivity

Waveform Measurements in Time and Frequency Domain



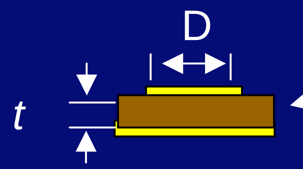
Time Domain
$v(t)=V_0\sin(\omega t+\phi)$

V_0 - amplitude
$\phi=\omega\tau$ - phase

Frequency Domain
$V=V_0\exp(i(\omega t+\phi))$

- Time domain - transient response, visualization
- Frequency domain - steady state phasor transforms convenient for calculating materials property - complex impedance

Experimental Set-Up

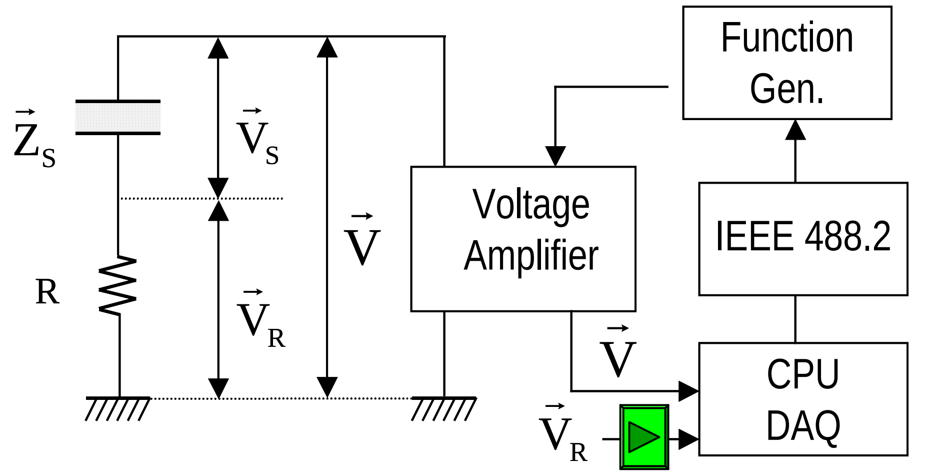


P3HT (Plextronics)

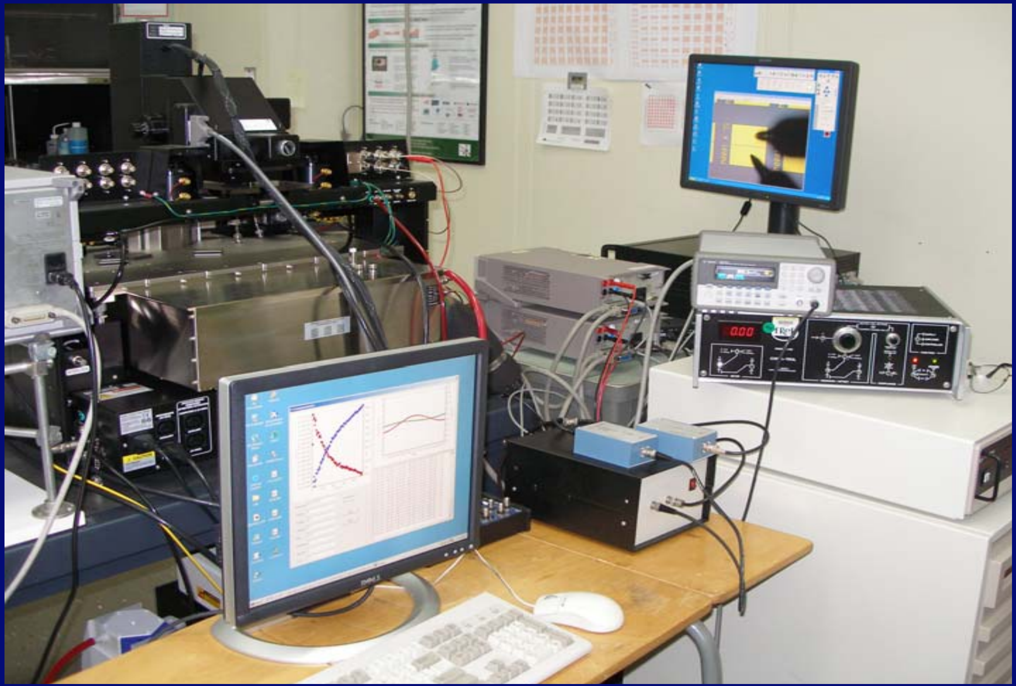
D = 3.0 mm

t = 50 µm

100 nm Au deposited by evaporation



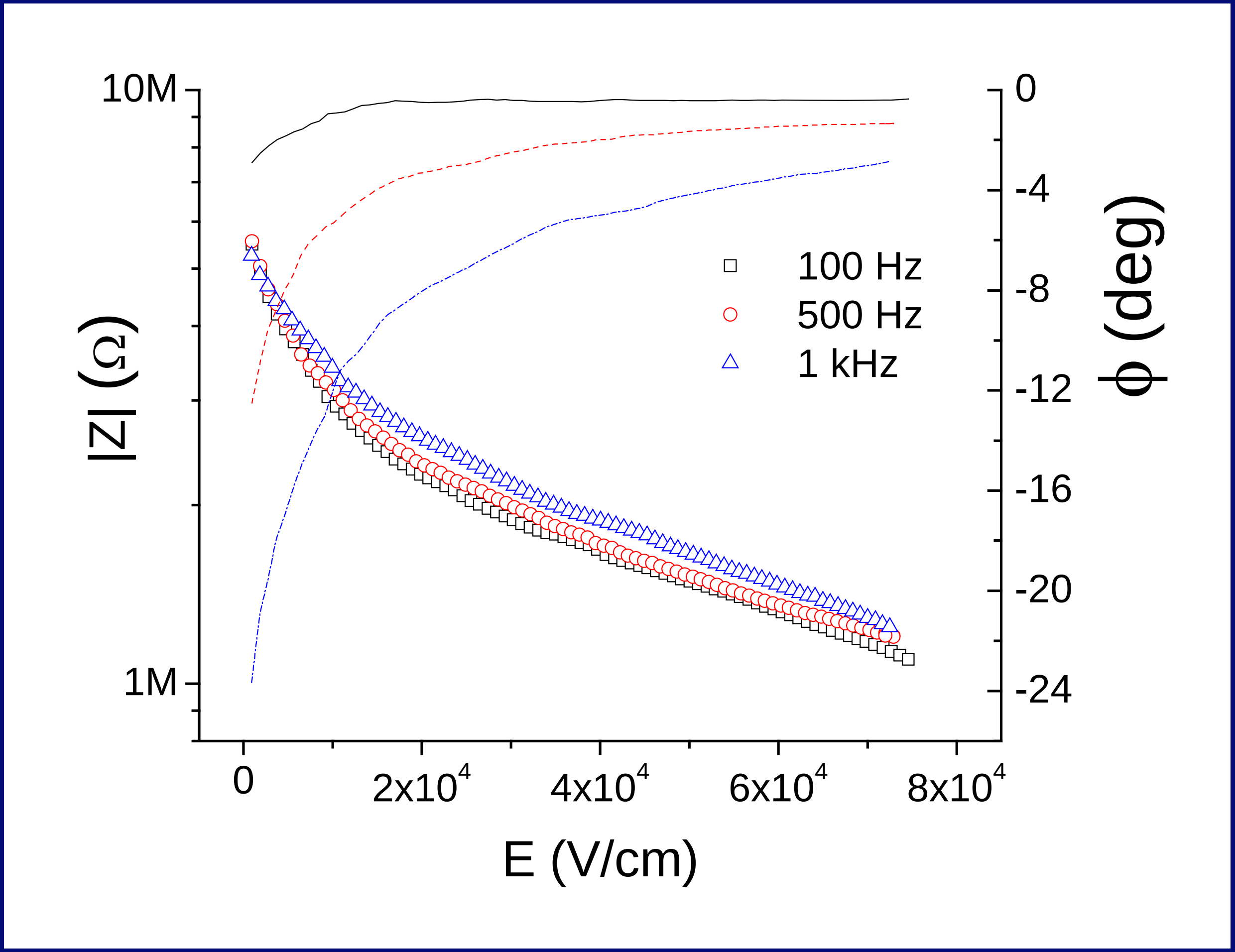
Voltage follower



$$\vec{Z}_S = R\frac{\vec{V}_S}{\vec{V}_R} = R(\frac{\vec{V}}{\vec{V}_R}-1)$$

J. Obrzut and K. Kano, IEEE Trans. Instr. Measurement. **54**, 1570 (2005)

Results: Impedance of P3HT

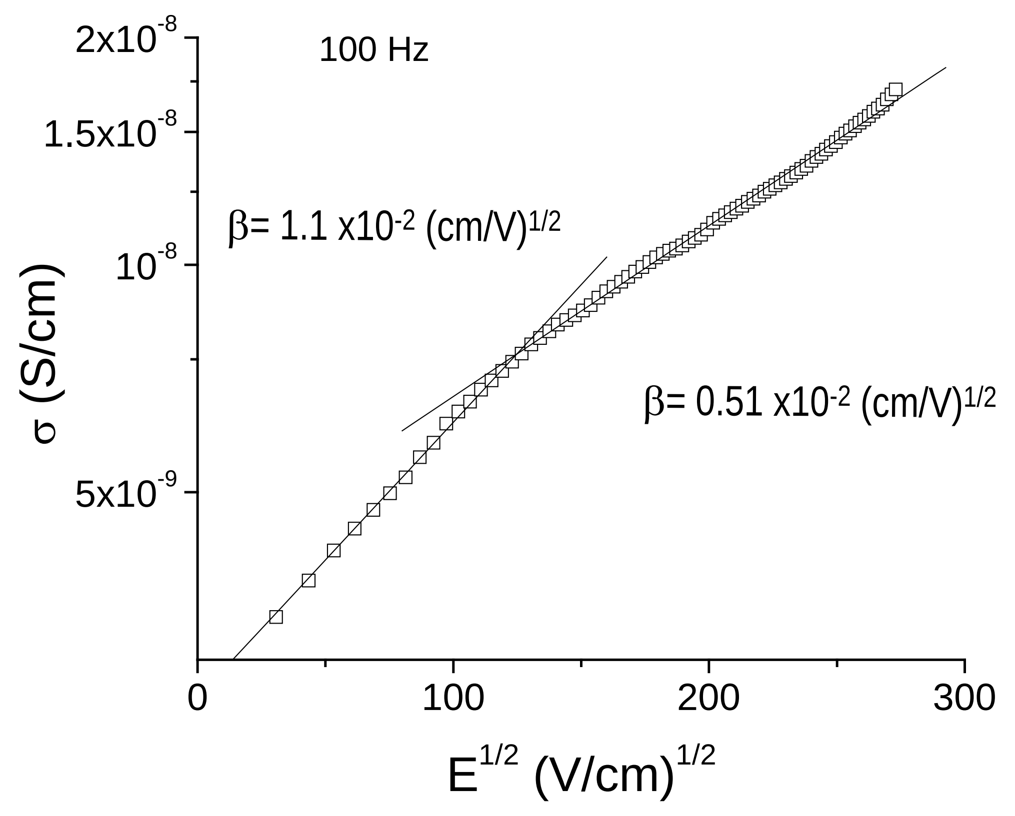


The impedance decreases with increasing electric field strength due to field activated charge transport

OFET operational field E = 50V/5 μm ≈ 10^4 V/cm

Charge transport in P3HT(pristine)

$$\sigma = \frac{d}{A}\frac{1}{|\vec{Z}|\cos(\phi)}$$



$$\sigma = \sigma_0 \exp(\beta E^{1/2})$$

Poole Frenkel model:

$$\beta_{PF} = (e/kT)(e/\pi\varepsilon_0\varepsilon_\infty)^{1/2}$$

$$T = 298\,\mathrm{K}, \varepsilon_\infty = 4.1,$$

$$\beta_{PF} = 1.4\times10^{-2}(\mathrm{cm/V})^{1/2}$$

Richardson-Schottky model:

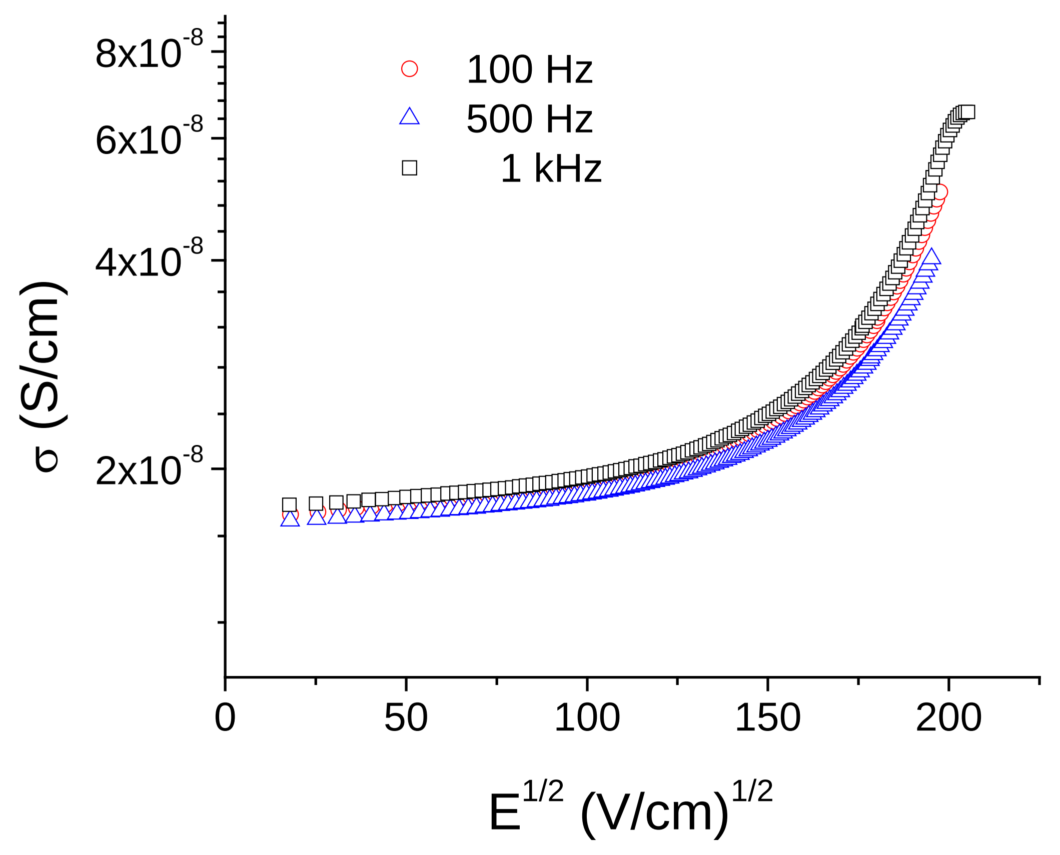
$$\beta_{RS} = \beta_{PF}/2$$

$$\beta_{RS} = 0.73\times10^{-2}(\mathrm{cm/V})^{1/2}$$

At low electric fields, the combined temperature and field dependent conductivity of P3HT obeys the bulk-limited Poole-Frankel (PF) model. At higher electric fields, the PF charge transport undergoes a transition to the electrode limited conduction - Richardson-Schottky (RS)

$\{\sigma, \varepsilon, \omega_{SD}, \beta, E_a\} \Rightarrow$ [PF] $\Rightarrow$ DOS, $\mu \approx 0.1$ cm^2/Vs

Conductivity of P3HT lightly doped with HCl



Lightly doped P3HT shows larger conductivity then P3HT(pristine)

Field effect is insignificant at $E < 1.5 \times 10^4$ V/cm

Conduction mechanism appears similar to that in lightly doped PPy

Nonlinear conductivity - harmonic analysis

$$j = \sigma_1 E + \sigma_3 E^3 + \dots$$

$$j(E) = -j(-E); \sigma_2 E^2 = 0$$

$E = (V_0/d)\sin(\omega t)$ - the input field is a sine AC voltage wave

$$j(t) = \sigma_1(E_0)\sin(\omega t) + \sigma_3(E_0)^3 \sin^3(\omega t) + ..$$

$\sin^3(\omega t) = (3/4)\sin(\omega t) - (1/4)\sin(3\omega t)$

$$j_3(t) = -1/4\sigma_3(E_0)^3 \sin(3\omega t)$$

3rd harmonic response at frequency 3ω

- π conjugated polymers,
- polarization reversal in ferroelectrics,
- dielectric breakdown

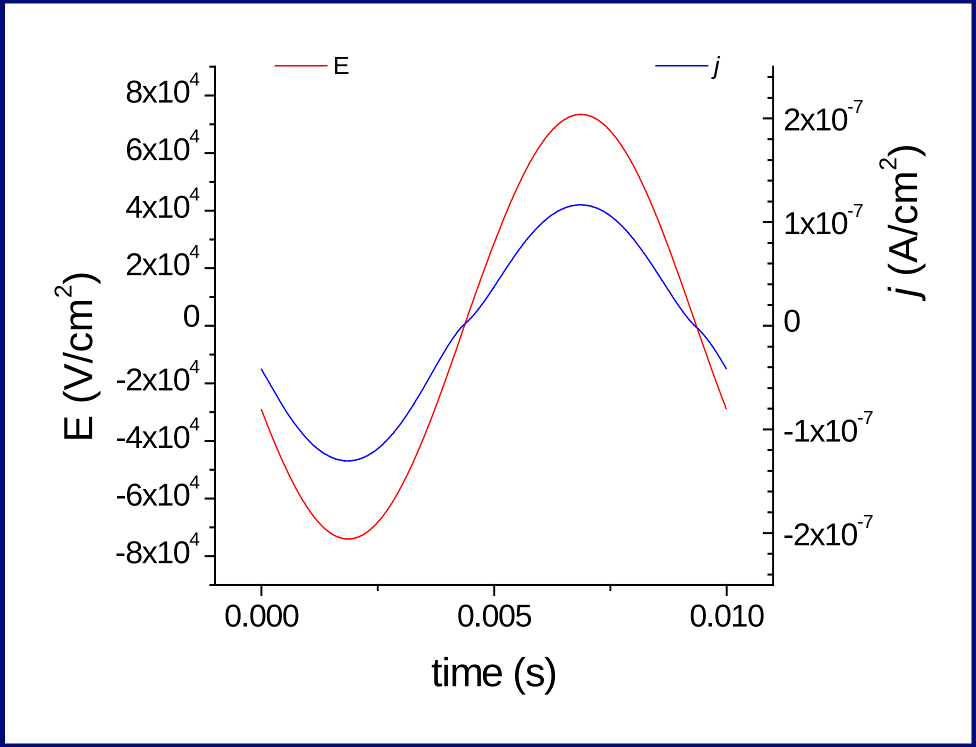
$$j(t) = j_\omega + j_{3\omega} + \dots$$

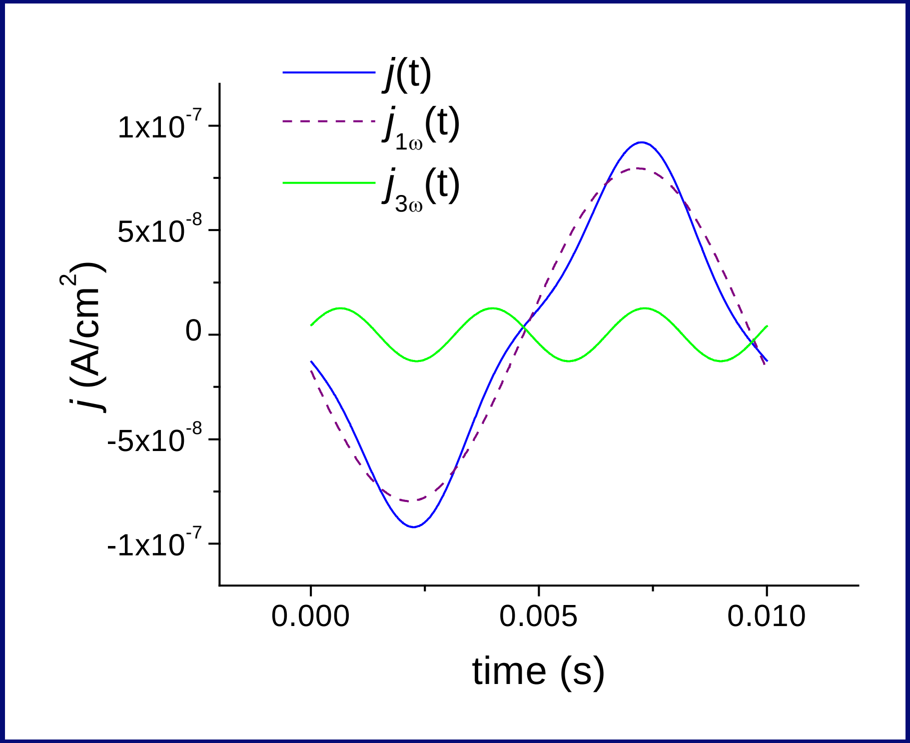
superposition of nonlinear components

the total nonlinear current consists of odd higher order harmonic components

T. Furukawa, Jpn. J. Appl. Phys. vol. 26, pp 1039 (1987), J.P. Huang, Phys. Rev., 011403 (2004)

Nonlinear conductivity of P3HT





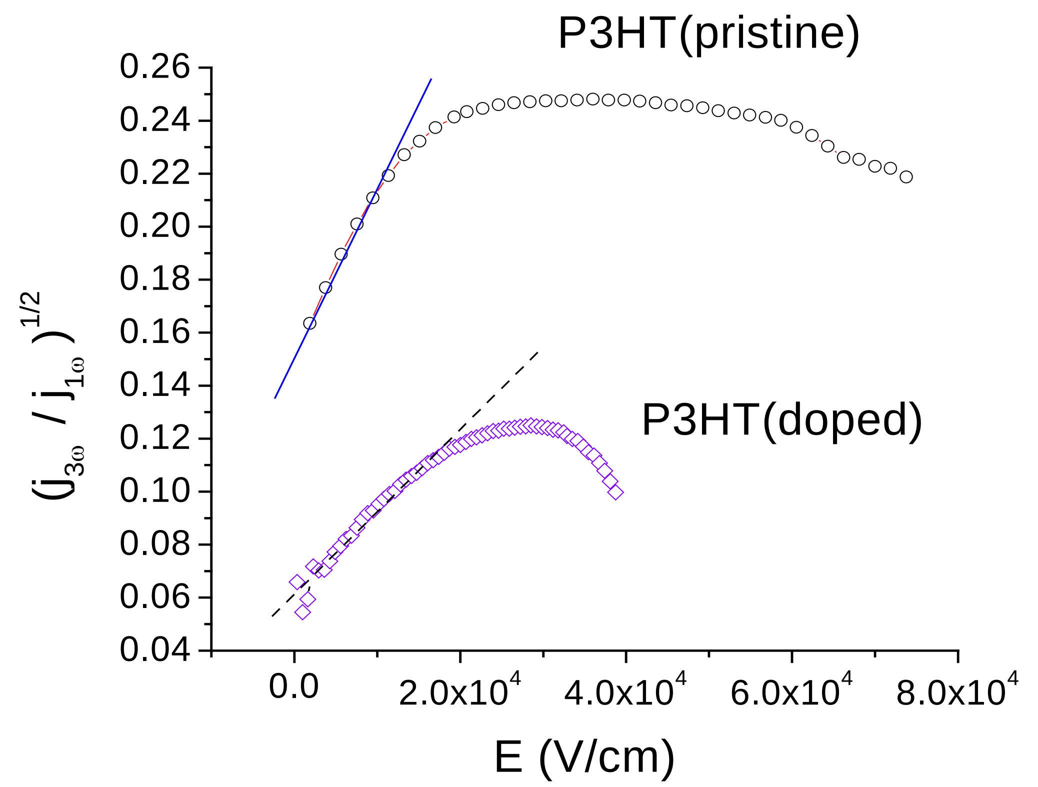
Calculating phasor transform of harmonics $|j_{n\omega}|$ (n=1,3, …) by DFT

$$|\vec{j}_{n\omega}| = \frac{|\vec{i}_{n\omega}|}{A} = \frac{2}{N}\left[\left\{\sum_{k=1}^{N}\frac{v_R}{R}(k)\cos(2\pi nk/N)\right\}^2 + \left\{\sum_{k=1}^{N}\frac{v_R}{R}(k)\sin(2\pi nk/N)\right\}^2\right]^{1/2}$$

$v_R/R(k)$ - a k-th current data point of n^th harmonic recorded at the time $t_k = (2\pi k)/(\omega N)$

Nonlinear conductivity of P3HT

slope of the $(j_{3\omega}/j_{1\omega})^{1/2}$ plot reflects the relative magnitude of the non-linear conductivity σ_3



The non-linear charge transport is dominated by the third-order conductivity, which originates from extended π-type electronic states in P3HT

The third order conductivity diminishes above 1.5×10^4 V/cm

Doped samples show smaller σ_3 and weaker field responsiveness than the corresponding P3HT(pristine) samples

Conclusion

- P3HT shows semiconducting and dielectric character.

$\sigma_{20} = 2 * 10^{-8}$ S/cm, $E_\sigma = 24$ kJ/mol

$\tau_{20} = 2.4 \times 10^{-4}$ s, $\Delta\varepsilon = 1.9$, $\varepsilon_\propto = 3.9$, $E_{diel} = 17$ kJ/mol
(β relaxation local molecular motions)

- There is a definite frequency f_{SD} at a fixed temperature at which semiconducting to dielectric transition first occurs.
- At frequencies f > f_{SD} P3HT is a dielectric; the relaxation time, $\tau_{25} = 3.1\ 10^{-5}$ s, reflects local molecular motions of the P3HT backbone.
- In the semiconducting range (f < f_{SD}) the conduction mechanism is bulk-limited at low electric fields of up to 1.510^4 V/cm, followed by a transition to electrode limited conduction at higher fields.
- Doping (increased conductivity) decreases field effect transport
- Our results demonstrate that the third order non-linear conductivity can be used to quantify the effect of an electric field on the conduction mechanism in organic semiconductors and to correlate the intrinsic mobility of the charge carriers with molecular structure.

Thank you

Contributors:

K. Kano

T. Psurek

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