Nonlinear charge transport in semiconducting polythiophene

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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.

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• Combinatorial Methods
• Polymer Processing
• Biomaterials
• Polymer Characterization
• Electronic Materials
Materials considered for Organic Electronics

- Poly(3-hexyl-thiophene), P3HT
Electrical properties of poly(3-hexyl-thiophene) (P3HT)

Desirable functional properties:

Operating voltage < 5V

\( \mu_h \approx 1 \text{ cm}^2/\text{Vs} \)

P3HT – a molecular solid with hopping conduction

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

field effect mobility

\( \mu_h \approx 10^{-5} \text{ cm}^2/\text{Vs} \) to \( 10^{-2} \text{ cm}^2/\text{Vs} \)

conductivity - \( 10^{-8} \text{ S/cm}^2 \) to \( 10^{-6} \text{ S/cm}^2 \)

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 $< 5$ V
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

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

$$\tan(\delta) = \frac{\varepsilon''}{\varepsilon'}$$

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 \( S_{11} \rightarrow \) impedance \( Z_{in} \)

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

\[ \varepsilon' < 100, \ t = 1 \mu m \text{ to } 100 \mu m, \ f \text{ to } 12 \text{ GHz (18 GHz)} \]

\[ Z_{in} = Z_0 \frac{(1+S_{11})}{(1-S_{11})} \]

\[ \varepsilon_r^* = \frac{xcot(x)}{j\omega C_p (Z_0 (1+S_{11})/(1-S_{11}) - j\omega L_s)} \]

\[ x = \omega a \sqrt{\varepsilon_r^*/2c} \]

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

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

Havriliak-Negami model
\(\sigma\) - conductivity
\(\tau\) - dielectric relaxation time
P3HT conductivity & dielectric relaxation

**Dielectric relaxation**

E\_\text{a} = 17 kJ/mol

\[ \text{relaxation time } \tau_{20} = 2.4 \times 10^{-4} \text{ s} \]
\[ \Delta \varepsilon = 1.9 \]
\[ \varepsilon_{\infty} = 3.9 \]

E\_\text{diel} = 17 kJ/mol

(\( \beta \) relaxation local molecular motions)

**Conductivity**

E\_\sigma = (20 to 35) kJ/mol

\[ \text{conductivity } \sigma_{20} = 2 \times 10^{-8} \text{ S/cm} \]
Electrical modulus – representation for conductivity

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

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

- Conductivity is represented in terms of its ‘relaxation time’ \((\tau_{\text{cond}})\) – gives opportunity to compare it with dipole relaxation time \((\tau_{\text{diel}})\)

\[
\sigma = \frac{\varepsilon_0 \varepsilon_\infty}{\tau_{\text{diel}}}
\]

- 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

\[ |Z| = \frac{1}{\omega C} \]

\[ f < f_{SD} \quad |Z| = \text{const} = R \quad \text{semiconductor}, \quad \varphi = 0 \]

\[ f > f_{SD} \quad |Z| = \frac{1}{\omega C} \quad \text{dielectric}, \quad \varphi = -90^0 \]

\[ f_{SD} \] depends on temperature
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, $Z = 1/\omega C$.

In the semiconducting range the conductivity $\sigma$ can be determined from $Z$.
- permittivity, dielectric relaxation time, local motions of the P3HT backbone
- conductivity, (merges with relaxation 55 °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 - transient response, visualization
- Frequency domain - steady state phasor transforms convenient for calculating materials property - complex impedance
Experimental Set-Up

\[ Z_S = R \frac{V_S}{V_R} = R \left( \frac{V}{V_R} - 1 \right) \]

\[ D = 3.0 \text{ mm} \]
\[ t = 50 \, \mu \text{m} \]

100 nm Au deposited by evaporation

Results: Impedance of P3HT

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

OFET operational field \( E = \frac{50V}{5 \mu m} \approx 10^4 \text{V/cm} \)
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)

\[ \sigma = \frac{d}{A |\mathbf{Z}| \cos(\phi)} \]

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

Poole Frenkel model:
\[ \beta_{PF} = \left(\frac{e}{kT}\right)\left(\frac{e}{\pi \varepsilon_0 \varepsilon_\infty}\right)^{1/2} \]
\[ T = 298 \text{ K}, \varepsilon_\infty = 4.1, \]
\[ \beta_{PF} = 1.4 \times 10^{-2} (\text{cm/V})^{1/2} \]

Richardson-Schottky model:
\[ \beta_{RS} = \beta_{PF} / 2 \]
\[ \beta_{RS} = 0.73 \times 10^{-2} (\text{cm/V})^{1/2} \]

\[ \{\sigma, \varepsilon, \omega_{SD}, \beta, E_a\} \Rightarrow \text{[PF]} \Rightarrow \text{DOS, } \mu \approx 0.1 \text{ cm}^2/\text{Vs} \]
Lightly doped P3HT shows larger conductivity than 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

\[ j = \sigma_1 E + \sigma_3 E^3 + \ldots \quad j(E) = -j(-E); \sigma_2 E^2 = 0 \]

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

\[ j(t) = \sigma_1(E_0) \sin(\omega t) + \sigma_3(E_0)^3 \sin^3(\omega t) + \ldots \]

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

3rd harmonic response at frequency \( 3\omega \)
- \( \pi \) conjugated polymers,
- polarization reversal in ferroelectrics,
- dielectric breakdown

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

\[ j(t) = j_\omega + j_{3\omega} + \ldots \]

superposition of nonlinear components

the total nonlinear current consists of odd higher order harmonic components

Nonlinear conductivity of P3HT

Calculating phasor transform of harmonics $|\mathbf{j}_{n\omega}|$ ($n=1, 3, \ldots$) by DFT

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

$v_{R}/R(k)$ - 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

The slope of the \((j_{3\omega}/j_{1\omega})^{1/2}\) plot reflects the relative magnitude of the non-linear conductivity \(\sigma_3\)

The non-linear charge transport is dominated by the third-order conductivity, which originates from extended \(\pi\)-type electronic states in P3HT.

The third order conductivity diminishes above 1.5 \(\times\) 10^4 V/cm.

Doped samples show smaller \(\sigma_3\) and weaker field responsiveness than the corresponding P3HT(pristine) samples.
Conclusion

- P3HT shows semiconducting and dielectric character.
  \[ \sigma_{20} = 2 \times 10^{-8} \text{ S/cm}, \quad E_\sigma = 24 \text{ kJ/mol} \]
  \[ \tau_{20} = 2.4 \times 10^{-4} \text{ s}, \quad \Delta \varepsilon = 1.9, \quad \varepsilon_\infty = 3.9, \quad E_{\text{dieel}} = 17 \text{ kJ/mol} \]
  (\(\beta\) 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, \(\tau_{25} = 3.1 \times 10^{-5} \text{ s}\), 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 \(1.5 \times 10^4 \text{ V/cm}\), 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

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