

## Non-linear charge transport in polythiophene under high AC field

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### ABSTRACT

Complex impedance and conductivity were measured for regioregular poly(3-hexylthiophene) (P3HT) at alternating current (AC) voltages using a waveform technique. The waveforms were Fourier transformed from time domain to frequency domain and analyzed at fundamental and higher order harmonic frequencies. It was found that the impedance of the semi-conducting P3HT decreases with increasing electric field strength. The non-linear charge transport is dominated by a third harmonic response that originates from extended polarizability of  $\pi$ -type electronic states. The third order non-linear conductivity can be used to quantify the effect of an electric field on the conduction mechanism and to correlate the intrinsic charge carriers mobility with molecular structure.

### INTRODUCTION

Semi-conducting conjugated polymers have been the focus of many studies due to their potential applications in organic field effect transistors (OFET), and light emitting diodes [1]. In particular, regioregular P3HT shows reasonable charge carrier mobility, which has been attributed to the self organization of this material [2, 3]. An analytical one-dimensional hopping model developed for semi-conducting polymers predicts strong dependence of conductivity on electric field [4]. Since in typical OFETs the thickness of the semi-conducting layer is in the range of about 100 nm, non-linear dielectric and conductivity effects can be induced by the operating electric field, which is typically larger than  $10^6$  V/cm.

A convenient method of probing the field-induced non-linear characteristics is to measure the higher-order harmonic components of the non-linear polarization under a sinusoidal alternating (AC) electric field. The amplitude of the harmonics reflects the magnitude of the non-linear effect. This methodology was pioneered by Furukawa [5] to measure non-linear dielectricity in ferroelectric polymers. The alternating current response in non-linearly conducting composite materials has been analyzed by Gu [6]. Several authors have extended this technique recently and applied it to study fundamental molecular dynamics in non-linear composites, dipolar fluids and molecular dielectrics [7, 8].

In this paper, we describe measurements of complex impedance and non-linear conductivity by recording and analyzing AC waveforms at their fundamental frequency, and at higher order harmonic frequencies. In particular, we are seeking to discover a correlation between the charge carrier transport mechanism and non-linear conductivity in organic semiconductors. We have examined and demonstrate this effect for semi-conducting regioregular poly(3-hexylthiophene).

## EXPERIMENTAL DETAILS

**Materials:** Poly(3-hexylthiophene) with head-to-tail regioregularity > 99% was obtained from Plextronics and used without further purification. Films of pristine P3HT 50  $\mu\text{m}$  thick were selected from the batch. Gold electrodes with a diameter of 3.0 mm and a thickness of 0.1  $\mu\text{m}$  were prepared by evaporation on both sides of the film. All samples were handled either under nitrogen or argon atmosphere.

**Measurements<sup>1</sup>:** We performed impedance measurements using a measurement system that we described previously [9]. An IEEE 488.2 controlled function generator (Agilent 33250A) was used to source a sinusoidal voltage wave at a fundamental frequency  $f$ . The source voltage wave was amplified by an operational voltage amplifier (Trek Model 610C), and a high AC voltage was applied to the specimen. The specimen's current is monitored using a standard reference resistor  $R$  shown in Figure 1. Separate channels of the data acquisition (DAQ) card recorded the

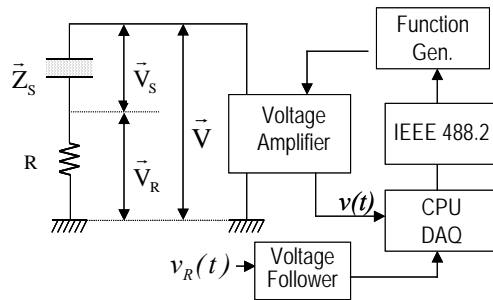


Figure 1. Measurement diagram.  $\bar{V}$  and  $\bar{V}_R$  are the phasor transforms of waveforms  $v_R(t)$  and  $v(t)$  from time domain to frequency domain.

waveform of the monitoring signal (which is proportional by a gain factor to the output voltage,  $v(t)$  from the voltage amplifier) and the voltage wave,  $v_R(t)$ , at the reference resistor via an impedance follower circuit. The  $v_R(t)$  is proportional to the specimen current. We used a two channel 12 bit analog-to-digital converter (NI PCI-6111), clocked at a frequency of 20 MHz, which has the capability to simultaneously sample both channels at frequencies of up to 100 kHz. The sampling was assumed to be coherent, i.e., containing an integer number of the sine-wave periods and an integer number,  $N$ , of the data points. In our experiments  $N$  equaled 1000 data points. The measurements were performed at fundamental frequencies of 100 Hz, 500 Hz and 1 kHz. During measurements, the specimen voltage amplitude was increased in steps of 5 V. The discrete quantization time and amplitude errors were assumed to be within the manufacturer's specification for the NI-6111. The experimental uncertainty depends primarily on the tolerance of the reference resistor and its phase characteristic. The combined relative uncertainty was 0.5 % for the measured voltage wave amplitude, and 1.5 % for the phase angle. The complex impedance of the specimen,  $\bar{Z}_S$ , can be obtained from (1) [9]:

$$\bar{Z}_S = R \left( \frac{\bar{V}}{\bar{V}_R} - 1 \right) \quad (1)$$

In (1)  $\bar{V}$  and  $\bar{V}_R$  are phasor transforms, from the time domain to the frequency domain representing complex quantities, each having an amplitude and a phase.

<sup>1</sup>Certain equipment, instruments or materials are identified in this paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology nor does it imply the materials are necessarily the best available for the purpose.

The amplitude of the n-th order harmonic current density response,  $j_n$ , can be calculated from (2):

$$j_n = \frac{i_n}{s} = \frac{2}{N} \left[ \left\{ \sum_{l=1}^N \frac{v_R}{R} (l) \cos(2\pi ml/N) \right\}^2 + \left\{ \sum_{l=1}^N \frac{v_R}{R} (l) \sin(2\pi ml/N) \right\}^2 \right]^{1/2} \quad (2)$$

where  $\frac{v_R}{R} (l)$  represents an individual data point of the specimen current,  $i(l)$ , recorded at the time  $t_l = (2\pi l)/(\omega N)$ ,  $n$  (1, 2, 3,..) is the harmonic order, and  $s$  is the specimen crosssectional area. The specimen impedance and the higher order harmonics of the current wave response are presented as a function of the specimen electric field  $E = |\bar{v}_s|/d$ , where  $\bar{v}_s = \bar{V} - \bar{V}_R$  and  $d$  is the specimen thickness. We assumed the non-linear current density - electric field characteristic to be of the form:

$$j = \sigma_1 E + \sigma_3 E^3 \quad (3)$$

$$j = \left\{ \sigma_1 E_0 \left( 1 + \frac{3}{4} \sigma_3 E_0^2 \right) \sin(\omega t) \right\} - \left\{ \frac{1}{4} \sigma_3 E_0^3 \sin(3\omega t) \right\} + \dots \quad (4)$$

where  $\sigma_1 = j_1/E$  is the low-electric field linear conductivity,  $\sigma_3$  is the third order non-linear conductivity term, and the higher order terms are neglected. Due to inversion symmetry ( $j(E) = -j(-E)$ ), we also neglected the quadratic term in equations (3). Thus, for a sinusoidal electric field  $E = E_0 \sin(\omega t)$ , oscillating at an angular frequency  $\omega = 2\pi f$ , we may consider the effective response as a sum of the fundamental and the third harmonic components at frequencies of  $\omega$  and  $3\omega$  respectively (4).

## RESULTS and DISCUSSION

The impedance and phase plots, measured as a function of the applied electric field for P3HT are shown in Figure 2 at fundamental frequencies of 100 Hz, 500 Hz and 1 kHz. Figure 2 demonstrates that the impedance is strongly dependent on the magnitude of the electric field and decreases exponentially with an increasing electric field. The drop of impedance is accompanied by an increase of the phase angle,  $\phi$ , where  $\phi = -90^\circ$  corresponds to phase angle of a loss-less dielectric, while  $\phi = 0^\circ$  corresponds to a real resistance. Small negative  $\phi$  values at low frequencies indicate that the material exhibits not only semi-conducting, but also a dielectric character. With an increasing electric field, P3HT becomes more semi-conducting as oppose to dielectric. The frequency of the AC field has an opposite effect on the impedance characteristic of P3HT than the electric field. The impedance increases with increasing frequency while the phase angle decreases. For example, at  $10^4$  V/cm,  $\phi$  is approximately  $-1^\circ$ , at the frequency of 100 Hz, and it decreases to about  $-12^\circ$ , when the frequency increases to 1 kHz (Figure 2).

The apparent semi-conducting character of P3HT ceases above a critical frequency, above which the material becomes a dielectric. Our broadband dielectric measurements indicate that at room temperature the semi-conducting to dielectric transition takes place at frequency of approximately 5 kHz. Consequently, applications utilizing the field-effect mobility are limited to this frequency.

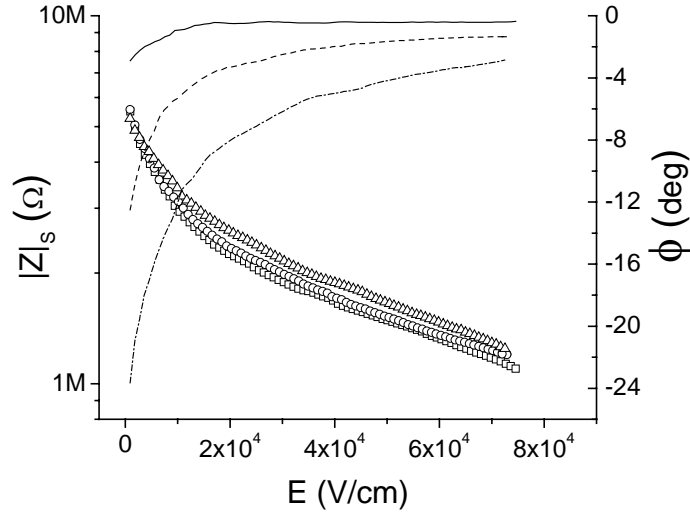


Figure 2. Impedance magnitude,  $|Z_S|$  (symbols), and phase angle,  $\phi$ , (lines) of P3HT at frequency of 100 Hz (squares, solid line), 500 Hz (circles, dot line), and 1 KHz (triangles, dash-dot line).

At frequencies below 5 kHz, P3HT shows a semi-conducting character, and the overall dielectric response is dominated by conductivity  $\sigma$ :

$$\sigma = (d/s)(1/|\vec{Z}_S| \cos(\phi)) \quad (5)$$

The conductivity of P3HT is thermally activated, with an activation energy of about 17 kJ/mol. Figure 3 shows that conductivity also increases exponentially in proportion to the square root of electric field  $E$ . The combined temperature and field dependent conductivity of P3HT can be expressed as:

$$\sigma = \sigma_0 \exp(\beta E^{1/2} / kT) \quad (6)$$

where,  $\sigma_0$  is the low-field conductivity, and  $\beta$  depends on mechanism of charge transport.

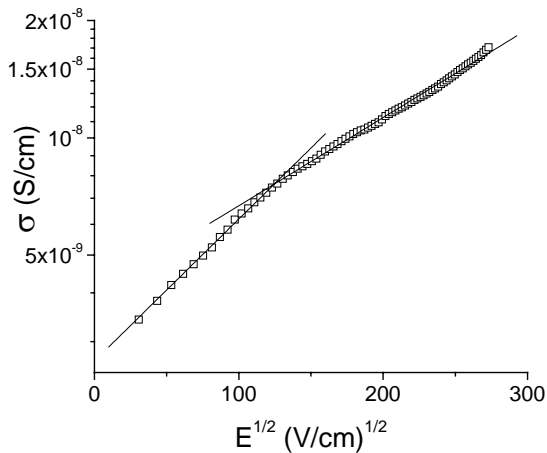


Figure 3. Conductivity,  $\sigma$ , of P3HT against electric field,  $E^{1/2}$ , at 100 Hz, 25 C.

In organic semiconductors and most organic solids, the high electric field changes the density distribution function of trapped charge carriers and decreases the trap barrier, which is referred to as a bulk-limited conductivity or the Poole-Frankel (PF) effect. In addition, when the electric field affects the rate of carrier generation or injection, the conduction process becomes electrode-limited, known as the Richardson-Schottky (RS) effect [9]. Both of these effects give the conductivity a field dependence of the form (3), where  $\beta_{PF}$  is larger than  $\beta_{RS}$ . Figure 3 shows that at low electric fields, the combined temperature and field dependent conductivity of P3HT obeys the bulk-limited PF model. At higher electric fields, above  $1.5 \times 10^4$  V/cm, the electric field affects the rate of carrier generation or injection, and the bulk limited charge transport undergoes a transition to the electrode limited conduction, which can be expressed as an RS effect. This mechanism is different than typically observed in organic solids, where at low electric fields the transport is controlled by the distribution of interfacial traps or by the space-charge-limited (SCL) transport [10,11].

To analyze the non-linear transport effects in more detail, we calculated the relative amplitude of the higher order harmonic current,  $(j_3/j_1)$ , using (2-4). The relative amplitude of the second harmonic current,  $j_2$ , is negligibly small, which confirms our earlier assumption that P3HT is inversely symmetric. Since the fundamental,  $j_1$ , is linearly dependent on  $E$ , the slope of the  $(j_3/j_1)^{1/2}$  plot reflects the relative magnitude of the non-linear conductivity  $\sigma_3$ . Figure 4 illustrates these results, where the relative amplitude of the square root of the third harmonic,  $(i_3/i_1)^{1/2}$ , is plotted as a function of the specimen voltage. The non-linear charge transport in P3HT is dominated by the third-order conductivity, which appears to be relatively constant at low electric fields of up to  $1.5 \times 10^4$  xV/cm, and thus likely reflecting the intrinsic electronic properties of P3HT. The third-order conductivity diminishes above  $1.5 \times 10^4$  V/cm, indicating a field induced saturation. This saturation threshold coincides with the transition in the conduction mechanism from the bulk-limited to the electrode-limited conduction (Figure 3).

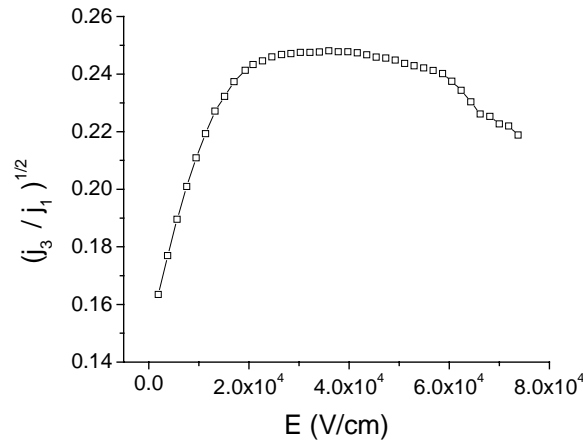


Figure 4. Normalized amplitude of the third harmonic current response for P3HT at 100 Hz.

The applicability of the PF model to describe the charge transport in disordered polymeric systems is often questioned because it requires the existence of a large and stable population of traps. Furthermore, the PF model assumes that the ground state electronic wave functions are spread over a large volume, which can lead to an enhanced mobilization of charge carriers when the external field is applied. The fact that the slope  $\beta$  at low electric fields (Figure 3) points to the

bulk-dominated charge transport implies the existence of highly delocalized electronic states, that form a band structure. Consistent with this observation, we believe that the non-linear conductivity identified in Figure 3 originates from extended  $\pi$ -type electronic states in P3HT.

## CONCLUSION

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. We found that the impedance of P3HT is highly non-linear and decreases considerably with an increasing electric field due to field activated charge transport. The semi-conducting character of P3HT is limited to frequencies below 5 KHz. The corresponding conduction mechanism is bulk-limited at low electric fields of up to  $1.5 \times 10^4$  V/cm,- with a transition to electrode limited conduction at higher fields. 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.

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