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# Broadband Dielectric Spectroscopy investigation of the electrical and structural heterogeneity of optically transparent organic semiconductor films

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## Abstract

Despite the high electrical conductivity of optically transparent organic semiconductor films, their structural and electrical heterogeneity induces capacitance effects. Broadband Dielectric Spectroscopy (BDS) is employed in order to investigate two distinct relaxation mechanisms of poly(3,4-ethylenedioxythiophene) with polyelectrolyte (PEDOT:PSS) films which constitutes a suspension of conducting PEDOT:PSS grains, shelled by an insulating layer of PSS. In this paper a general methodology is proposed in order to get an insight into the local conductivity of mesoscopic conducting phase and to calculate the activation energies of the relaxation mechanisms.

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## 1. Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT) is the most successful conducting polymer due its optical transparency in the visible region, its stability and the ability to become good electrical conductor after doping. PEDOT exhibits low solubility by itself, but, when water polyelectrolyte (PSS) solution is used as a charge balancing dopant, PEDOT:PSS mixture form in water a micro-dispersion that forms thin transparent films by the spin-coating technique. PEDOT:PSS is a phase-segregated material consisting of lentic-like PEDOT:PSS conductive

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grains of about 25 nm width, which are covered by a thin layer of a few nanometers of PSS resulting to a film with overall poor conductivity. The conductivity of the films is mainly determined by the ratio of PSS to PEDOT and also from the size of the formed PEDOT:PSS dispersions/grains [1, 2, 3, 4, 5, 6].

In this work, by employing broadband dielectric measurements we shall explore the dynamics of charge carriers at a structurally and electrically heterogeneous material such as PEDOT:PSS films at different time scales. The methodology can be used at a variety of different materials with similar structure and electrical properties in order to come to some conclusions regarding the local conductivity of the interior meso-scopic phases.

## 2. Theoretical concepts

PEDOT:PSS film consists of lentil-like PEDOT:PSS grains of about 25 nm width, shelled by a thin layer of PSS [3,4,5]. We can simplify the system as a material with conductivity  $\sigma_h$  which hosts spheres with greater conductivity  $\sigma_{sp}$  but which are covered by a thin and much less conductive material  $\sigma_{sh}$ .

When suspensions of conducting spheres, covered by a thin layer of insulator are dispersed into a less conducting medium, compared with the interior conductivity, they yield two distinct relaxation mechanisms in the frequency domain [7, 8]. At first, a low frequency (LF) mechanism, which corresponds to a suspension of homogeneous spheres of radius equal to the overall radius of the shelled spheres and effective permittivity and conductivity equal to the corresponding effective ones of the bi-phase shelled particles i.e. a relaxation mechanism due to the presence of the insulating shells. Additionally, there is a high frequency (HF) mechanism, which corresponds to the interfacial polarization of the thin-shelled conductive spheres inside the less conductive host matrix i.e. a mechanism due to the polarization of the conducting grains.

So, the HF relaxation mechanism, according to Hanai's model [9], PEDOT:PSS is modeled by a suspension of conducting spheres (with conductivity  $\sigma_2$ , and relative static permittivity  $\epsilon_2$ ) covered with insulating thin shells, which are embedded into a host matrix (with conductivity  $\sigma_1$  and relative permittivity  $\epsilon_1$ ) with  $\sigma_2 \gg \sigma_1$ . The maximum frequency  $f_{max}$  and the intensity of the corresponding relaxation mechanism is given by the reduced relations (338) and (337) of Hanai's theory [9]

$$2\pi f_{max} = \frac{(1-\Phi)\sigma_2}{\epsilon_0((1-\Phi)\epsilon_2 + (2+\Phi)\epsilon_1)} \quad (1)$$

and

$$\Delta\epsilon = \frac{9(\epsilon_1\sigma_2)^2\Phi(1-\Phi)}{[\epsilon_0(1-\Phi)\epsilon_2 + \epsilon_0(2+\Phi)\epsilon_1](1-\Phi)^2\sigma_2^2} \quad (2)$$

respectively, where  $\Phi$  is the volume fraction and  $\epsilon_0$  is the permittivity of free space. Combining the two equations to one we get

$$\sigma_2 = 2\pi\epsilon_0 \left[ \frac{9\epsilon_1^2\Phi}{(1-\Phi)^2\Delta\epsilon} \right] f_{max} \quad (3)$$

or even simpler  $\sigma_2 = g(\Phi, \epsilon_1, \Delta\epsilon) f_{max}$ .

It is worthy noticing that eq. (1) resembles the empirical Barton - Nakajima – Namikawa (BNN) relation [10, 11, 12], which implies a simple proportional connection between the conductivity of a material and the maximum frequency of conductivity relaxation assuming that  $g(\Phi, \epsilon_1, \Delta\epsilon)$  is constant which is actually the case as it is going to become obvious from the experimental results. The above proportionality implies something more, that the activation energy for the dc conductivity inside the inclusion is the same as the relaxation activation energy value.

So, the characteristic relaxation frequency of the HF mechanism has the same temperature variation as that of the dc conductivity in the interior of the conducting phase.

### 3. Experimental

PEDOT:PSS films with thickness 50 nm, coated on PET were made from an aqueous dispersion of PEDOT:PSS (CLEVIOS PH 500, H.C. Starck), where the ratio PEDOT-to-PSS was 1:2.5 by weight [13]. A sample holder was constructed in order to place the PEDOT:PSS films. Details of the holder can be found elsewhere [2]. A vacuum cryostat, operating from the liquid nitrogen temperature to 420 K, accommodated the sample holder described above. Isothermal conditions could be achieved with an accuracy of 0.2 K. A Solartron 1240 Gain Phase Frequency Response Analyzer with a BDC pre-amplifier was used to measure complex impedance in the frequency range from 1 mHz to 1 MHz while the amplitude of the applied ac voltage was 50mV. The imaginary part of the (relative) complex permittivity  $\epsilon^*$  is connected to complex electrical conductivity  $\sigma^*$  through the relation  $\text{Im}(\epsilon^*) = \text{Re}(\sigma^*) / (2\pi f \epsilon_0) \propto G(f) / f$ , where  $f$  denotes the frequency of the harmonic voltage applied to the specimen and  $G(f)$  is the measured conductance.

### 4. Results and discussion

The  $G/\epsilon_0 f$  plot versus frequency consists of the dc contribution i.e. a line with slope -1 and possibly a number of relaxation mechanisms i.e. peaks with amplitude and width depending on their particular characteristics. If though the dc component is strong compared to the dielectric relaxation peaks, the former shall mask the latter, as can be seen in this case in Figure 1 for room temperature. Nevertheless, there are several methods which can be employed in order to reveal the underlying mechanisms. Two of these are, lowering the temperature and thermal aging under the condition that these affect the different mechanisms in such a way that they can finally be distinguished.

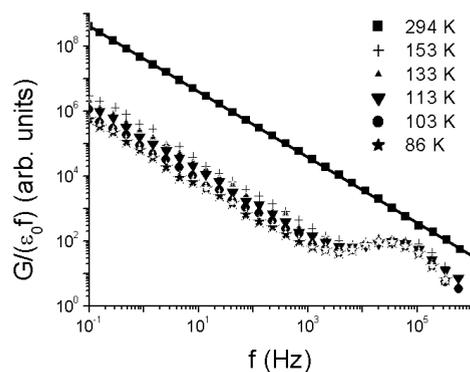


Fig. 1. Isotherms of the quantity  $G/(\epsilon_0 f)$  versus frequency. Data points at room temperature ( $T=294$  K) are fitted with a line with slope  $-1$ .

In Figure 1,  $G/\epsilon_0 f$  is plotted as a function of frequency at various temperatures. A dominant high frequency (HF) one has its maximum around  $10^4$  Hz and a strongly masked mechanism around  $10^2$  Hz (LF) as can be seen in Figure 2.

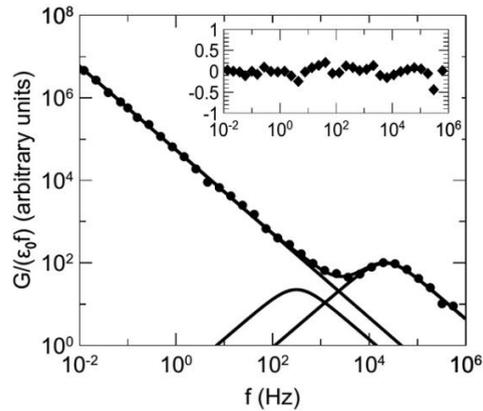


Fig. 2. Fitting curve consisting of a conductivity component (straight line) and a couple of Debye-type relaxation peaks at 86 K. Inset: The reduced residuals versus frequency.

In order to expose the low frequency mechanism the specimen was thermally aged so the dc conductivity was further reduced. The specimen was heated at ambient atmosphere at 423 K for 7 h.

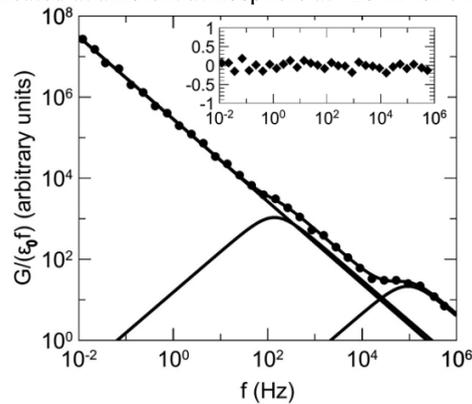


Fig.3.  $G/(\epsilon_0 f)$  vs frequency of a PEDOT:PSS specimen at  $T=86$  K heated at ambient atmosphere at 423 K for 7 h. Inset: The reduced residuals vs frequency.

The results (Figure 3) were remarkably illuminating; the LF relaxation appeared clearly as a 'knee' around  $10^2$  Hz. Thermal annealing affects the percolation network by breaking cross-linking and subsequently the total  $\sigma_{dc}$  reduces. As a result of this, charge carriers that initially contributed to dc conductivity are now trapped within short scale regions and enhance the intensity of the LF relaxation mechanism (capacitance effects) relatively to HF relaxation mechanism which according to eq. (1) involves relaxation within the interior of the grains.

Dielectric relaxation is observed in PEDOT PSS films of even higher dc conductivity [3], such as that depicted in the Figure 4 whereas the film was developed on cellulose substrate. In this experiment, isotherms were extended up to 15 K using a Leybold-Heraeus liquid helium cryostat modified to collect ac conductivity data from the open surface of a film on insulating substrate. In such specimens with high dc conductivity, it is necessary to freeze the specimen at significantly low temperature, so as to reveal the HF relaxation.

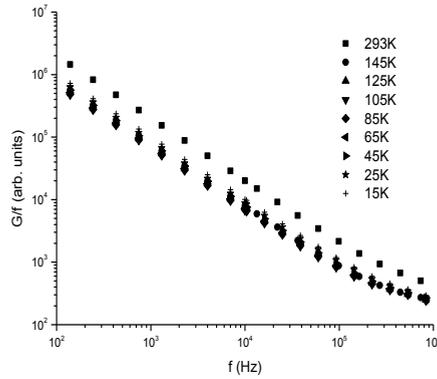


Fig. 4. Isotherms of the quantity  $G/(\epsilon_0 f)$  versus frequency of a PEDOT:PSS specimen developed on cellulose substrate.

In Figure 5, the natural logarithm of the frequency-independent ac conductance  $G_{dc}$  i.e. the low frequency dc region ( $G_{dc} = C \exp(-E_{dc}^{act} / kT)$ ), is plotted against reciprocal temperature. A linear fit to the data points yields the dc activation energy

$$E_{dc}^{act} = -(d \ln G_{dc} / d(1/kT)) = (0.017 \pm 0.002) eV,$$

where  $k_B$  denotes the Boltzmann’s constant and  $T$  is the absolute temperature.

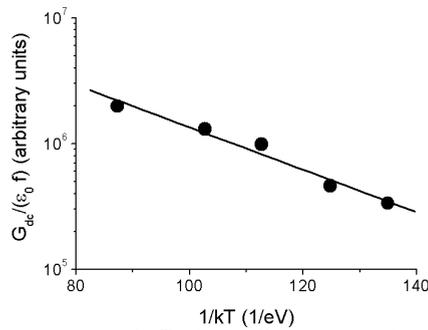


Fig. 5. The quantity  $G/(\epsilon_0 f)$  at low frequency versus  $1/kT$ , whereas  $G$  is proportional to the dc conductivity of the film.

An Arrhenius equation  $f_{max} = f_0 \exp(-E^{act} / kT)$ , where  $f_0 \equiv f_{max}(T \rightarrow \infty)$  is constant, is perfectly fitted to the data points of  $\ln f_{max}(1/kT)$  diagram (Figure 6), yielding an activation energy

$$E_{HF}^{act} = -(d \ln f_{max} / d(1/kT)) = (0.015 \pm 0.002) eV.$$

$E_{HF}^{act}$ , which is identical to the activation energy for dc conductivity within the interior of the conducting grains. As mentioned earlier,  $\Delta\epsilon$  is practically constant with temperature as can be seen in the inset diagram of Figure 6.  $E_{HF}^{act}$  is lower than the macroscopic  $E_{dc}^{act} = (0.017 \pm 0.002) eV$ , which incorporates the contribution from the percolation network as well as the energy barriers set by the insulating shells.

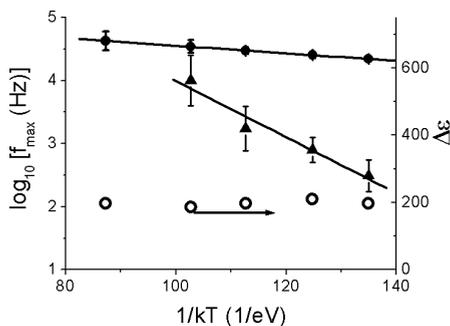


Fig. 6. Arrhenius plot for HF (full circles) and LF (full triangles) relaxations and the relaxation strength  $\Delta\epsilon$  (open circles) vs  $1/kT$ .

For LF relaxation mechanism, the analogous calculations yield

$$E_{LF}^{act} = (0.15 \pm 0.02) eV.$$

This energy is an order of magnitude bigger than both  $E_{dc}^{act}$  and  $E_{HF}^{act}$  implying an increased effective potential barrier in accordance with a model of thermal degradation mechanism proposed for PEDOT:PSS [13]. When thermally treated, PEDOT oligomers and PSS chains separate and the latter concentrate at the surface of the grains, increasing the height of the potential barriers.

## 5. Conclusion

In conclusion, PEDOT:PSS is a promising material for optoelectronic devices, which constitutes a suspension of conducting PEDOT:PSS grains, shelled by an insulating layer of PSS. Broadband Dielectric Spectroscopy (BDS) is employed in order to investigate two distinct relaxation mechanisms as predicted by bi-phase suspension dielectric theory. BDS can also be employed in order to explore the influence of thermal annealing on the dc conductivity and the relaxation mechanisms. We propose a methodology to gain an insight into the local conductivity of the interior of mesoscopic conducting phase and to calculate the activation energies of the relaxation mechanisms.

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