DENSITY OF STATES OF POLY(3-ALKYLTHIOPHENE)S DETERMINED USING ENERGY RESOLVED ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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1. Introduction

Determination of electronic structures of conjugated polymers is essential for the study of novel organic materials for photoelectronic applications. Poly(3-alkylthiophene)s (PAT)s were synthesized to improve the solubility of electrically conductive polythiophenes by installing the alkyl side groups on the thiophene cores [1]. PATs are semi-crystalline polymers with an orthorhombic crystal lattice where polymer backbones are separated from one another by side alkyls (a-axis). X-ray diffraction studies have revealed that the above-indicated polymers form the layered structures inside orthorhombic lattices [2]. Planar lattices are superimposed upon each other in three-dimensional structures and formed by a regular trans-arrangement of thiophene cores. It is know that polaron states play a dominant role in the charge transport in π-conjugated heterocyclic chains [3]. In particular conditions, the polarons interaction can stimulate the formation of the bipolaron, the ground energetic state of which is lower than that observed in the case of polaron [4]. Polarons and bipolarons are two potential configurations of the charge carriers of polymers in the non-degenerate state, the concentration of which can be changed by doping or photoexcitation. Substitution of an alkyl group results in a soluble polymer in conventional solvents, which exhibits absorption and emission bands in the visible region. Colour of the poly (3-alkylthiophene)s can be tuned sequentially by changing the length of the alkyl side group [5]. An important property of real PATs samples is their regioregularity, which strongly affects the geometry of the polymer chain. In the case of the totally regioregular sample, all neighbouring PATs monomer units are connected in a head-to-tail (H-T) pattern, permitting a coplanar structure. Therefore, the 100% regioregular form represents the lowest energy configuration of the polymer backbone and results in the lowest band gap [6]. In fact, the real samples involve some head-to-head (H-H) or tail-to-tail (T-T) dyads in the polymer chain, which cause conformational defects.

The major problem for the study of organic materialsisthe lack of the spectroscopic methods for the measurements of the electronic structureexpressed bythe density of states (DOS)that would enable a faster progress in the material optimization. Methods used for characterization of inorganic semiconductors are not always appropriate due to the weaker intermolecular coupling and different nature of the structures formed by the organic molecules.

In this paper we present the DOS structure of thin PATs films with different alkyl length on the thiophene cores in a wide energy region between the HOMO and LUMO bands.The new spectroscopic method, energy resolved electrochemical impedance spectroscopy (ER-EIS) [7], is used for DOS measurements. Experiments demonstrate a high sensitivity of the ER-EIS method to detect small changes in the DOS structure caused either due to polymer chain modification or the way of the thin polymer layer preparation.

2. Materials and sample preparation

Three polymers under investigation [poly(3-pentylthiophene) (P3PT), poly(3-dodecylthiophene) (P3DDT) and poly(3-hexadecylthiophene) (P3HDT)] were synthesized according to Mao and Holdcroft [8] through a Grinard reaction of intermediate monomers. The regioregularity of all of these polymers was around 60%. Molar mass of P3PT and P3HDT was $6x10^4$g/mol and $9x10^4$g/mol, respectively. P3DDT polymer was prepared with two different chain length with molar masses of $7x10^4$ g/mol and $13x10^4$ g/mol. Poly(3-hexylthiophene) (P3HT) was commercially available from Sigma-Aldrichwith 99.9 % regioregularity and average molar mass of $4.5x10^4$ g/mol.

Thin films (≈ 80 nm) of all polymers were prepared by spin coating from polymer solutions dissolved in dichlorobenzene (DCB), chloroform ($CHCl_{6x}$), and mixture of DCB+$CHCl_3$. The samples were left to dry in solvent vapor a subsequently thermally annealed (110 ˚C, 5 minutes).

3. Method

The ER-EIS method is based on interaction between a thin organic film and an electrolyte via redox reactions in an electrochemical cell [8]. Exchange of electrons through electrolyte/semiconductor interface gives rise to current density:

$$j = ek_{ct}n_s[A], \tag{1}$$

where e is elemental charge, k_{ct} is charge transfer coefficient, n_s is electron concentration on the polymer surface, and $[A]$ is concentration of redox (donor/acceptor) pairs in the electrolyte. Various elementary processes of the semiconductor/electrolyte system respond to the system perturbation at different rates and the corresponding relaxation processes become dominant in impedance spectra measured at different frequencies ω. Determination of DOS is based on the measurement of the impedance of electrolyte/semiconductor system. The DOS function in the polymer at the Fermi level $g(E_F)$ can be derived in terms of the charge transfer resistance $R_{ct}(U)$ measured under applied voltage U as:

$$g(E_F = eU) = \frac{dn_s}{d(eU)} = \frac{1}{ek_{ct}[A]S}\frac{d(jS)}{d(eU)} = \frac{1}{ek_{ct}[A]SR_{ct}} \tag{2}$$

We can map the function $g(E)$ at Fermi energy $E_F = eU$ by direct measurement of $R_{ct}=dU/d(jS)$ at the applied voltage U with superimposed perturbation dU with a frequency of 0.5 Hz. The measurements were performed using a three-electrode electrochemical cell.

4. Results

Measurement of DOS function using ER-EIS for polythiophenes with different length of the alkyl side group on the thiophene core is shown in Fig. 1. On the left graph is shown $g(E)$ in linear scale. We can see definite broadening of the bandgap with the increasing length of polymer side chain. Linear scale allows us to determine actual value of the width of the bandgap for individual polymers. The bandgap of P3PT, P3HT, P3DDT, and P3HDT are 2.20, 2.22, 2.25 and 2.65 eV, respectively. Logarithmic scale (right graph of Fig. 1) gives insight into the actual fine DOS structure in the bandgap. The satellite peak located in the gap at the edge of HOMO band is lesser pronounced as the length of alkyl side group increases.

The peak amplitude of P3DDT is smaller by more than one order of the magnitude compared to P3HT. Differences are also observed for the depth of the bandgap: longer alkyl side group lower density of defect states. The band structure of commercial P3HT is shifted by 0.15 eV towardsvacuum energy in comparison with thesynthesized polymers. This shift is consequence of a much higher regioregularity of P3HT.

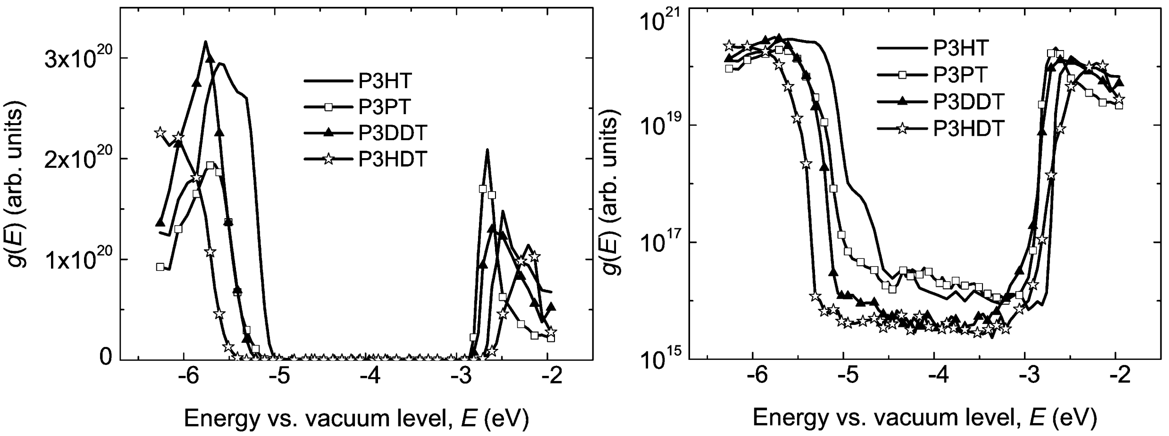

Fig.1: *Measured g(E) in HOMO/LUMO region of polythiophenes with various-length of alkyl side group. Left (right) figure shows g(E) in linear (logarithmic) scale.*

Figure 2 demonstrates influence of the preparation procedure on the structure of the DOS function, namely the usage of different solvents. The rate of drying of different solutions affects the character of polymer chain alignment in the layer which influences the layer structure. Tuning of this fine bandgap structure is essential in the process of electronic device preparation. Left graph of Fig. 2 shows *g*(*E*) for P3PT prepared using DCBand mixture of $CHCl_3$and DCB (boiling point of 180 ˚C for DCB and 61.2 ˚C for $CHCl_3$). The high sensitivity of ER-EIS method on subtle structural changes can be seen. The higher degree of structure disorder manifests itself in the extra states under the edge of HOMO slope. The DOS function of P3DDT dissolved in DCB and $CHCl_3$ is depicted on the right graph of Fig. 2. The steeper slope of the LUMO edge for DCB (graph (a)) relates to the higher crystallinity of the layer achieved by a slower drying.

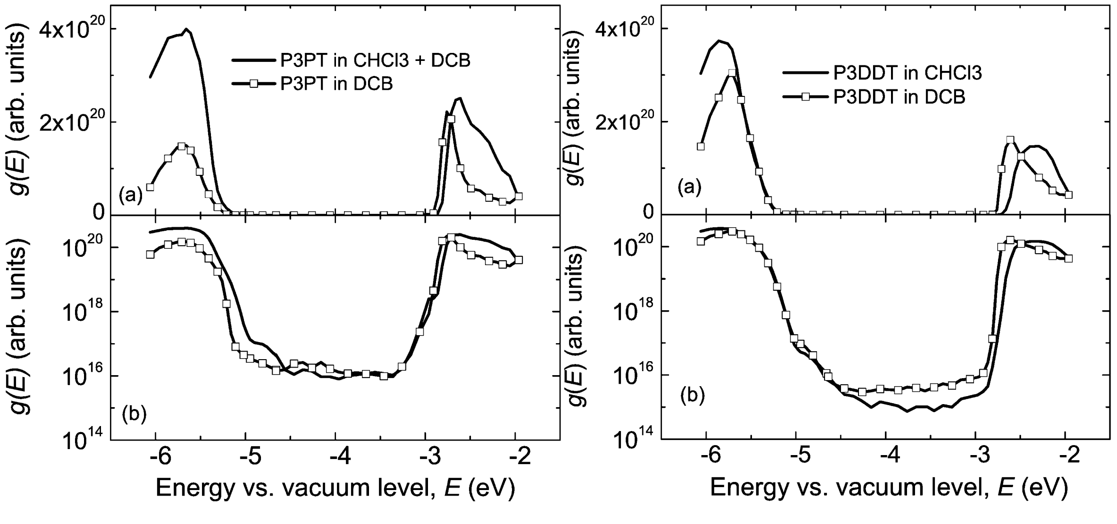

Fig. 2: *Influence of solvents on measured g(E) in HOMO/LUMO region of P3PT (left) and P3DDT (right). (a) linear scale; (b) logarithmic scale.*

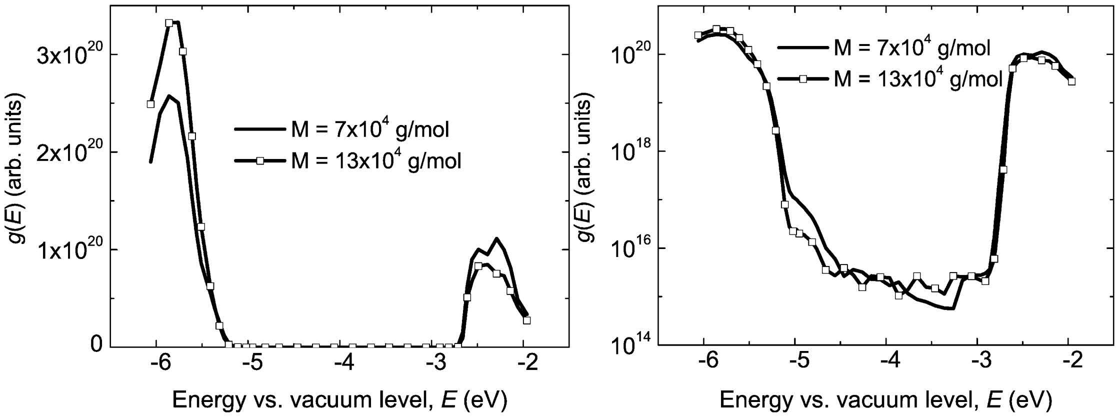

Fig. 3: *Measured g(E) in HOMO/LUMO region of P3DDT for two different length of the polymer chain. Both layers were prepared from the DCB solution. Left (right) graph shows g(E) in linear (logarithmic) scale.*

Material influence on fine bandgap structure is depicted in Fig. 3. Two types of P3DDT polymer with different length were measured. Both materials were dissolved in DCB and prepared by the same annealing procedure. Left (right) figure uses linear (logarithmic) scale for *g*(*E*). It can be seen that bandgap width and depth are same for both materials but they differ in the height of satellite peak at the bottom of the HUMO slope. The higher peak indicates better polymer ordering for shorter polymer chain.

5. Conclusion

We demonstrated the sensitivity of the new ER-EIS method on structural features and subtle alignment of polythiophenes. This method is appropriate for DOS study and fine bandgap structure of organic semiconductors. We showed the influence of the alkyl side-group length of poly(3-alkylthiophene)s on the bandgap structure as well as an importance of the chosen process for the sample preparation in respect of their DOS structure.

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