Comparison of the optical and electrical energy band gap of a thin layer of polyelectrolyte based on MEH-PPV and KI

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Abstract. A thin layer of polyelectrolyte based on Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and potassium iodide (KI) was prepared using the sol-gel method. Comprehensive studies of the optical and electrical energy gap of the produced material were carried out. Using the Thermo Scientific Evolution 220 spectrophotometer equipped with a xenon lamp in the wavelength range from 190 to 1110nm, the absorbance \(A\) was measured. The optical energy gap (\(E_{\text{g, opt}}\)) was calculated. With the change in the concentration of potassium iodide, the change in the energy band gap of polyelectrolyte thin film was registered. In this paper, the cyclic voltammetry (CV) for testing electrochemical properties was used. The location of energy levels HOMO, LUMO and the value of the energy band gap were calculated, which is very important for polymeric materials that conduct electricity and the possibility of their use in solar cells.

1. Introduction
Polymeric materials thanks to their properties find application in various fields of modern technology, being an important material for an engineer constructor. The development of science about polymeric materials and their mass production can undoubtedly be considered as one of the greatest technological achievements of the 20th century. At the turn of the 20th and 21st centuries, their production amounted to about 180 million tons, and in 2006 it already reached the level of 245 million tons. In recent years, this production has been increasing every year by 5-5.5%, and the consumption of polymeric materials per capita in highly industrialized countries exceeded 150 kg. Of the general-purpose polymeric materials, many products of great practical importance are manufactured, among others packaging, tires, conveyor belts, drive belts, seals, thermal insulation (foams) and electrical (cable coatings), textiles, furniture, linings, casings, window frames, toys, etc. An important element in the development of production of more specialized polymers and resins is the mutual struggle for a place on the market of large recipients of polymeric materials, such as the aerospace, automotive, construction, electronic, electric and photovoltaic industries. Until recently, electronics was based on materials of inorganic origin (primarily on metals, as well as physical phenomena occurring in semiconductors and dielectrics). However, the characteristic properties of metals, i.e. opacity, lack of flexibility, the inability to obtain a strong conductivity anisotropy, the lack of possibility of processing in solutions, high density or susceptibility to corrosion, often constitute a barrier to their use [1-9]. Technological progress, continuous improvement and minimization of devices, forces searching for new materials and improving existing ones. The rapid development of electronics and materials engineering, especially regarding semiconductor technology and chemistry of polymer materials is
related to the introduction of modern engineering materials, including polymeric materials that conduct electricity. Professor Hideki Shirakawa is considered to be the discoverer of conductive polymers. In 1975 he made acetylene polymerization, resulting in the reaction of polyacetylene (an organic conductive polymer). In 1976, to collaborate on conducting polymers joined by Professor Alan G. MacDiarmid and Professor Alan J. Heeger, which resulted in the doping polyacetylene with iodine and bromine, significantly increasing its electrical conductivity. In 2000, "for the discovery and development of conductive polymers" professors Hideki Shirakawa, Alan G. MacDiarmid and Alan J. Heeger received the Nobel Prize. This led to increased interest in this group of materials [7-16]. Polymeric materials with semiconductor properties show some common feature: they are made of macromolecules in which, in spite of all complexity, more or less regular repeating sequences of specific atomic groups can be distinguished, e.g. chains of conjugated bonds. The greater its extent, the more favorable are the electron flow conditions through the material, and hence its higher conductivity. Conductive polymers in the undoped state are multiparticulates semiconductors. They are part of a wider group of organic semiconductors. In the group of electronically conducting polymers, Π-electron aliphatic systems are often distinguished. By doping a polymer material, it is possible to obtain an electrical conductivity similar in size to the conductivity of metals. An example is poly (acetylene). This polymer in the undoped state is a semiconductor with a specific conductivity of $10^{-7}$ S/cm. The introduction of an acceptor-like admixture (eg AsF$_5$) or a donor (Li, K) to poly (acetylene) increases its conductivity by $10^{-12}$ orders of magnitude [11-20].

The main problem in the development of solar cells with polymer material is to choose the appropriate energy levels of each material to ensure the oriented movement of electrons. In these kinds of solar cells the HOMO and LUMO energy levels of each component must be selected that guarantees the oriented transport of electrons. A novelty in the article is the preparation of a thin layer of MEH-PPV polymer doped with potassium iodide which can be used in polymeric and dye sensitized solar cells. Then, the optoelectric properties of this layer were characterized. Optical and electrical energy band gap and HOMO and LUMO levels were determined.

2. Materials and methodology

Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene], anhydrous potassium iodide (KI) and other chemicals were supplied by Sigma Aldrich. N-Methylpyrrolidine (NMP) was used to dissolve the polymer and salt, and the liquid solutions were spin-coated to form polyelectrolyte thin films. Using the Thermo Scientific Evolution 220 spectrophotometer equipped with a xenon lamp in the wavelength range from 190 to 1110nm, the absorbance $A$ was measured. This is the logarithm of the ratio of the incident radiation ($I_0$) to the intensity of the outgoing radiation ($I_t$), which is defined as the decimal logarithm of the transmittance:

$$A = \log \frac{I_0}{I_t}$$  

The optical energy gap ($E_{\text{opt}}$) was calculated by plotting on the normalized absorption spectrum a straight line indicating the wavelength ($\lambda_{\text{onset}}$) for the recorded absorption edge and using the formula:

$$E_{\text{opt}} = \frac{hc}{\lambda_{\text{onset}}}$$  

The location of energy levels HOMO, LUMO and the value of the energy band gap are very important for polymeric materials that conduct electricity and the possibility of their use in solar cells. One indirect methods of determining energy levels are electrochemical measurements. In this paper, the cyclic voltammetry (CV) for testing electrochemical properties was used. In the voltammetric measurements, the dependence of the intensity of the electric current on the applied voltage or potential of the electrode is examined. The change in potential causes that the molecules chemically take or get rid of the electron, which means that they can undergo oxidation and reduction processes. As a result, an electric current flows, which depends on the rate at which the electrons move at the electrode-solution interface. The tests were performed in a three-electrode system with a platinum auxiliary electrode and a silver-chloride reference electrode. The working electrode was an ITO tile covered with a thin layer of polymer. In order to calculate the position of energy levels, first the
oxidation process of $E_{\text{ox}}$ was determined, which is connected with the removal of the electron from the HOMO level, and the beginning of the first reduction process $E_{\text{red}}$, which corresponds to the introduction of the electron to the LUMO level.

3. Results

The recorded electron absorption spectra are presented as a function of the dependence of the absorbance on the wavelength (Figure 1). The thin layer of MEH-PPV polymer material, dissolved in NMP, has the highest absorption band at a wavelength of 416 nm. The highest absorption band of the MEH-PPV layer dissolved in the same solvent but with 5% KI was recorded at 428 nm. The highest absorption band for the MEH-PPV layer with 10% KI was recorded at the wavelength of 431 nm, and for the layer with 15% KI at 435 nm. Along with the increase in the proportion of potassium iodide in the polymer material in the recorded spectra, bathochromic shifts of bands towards longer wavelengths were found. In the analysed spectra, along with the increase in the percentage of KI, a small hyperchromic effect of the absorption bands was registered. A slight widening of the absorption band was observed along with the increase in KI content.

![Figure 1. The dependence of the absorbance on the wavelength for a thin layer of MEH-PPV deposited on a glass substrate together with MEH-PPV graphs with an increasing contents of potassium iodide](image)

The optical energy gap ($E_{\text{opt}}$) was calculated by plotting on the normalized absorption spectrum a straight line indicating the wavelength ($\lambda_{\text{onset}}$) for the recorded absorption edge, and the results obtained are summarized in Table 1. For the thin layer of MEH-PPV dissolved in NMP, the wavelength of the absorption edge was 510 nm, and calculated on this basis the optical band gap is 2.43 eV. The MEH-PPV layer with 5% KI is characterized by $\lambda_{\text{onset}} = 520$ nm, and the optical band gap at this wavelength is equal 2.39 eV. For a 10% share of KI in MEH-PPV, the graphically determined wavelength for the absorption edge was 535 nm, and the optical band gap is equal 2.32 eV. The wavelength of the absorption edge determined from absorption of MEH-PPV with 15% was 540 nm, and the $E_{\text{opt}}$ calculated on this basis is 2.3 eV. Along with the change in the share of KI in the polymeric material, its optical energy break has changed (Table 1). These changes were small, by 0.13 eV. However, it has an impact on its electrical conductivity. With the change in the concentration of KI in the polymeric material, changing its optical energy band gap (Figure 2). The measurements of electrochemical properties of polymeric materials deposited by the sol-gel method on a glass substrate with an ITO layer were made by means of cyclic voltammetry. The results of measurements are presented in the form of current-voltage diagrams (Figure 3).

The potentials of reduction and oxidation of polymer layers and the energy levels HOMO and LUMO calculated on their basis, as well as the value of the energy band gap are summarized in table 2.
The oxidation and reduction potentials for the thin layer of non-doped MEH-PPV polymer material are 0.69 and -1.47 respectively. The calculated HOMO energy level is 5.09 eV, and the LUMO energy level is 2.93 eV. The contribution of 5% potassium iodide influenced on the energy levels of the MEH-PPV by increasing the HOMO level to 0.08 eV, while the LUMO level by increasing to 0.29 eV. The energy band gap has consequently decreased from 2.16 eV to 1.95 eV. Further doping up to 10% KI had a slight impact on the HOMO and LUMO energy levels of the MEH-PPV polymer material. For a thin layer of polymer material MEH-PPV with 10% potassium iodide the energy gap was equal 1.88 eV.

**Table 1.** Values determined on the basis of absorbance curves, wavelengths and optical band gap of thin layers calculated on this basis

| Layer                | $\lambda_{\text{max}}$ [nm] | $\lambda_{\text{onset}}$ [nm] | $E_{\text{gopt}}$ [eV] |
|----------------------|-------------------------------|-------------------------------|-----------------------|
| MEH-PPV              | 416                           | 510                           | 2.43                  |
| MEH-PPV + 5% KI      | 428                           | 520                           | 2.39                  |
| MEH-PPV + 10% KI     | 431                           | 535                           | 2.32                  |
| MEH-PPV + 15% KI     | 435                           | 540                           | 2.30                  |

**Figure 2.** The influence of KI doping on the optical band gap value of the polymer thin film MEH-PPV

**Figure 3.** A cyclic voltamperogram of a thin layer of MEH-PPV deposited on a glass substrate with ITO
Table 2. Comparison of the values of reduction potentials and oxidation of thin polymer layers and the energy levels of HOMO, LUMO and energy gap values calculated on their basis

| Layer                  | $E_{\text{ox}}$ [V] | $E_{\text{red}}$ [V] | $E_{\text{Homo}}$ [eV] | $E_{\text{Lumo}}$ [eV] | $E_{g}$ [eV] |
|------------------------|---------------------|----------------------|------------------------|------------------------|--------------|
| MEH-PPV                | 0.69                | -1.47                | 5.09                   | 2.93                   | 2.16         |
| MEH-PPV + 5% KI       | 0.77                | -1.18                | 5.17                   | 3.22                   | 1.95         |
| MEH-PPV + 10% KI      | 0.78                | -1.1                 | 5.18                   | 3.3                    | 1.88         |

4. Conclusion

The suitability of the tested materials for the construction of dye sensitized solar cells was confirmed using a UV-VIS spectrophotometer, determining their optical properties. In the analyzed UV-VIS spectra, together with the increase in the concentration of potassium iodide in the polymer material, bathochromic shifts of bands towards longer wavelengths and the hyperchromic effect of absorption bands were registered. In polymeric materials, the shift of absorption bands is related to the change of the chain length, the shifting of the bands towards the longer wavelengths indicates the increase of the chain length in the oligomers. The optical energy band gap for the material of MEH-PPV is 2.43 eV, which is confirmed in the literature. With the change in the concentration of KI in the polymeric material, changing its optical energy band gap. Significance for polymeric conductive materials and the possibility of their use in solar cells not only has an energy band gap, but also the location of their energy levels HOMO and LUMO. By adding potassium iodide to the meh-ppv polymer it is possible to reduce its energy band gap from 2.16 eV to 1.88 eV and slightly influence on the HOMO and LUMO energy levels.

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