

Article

The Determination of the Electronic Parameters of Thin Amorphous Organic Films by Ellipsometric and Spectrophotometric Study

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Abstract: The aim of this work was the determination of the basic optical parameters and electronic structure of conjugated polymer films by two commonly used techniques—spectrophotometry and ellipsometry. Poly(3-hexylthiophene (P3HT) and poly(3-octylthiophene (P3OT) conductive polymers films deposited on a glass substrate by the spin-coating technique showed very comparable surface structures composed of grains of similar sizes and shapes. X-ray tests confirmed that the polythiophene layers are amorphous, which confirmed the correctness of the choice of the optical models used. Selected optical models (Lorentz, Tauc–Lorentz and Cody–Lorentz) have been applied in order to determine the thickness, and optical parameters such as refractive index and extinction coefficient, absolute absorption and electronic parameters (energy gap E_g , amplitude A and broadening B). Spectral absorption determined from spectrophotometric measurement is similar to the absorption spectrum obtained from the ellipsometry method with the application of oscillator models.

Keywords: polythiophenes; spectroscopic ellipsometry; spectrophotometry; optical constants

1. Introduction

For many years, conjugated polymers have been the subject of interest of many scientists in the field of organic semiconductors. It is their optoelectronic properties that make them suitable to use in solid-state devices such as field effect transistors (FETs) [1,2], organic light emitting diodes (OLED) [3,4] and photovoltaic cells (PV) [3,5,6]. The polythiophene thin films may also be used as sensors of volatile organic compounds in the atmosphere such as dichloromethane or tetrahydrofuran [7,8]. Polymers may also be used as a replacement for glass in optical fibers [9]. The unique optoelectronic properties of conjugated polymers are the result of the existence of π bonds in the electronic structure of the polymer. The π bonds are not particularly strong; therefore, it is possible to excite the electronic state of electrons in the π bonds by the photons in the visible range. Electrons from σ bonds are usually not taken into consideration [10]. Moreover, polythiophenes possess attractive optoelectronic properties such as easy solubility, environmental stability, solution processability and cost effectiveness [2]. The optoelectronic properties of the π conjugated polymers are a function of their chemical nature, the spatial arrangement of the polymeric chain and film morphology. Furthermore, the polymer microstructure and film morphology are strongly dependent on the processing conditions.

It is well known that the optoelectronic properties of conjugated polymers vary with the changing of molecular weight, [11,12] the deposition method [10], the concentration of the solution and film

thickness [13]. For many types of polymer, a strong relationship between the thickness of the polymer layer and the refractive index can be observed. The thinner the polymer film, the stronger the dependence of the refractive index is, especially at longer wavelengths (above 500 nm). For thicker polymer films, the influence of the layer thickness on the refractive index is negligible [14].

Spectroscopic ellipsometry (SE) is an especially useful, fast, non-destructive measurement technique for determining the optical properties and thickness of samples and it enables evaluation of the morphology of the samples. SE uses polarized light to illuminate the sample. The changes in the polarization state for *s* and *p* polarization components of the electric field after interaction with the sample are registered. These changes are recorded as Ψ and Δ spectra. Ψ presents the amplitude ratio between the Fresnel reflection coefficients of *s* and *p* polarization types and Δ presents the phase difference between the components of reflected light in *s* and *p* plains, before and after reflection [15].

The biggest disadvantage of ellipsometry is fact that it is an indirect technique. In order to obtain any information characterizing the sample, the application of an appropriate model of dispersion is required. The Kramers–Kronig consistency ensures the compatibility of the measured and fitted data in a wide spectral range and provides physically consistent results.

Obtaining the same transmittance spectra and the absorption coefficients in two different measurements is hard to achieve in the case of polymer layers. In the literature, many models are used to describe conductive polymer layers [16,17]. In our article, we present the usefulness of the models described in the literature to determine the optical parameters of poly(3-hexylthiophene) (P3HT) and poly(3-octylthiophene) (P3OT) layers deposited by the spin-coating method on glass and silicon substrates. Although the depolarization of light reflected from the polymer samples is high, the obtained ellipsometric results enable the fitting of three independent models and the determination of the electronic parameters of the tested polymer layers. However, the use of models alone does not yield reliable results. Such a procedure is new to this work.

2. Materials and Methods

2.1. Optical Modelling

There are many dispersion relations utilizing oscillator theories to describe optical properties of particular substances such as absorption, reflection, refraction and transmission. We used the Lorentz model including the extended versions of Tauc–Lorentz and Cody–Lorentz for determining the results of the ellipsometric studies of thin polythiophene films. Additionally, we used the Gauss model because it effectively describes the interband transitions [18]. The Lorentz and Gaussian oscillators both have a symmetrical shape.

The Lorentz oscillator model is often applied for describing the behavior of transparent or semi-transparent semiconductors and insulators. For disordered materials, such as polythiophenes, any oscillator model may be applied successfully. According to the Lorentz model [19], the imaginary part of the dielectric function ϵ_L is given as:

$$\epsilon_L(E) = \frac{A B E_c E}{(E^2 - E_c^2)^2 + B^2 E^2} \quad (1)$$

where *A* is the amplitude, *B* is the broadening term of the peak, E_c is the peak transition energy (center energy) and *E* is the photon energy.

The imaginary part of the dielectric function for the Gaussian oscillator ϵ_G is given in Equation (2):

$$\epsilon_G(E) = A \left(\exp \left[-\left(\frac{E - E_c}{\sigma} \right)^2 \right] + \exp \left[-\left(\frac{E + E_c}{\sigma} \right)^2 \right] \right) \quad (2)$$

where $\sigma = \frac{B}{2\sqrt{\ln 2}}$.

In order to obtain optimum compatibility between the applied model and the experimental data, the Gauss model is often used in optical modelling. Gaussian models are included as multiplicative factors on spectral dependences in the Tauc–Lorentz and Cody–Lorentz models. In optical modelling, the Tauc–Lorentz (TL) [20] or Cody–Lorentz (CL) [21] oscillators give a more realistic shape of dielectric function than the Lorentz or Gauss models.

Neither Lorentzian nor Gaussian theorems are able to determine the common energy gap E_g . The Gaussian-shaped functions are usually used for fitting energies below the band gap related to molecular lattice vibrations, while TL and CL are used for fitting the band gap and the energies in the UV region [22]. The CL model is analogous to the TL model because both define the optical band gap and the Lorentzian absorption peak. The main difference between TL and CL is in the absorption onset region with energy slightly higher than E_g , where the TL model gives poor results while the CL model gives a good output. The large number of fitting parameters in the TL model refers to the properties of the measured material.

The imaginary part of the dielectric function for TL ε_{TL} is the product of the Lorentz function (Equation (1)), the Tauc function is given as presented in Equation (3) [20]:

$$\varepsilon_T(E > E_g) \propto \left(\frac{E - E_g}{E} \right)^2 \quad (3)$$

The imaginary part of the dielectric function for CL ε_{CL} is similar to TL and the Cody formula is given as follows in Equation (4):

$$\varepsilon_C(E < E_g) = (E - E_g)^2 \quad (4)$$

The CL model has one extra dispersion parameter in comparison to TL, which makes it more versatile than the TL model. At energies below band gap, the Urbach absorption tail term is included in the CL oscillator.

Both TL and CL are Kramers–Kronig consistent and appropriate for analyzing amorphous semiconductor data. For all discussed oscillators, the real part of dielectric function ε_1 (Equation (5)) can be obtained by a Kramers–Kronig integration of the ε_2 functions [23]:

$$\varepsilon_1 = \frac{2}{\pi} P \int_{E_g}^{\infty} \frac{\xi \varepsilon_2(\xi)}{\xi^2 - E^2} d\xi \quad (5)$$

where P is the principal values of the integral.

2.2. Materials

Poly(3-hexylthiophene (P3HT) and poly(3-octylthiophene (P3OT) thin films were deposited by a spin coating technique on glass slides and monocrystalline silicon (001) substrates using the SCV-15 spin coater made by LOT-Oriel GmbH. Both polythiophenes were purchased from Sigma Aldrich and their chemical structure is presented in Figure 1. The methods of preparation of the polythiophene derivatives have been described in [24,25].

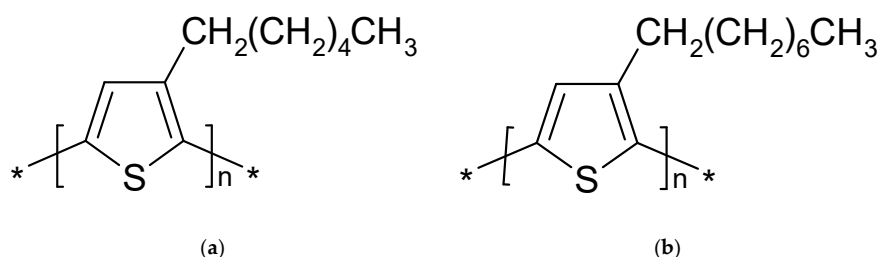


Figure 1. Chemical structure of (a) poly(3-hexylthiophene (P3HT), (b) poly(3-octylthiophene (P3OT).

Both polymers were dissolved in tetrahydrofuran 10 mg/mL. The silicon and glass substrates were first cleaned in an ultrasonic bath for 10 min in water with detergent and next for 10 min in 2-propanol in order to remove any impurities from the substrate surface. Polymeric films were deposited with an aligned rotational speed of 2000 rpm for 60 s in ambient conditions (21 °C, 35% humidity). The thickness of the thin film in the spin coating method depends on the rotational speed. The higher the speed of rotation, the thinner the layer is. The thickness is also influenced by the solution concentration. P3HT and P3OT thin films have been examined by ellipsometric and spectrophotometric methods. In this work, we present the results of ellipsometric measurements only for thin films on silicon substrate. This is due to the fact that the thermo-optical properties of crystalline silicon are well defined across a wide range of temperatures [26]. Moreover, the sensitivity of ellipsometry measurements is better when the difference between the refractive indices of layer and substrate Δn is higher. For the polythiophenes–Si interface, it is about 1.9 at wavelength of 633 nm, while for the polythiophene–glass interface, it is about 0.4. This is due to the formulas for amplitude Fresnel coefficients.

The optical and electronic properties of deposited organic thin films were investigated using two measurement methods: spectroscopic ellipsometry and spectrophotometry. The spectral dependencies of transmission and reflection for both polymers deposited on glass slides were measured by the AvaSpec-ULS2048LITEC-RD-US fiber optics spectrometer (Avantes, Louisville, CO, USA), produced by Avantes, in the wavelength range of 300 to 1000 nm. The spectrophotometer was equipped with an integrating sphere with a diameter of 80 mm and coated with SpectralonTM. The sample was illuminated with a 15 mm diameter light beam and the reflected light signal was collected under an angle of 8° to the normal. As a reference, a white standard made from Spectralon was used. Based on the transmission and reflectance measurements for both polymers, the absorption coefficients were determined, and the band gap values were estimated. The obtained results were compared with the data achieved from ellipsometric measurements.

The ellipsometric method measures changes in the polarization state of light due to its reflection from the sample [23,27]. The ratio ρ between the Fresnel reflection coefficients for p and s polarized light (r_p, r_s) is termed as a fundamental equation of ellipsometry and is given in Equation (6) [28]:

$$\rho = \frac{r_p}{r_s} = \tan \Psi \Delta e^{i\Delta} \quad (6)$$

where Ψ represents the amplitude ratio for the s and p polarization types before and after reflection and Δ represents the phase shift before and after reflection, also for the s and p polarization types. The polarization changes as a result of light reflection from the investigated sample surface. Based on Equation (6), information about the thickness, the spectral dependencies of refractive and extinction coefficients and the band structure of the sample could be found. Ellipsometric measurements were performed using the M2000 spectroscopic ellipsometer (Woollam Co. Inc., Lincoln, NE, USA). The samples were measured for three angles of incidence: 60°, 65° and 70° for a wavelength range of 190 to 1700 nm. During the same experiment, the reflected light intensity and depolarization coefficients were investigated. To analyze the data, all angular spectra were combined, and all data were fitted simultaneously using the CompleteEASE 5.2 software package.

Atomic force microscopy (AFM) imaging was performed by scanning-probe microscope CoreAFM (Nanosurf AG, Liestal, Switzerland) operating in a contact-force mode. A 256 × 256 pixel resolution was used for all AFM topography images. X-ray powder diffraction measurements of the polymer films were performed on the X'Pert Phillips diffractogram using Cu K α radiation source ($\lambda = 1.54178$ Å) for $2\theta = 10^\circ$ – 70° with a step size of 0.01° . The adhesion of the polymer films to the substrate was measured by a scratch test with a nanoscratchtester (CORE Nano-Scratch Tester-Micro Materials, Micro Materials Limited, Wrexham, UK) using a diamond cone indenter.

3. Results and Discussion

The electro-optical properties of thin polymer films are closely related to surface morphology and the fabricated method. Figure 2a,b shows a two- and three-dimensional perspective views of $27 \times 27 \mu\text{m}$ AFM images of P3HT and P3OT polymers films deposited on glass plates. Both polymer films have very comparable surface structures composed of grains of similar size and shape. These films are also characterized by an exceptionally smooth surface with high integrity and strong adhesion to the glass substrates.

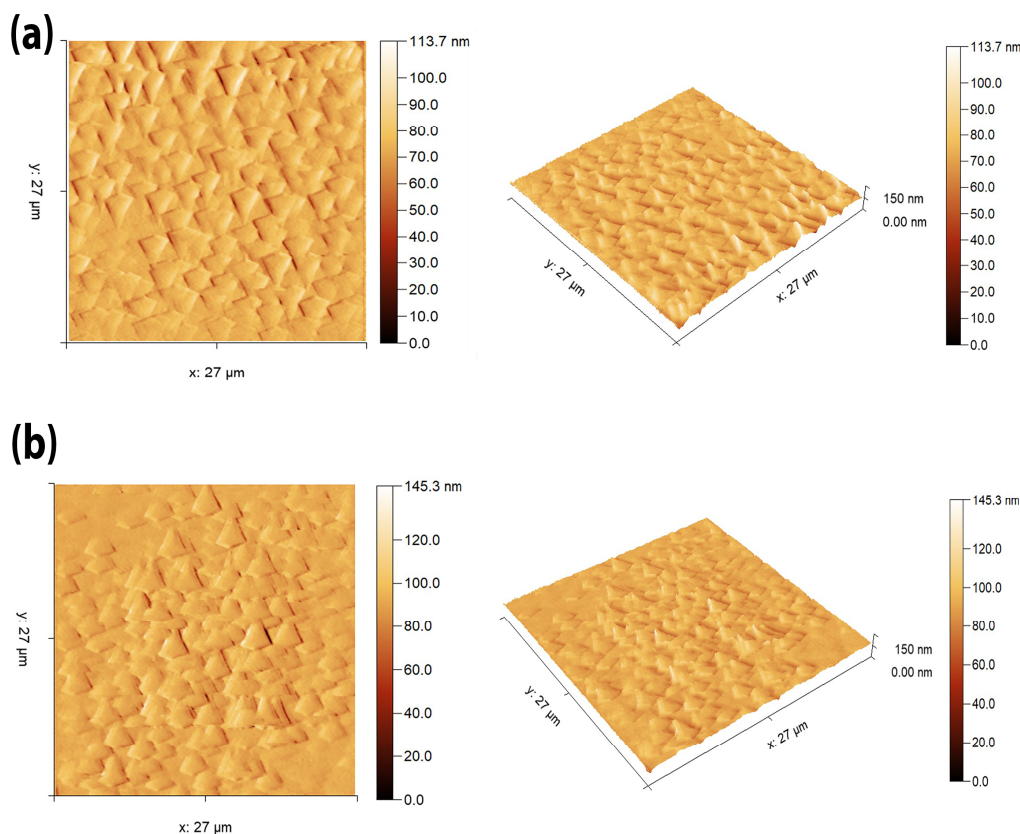


Figure 2. AFM images of (a) P3HT and (b) P3OT samples.

The orientation of the surface structure of both polymer films significantly differ from those obtained by popular fabrication methods such as vapor-phase polymerization and the dip-coating technique. It is characterized by the presence of fine particles with a triangular shape of around $3 \mu\text{m}$. They are all oriented in one direction and are formed as a result of the vortex movement of the glass substrate and gradual evaporation of the organic solvent. The P3OT polymer film was also characterized by small protrusions on the film surface. The mean roughness (S_a) value for the P3HT sample is 5.02 nm and for the polymer films of P3OT, the value of this parameter is 4.65 nm . The X-ray diffraction study of the P3HT and P3OT films presented in Figure 3 excluded the presence of any crystalline phase on the surface of the substrates covered with the tested polymers. In both investigated samples, only the broad peak in the 2θ range of 10° – 40° corresponding to the amorphous substrate glass is clearly visible. There are no diffraction reflections on any diffraction pattern that would indicate the presence of a crystalline phase. Tests of polymer films using a scratch tester allowed them to be scratched with a diamond cone with increasing pressure of the indenter (from 10 to 100 mN). In both cases (P3HT and P3OT), the study confirmed their high adhesion to the substrate. At high pressure (several dozen mN), the cracks in the layers were observed in both tested polymers (they appeared with significant deformation of the material under the indenter). These defects were small, located at

an angle of approximately 45 degrees to the fracture axis. No crumbling or delamination from the substrate was observed with any of the tested polymer films.

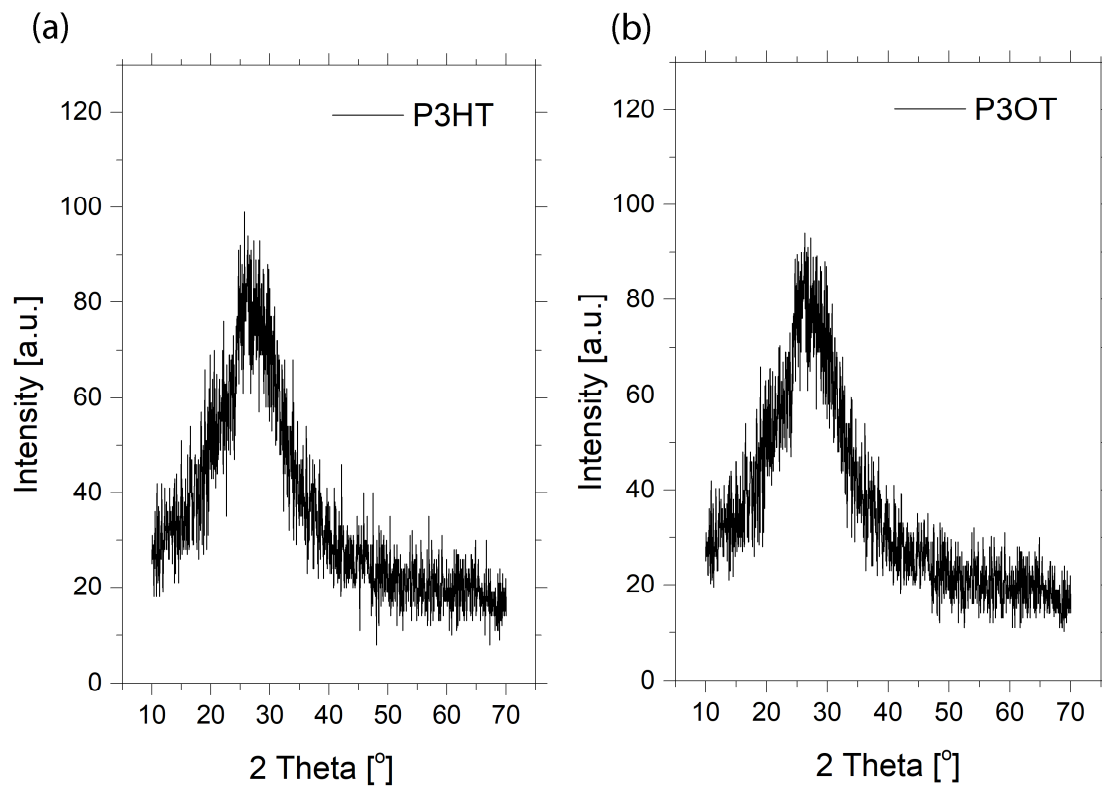


Figure 3. XRD diffraction patterns of the P3HT and P3OT polymers films deposited by a spin-coating method, (a) P3HT; (b) P3OT.

The results of the X-ray powder diffraction studies showed that the tested polythiophene films are completely amorphous, which justifies the choice of TL and CL optical models. These models make it possible to reliably determine the electro-optical properties of polymer films. The spectral characteristics of transmission and the reflectance of P3OT and P3HT films deposited on glass slides were registered by the spectrophotometer. Additionally, transmission spectra were registered by the spectroscopic ellipsometer for the comparison of both methods. Figure 4 presents the transmission and reflectance characteristics for the photon energy range of 1.2 to 3.5 eV. The shapes of the transmittance and reflectance spectra of both studied polymers are similar. However, the transmittance of P3OT is higher than the transmittance of P3HT and simultaneously, P3OT reflectance is lower than P3HT reflectance. This is due to the different absorption coefficients and the thickness of the samples. In the spectrophotometry method, the total transmittance (directional plus diffusion) has been determined. The differences between the transmittance spectra obtained from the ellipsometry and spectrophotometry methods are the result of the fact that in spectrophotometry, only directional transmittance has been measured. The differences between the spectrophotometer and ellipsometer transmittance spectra may be also caused by the fact that it is difficult to take the measurement in exactly the same spot on the sample. However, the overall shape of the spectrum is very similar. Regardless of the measurement method, the spectra designated for polarized light (SE) and non-polarized light (spectrophotometry) are nearly the same.

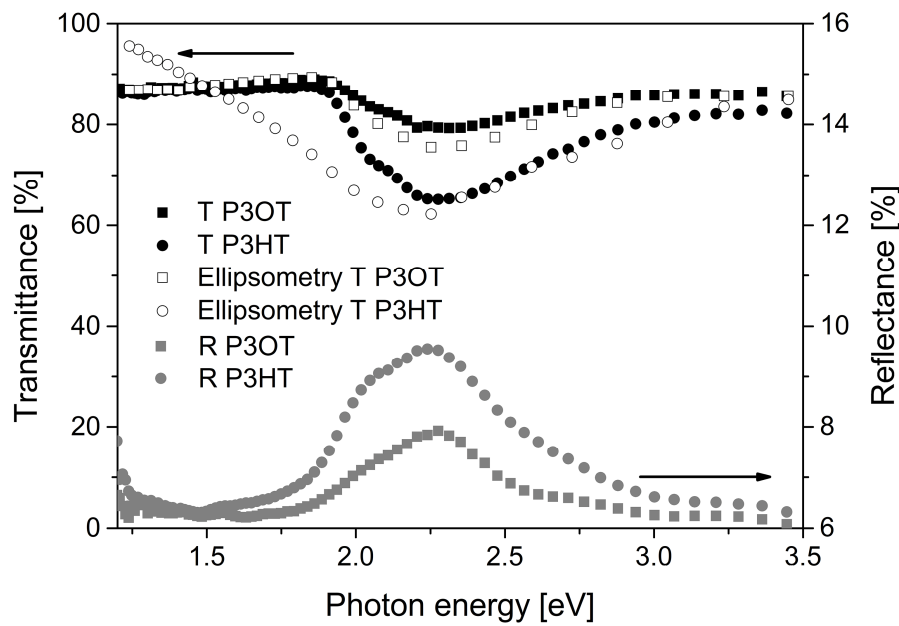


Figure 4. Spectral dependencies of transmission and reflectance of P3HT and P3OT.

Based on the transmission and reflection spectra, the absorption coefficients of the layers were calculated according to Equation (7):

$$\alpha = -\frac{1}{d} \ln\left(\frac{T}{1-R}\right) \quad (7)$$

where d is the film thickness, T is the fraction of incident light transmitted through the film and R is the fraction of incident light reflected by the film. The thickness values of the P3OT and P3HT films were determined by ellipsometric measurements performed for layers deposited on glass slides. The obtained thicknesses amounted to 163.2 nm for P3OT and 135.6 nm for P3HT. The thickness of the layers on the silicon substrate was determined using the Cauchy model fitted to the ellipsometric results in the near-infrared (NIR) region (1.24–0.73 eV). In this range, absorption is not observed. In the applied models (Lorentz, Tauc–Lorentz and Cody–Lorentz), we used a fixed constant value of layer thickness.

The absolute absorption coefficient determined from spectrophotometry for P3HT and P3OT is presented in Figure 5. Absorption determined from ellipsometric data with the use of Lorentz, TC and CL oscillator modelling are also presented in Figure 5.

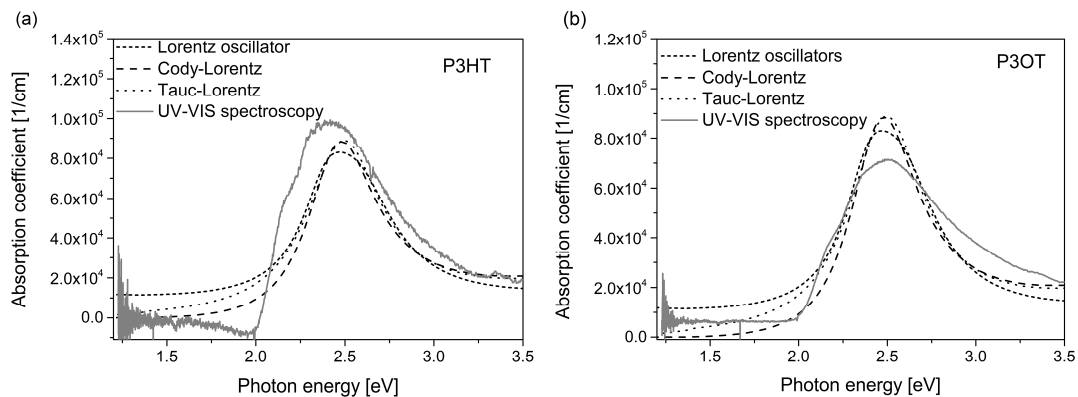


Figure 5. Absolute absorption coefficient determined from spectrophotometry compared with absorption modelled from ellipsometric data (a) P3HT, (b) P3OT.

The shape of the absorption coefficient curves for both polymers are similar, which means that the absorption mechanism is the same, but the value of absorption coefficient for P3HT is higher than for P3OT. This is important because materials with high absorption coefficients are required for application in polymer solar cells. This is due to the fact that the film thickness of the photoactive layer should normally not exceed a few hundred nanometers (typically 100–300 nm). This limitation is determined by the much lower charge carrier mobility. The exciton diffusion length is distinctively shorter in semiconducting polymers compared with inorganic semiconductors [29]. The absorption maximum ($\alpha_{\max}$) of P3HT and P3OT was registered at 2.43 eV (510 nm) and 2.51 eV (494 nm), respectively. The transmittance, reflectance and absorption coefficient spectra obtained in this work are consistent with the results presented elsewhere [30,31].

Ellipsometric measurements were performed for P3HT and P3OT thin films for three angles of incidence: 60°, 65° and 70° in the wavelength range of 190 to 1700 nm. To analyze the data, all angular spectra were combined, and all data were fitted simultaneously. The data were analyzed using CompleteEASE 5.2 software. Psi and Delta values registered for P3HT and P3OT layers deposited on a silicon substrate are shown in Figures 6 and 7. In order to identify the spectral dependencies of refractive indices and extinction coefficients for P3HT and P3OT, optical model fitting was required.

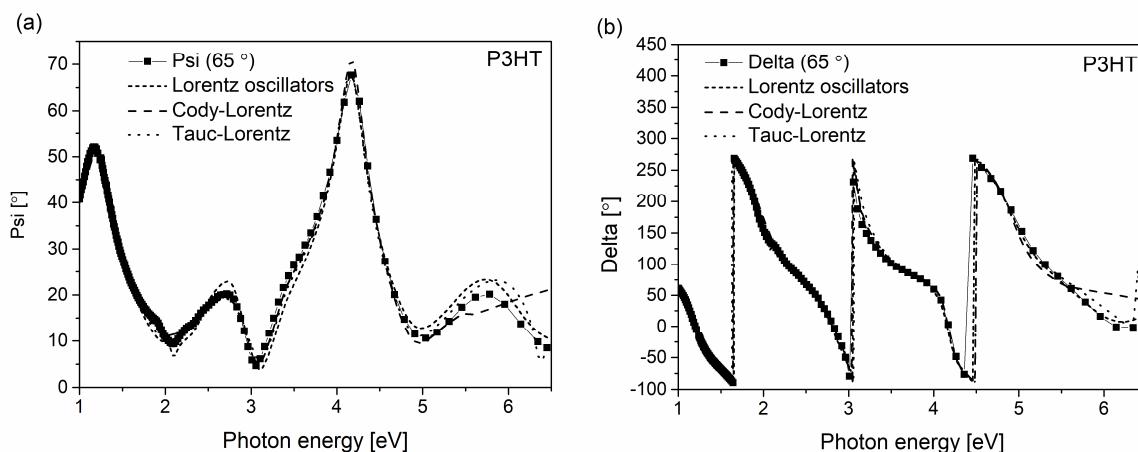


Figure 6. Spectra of P3HT ellipsometric angles (a) Psi, (b) Delta.

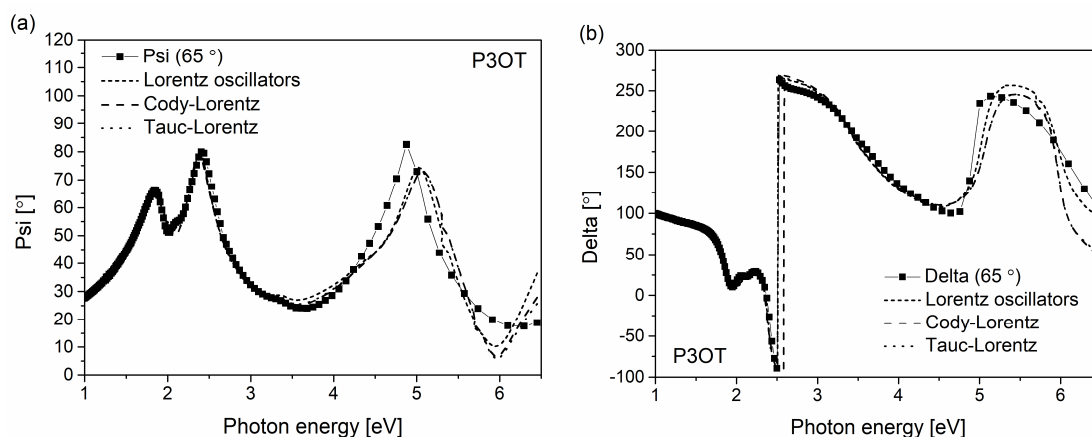


Figure 7. Spectra of P3OT ellipsometric angles (a) Psi, (b) Delta.

For preliminary modelling, the B-spline function was fitted [32,33]. The fitting was performed on the assumption that the refractive index and extinction coefficient are related by the Kramers–Kronig relation to ensure the consistency of the model with experimental data. Next, the experimental data were parametrized using Lorentz oscillators, the TL model and the CL model. The results of the assumed

models are presented in Figures 6 and 7. The most important parameters characterizing applied oscillator models, such as energy gap E_g , amplitude A , broadening parameter B and mean square error (MSE), are presented in Table 1. The CompleteEASE software uses the Levenberg–Marquardt method to minimize the MSE by adjusting the model fit parameters. The values of the A and B parameters for all applied models are similar. The determined values of E_g have been confirmed in other works [30,34].

Table 1. Electronic parameters and mean square error (MSE) values of P3HT and P3OT determined from ellipsometric data with an estimated uncertainty.

Sample	P3HT				P3OT			
Opt. Par.	A	B	E_g	MSE	A	B	E_g	MSE
Lorentz	0.647(56)	0.127(37)	-	25.491	0.883(23)	0.368(39)	-	22.632
Tauc-Lorentz	0.729(12)	0.067(41)	1.91(38)	23.174	0.765(31)	0.667(61)	1.97(73)	22.412
Cody-Lorentz	0.655(39)	0.109(82)	1.87(51)	22.228	0.881(62)	0.775(38)	1.92(42)	20.382

The determination of optical E_g is not possible through the application of Lorentz oscillators. Therefore, to determine common E_g , Cody–Lorentz and Tauc–Lorentz models were applied. The Cody–Lorentz model is more suitable for identifying the absorption of polymer layers because it takes into account the existence of Urbach’s tails below the main energy gap. By using each of these models, we could achieve good fitting in the photon energy range of 1 to 6.5 eV. In the UV range, some discrepancies between the measurement data and the applied models can be noticed. The Lorentz oscillators describe the optical properties of both layers in the UV region in the best way. Below the band gap, the Cody–Lorentz model ensures the best fitting.

The application of three types of models enabled us to determine the spectral dependencies of refractive indices and extinction coefficients. Figures 8 and 9 present the spectral dispersion relations of the refractive index and the extinction coefficient for P3HT and P3OT, respectively. The region of anomalous dispersion of refractive index n occurs between 2 and 2.8 eV. This is the absorption area as confirmed in Figure 5 where the experimental data from a spectrophotometric measurement are presented. In all other areas of the refractive index spectrum, normal dispersion occurs. This relation is observed for both tested polymers.

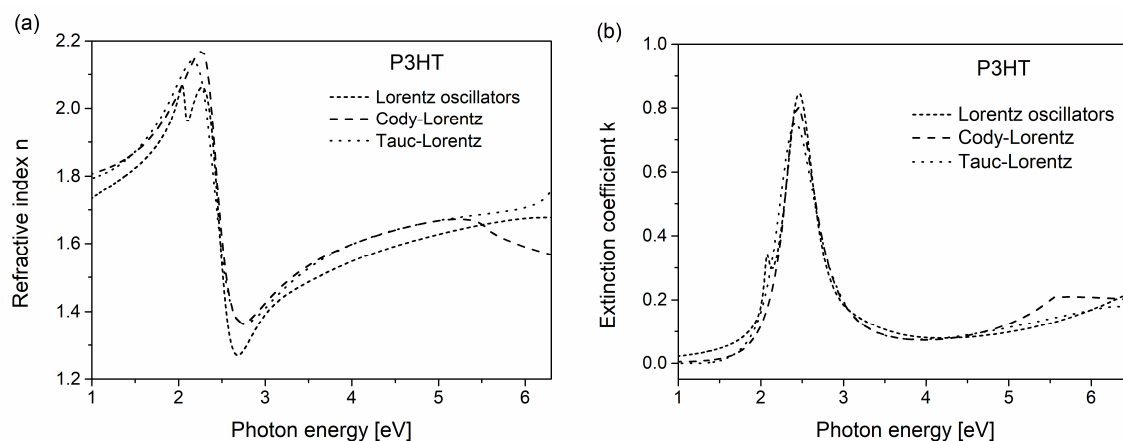


Figure 8. Dispersion relations of optical constant for P3HT (a) refractive index, (b) extinction coefficient.

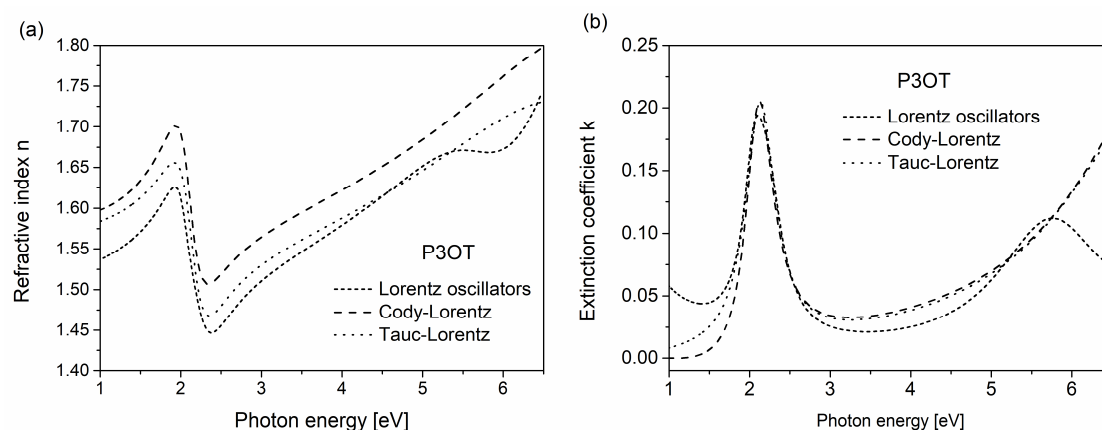


Figure 9. Dispersion relations of optical constant for P3OT (a) refractive index, (b) extinction coefficient.

4. Conclusions

The P3HT and P3OT conductive polymers films deposited on glass substrate by the spin-coating technique showed very comparable surface structures composed of grains of similar size and shape. The films were also characterized by their exceptionally smooth surface with high integrity and strong adhesion to the substrates. The samples also had a relatively low surface porosity. The mean roughness (S_a) value for the P3HT and P3OT samples was 5.02 and 4.65 nm, respectively. X-ray tests confirmed that the polythiophene layers are amorphous, which confirmed the correctness of the choice of the optical models used. In this work, we have presented the experimental results of ellipsometric and spectrophotometric measurements. Selected optical models (Lorentz, Tauc–Lorentz and Cody–Lorentz) have been applied in order to determine thickness, optical parameters such as refractive index and extinction coefficient, absolute absorption and electronic parameters (energy gap E_g , amplitude A and broadening B). All of the applied models gave similar results with regard to fitting optical and electronic parameters. The energy gap E_g values are similar for both the Tauc–Lorentz and Cody–Lorentz models. This means that the values of the obtained parameters are not dependent upon the type of oscillator applied. Spectral absorption determined from spectrophotometric measurement is similar to the absorption spectrum obtained from the ellipsometry method with the application of oscillator models.

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