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Optical anisotropy in thin films of poly(3,4-ethylenedioxythiophene)–poly(4-styrenesulfonate)

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Abstract

Anisotropic optical constants spectrum of spin-coated thin films of poly(3,4-ethylenedioxythiophene)–poly(4-styrenesulfonate) (PEDOT–PSS) from 200 to 1700 nm were determined using variable-angle spectroscopic ellipsometry and polarized intensity transmission data together with absorption spectroscopy. PEDOT–PSS was found to be very anisotropic, uniaxial with the optic axis parallel to the surface normal. The result is in good agreement with results obtained of chemically polymerized PEDOT layers doped with toluenesulfonate. By adding sorbitol to the PEDOT–PSS dispersion before spin-coating, layers with a higher conductivity were obtained. A detailed study was made of the optical response of these layers in comparison to the PEDOT–PSS prepared from dispersions without sorbitol. The optical anisotropy is important to consider when using PEDOT–PSS in optoelectronic devices, such as polymer light-emitting diodes and photovoltaic devices.

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1. Introduction

The conjugated polymer poly(3,4-ethylenedioxythiophene) (PEDOT) is a low band-gap polymer with high charge mobility and good thermal and chemical stability [1]. PEDOT doped with the polymeric counteranion poly(4-styrenesulfonate) (PEDOT–PSS), Fig. 1, has good transparency in the visible spectrum, high conductivity and very good film forming properties. PEDOT–PSS is used as antistatic coatings [2] and has become one of the most important and widely used transparent electrode layers in polymer based and organic electronic devices [3–7]. PEDOT–PSS is often used in both light-emitting devices as hole injecting layer [3] and in photovoltaic devices as hole-collecting layer [4,5] due to the high work function of the material. Much progress has been made in understanding the fundamental physics that controls the properties of these optoelectronic devices even though all aspects still are not fully understood. Consequently, modeling of the device properties is a vital part of obtaining the fundamental understanding and to improve the device performance [8]. In this perspective detailed knowledge and

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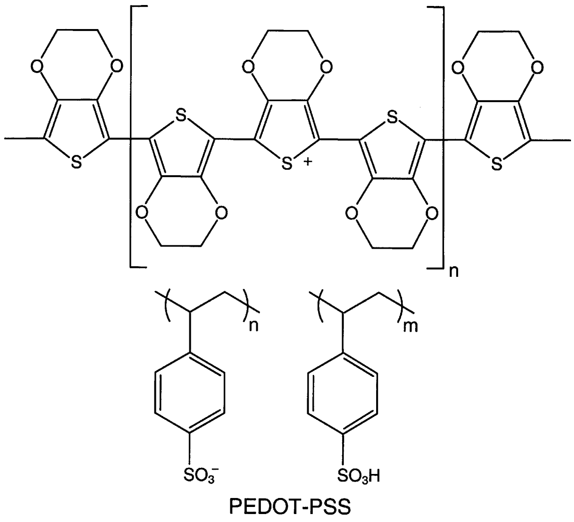

Fig. 1. The chemical structure of PEDOT–PSS.

analysis of optical properties and structure/morphology of the materials inside the devices is of paramount interest. When modeling organic optoelectronic devices, the optical properties of the layers have typically been considered to be isotropic, which however in general is not the case. For thin films of conjugated polymer molecules the macroscopic optical response is not only dependent of the intrinsic electronic structure of the chain but also on inter-molecular interaction determined by their relative orientation and position. Spin-coated thin films of conjugated polymers have previously been shown to be uniaxial anisotropic with the optic axis parallel to the surface normal of the film [9–12]. The anisotropy was considered to attribute from a preferential orientation of the conjugated polymer with the chains primarily in the surface plane. For such layers (Fig. 2), the linear optical response is described by the principal indices of refraction, the ordinary complex index of refraction (||, parallel to the surface plane of the film; $\tilde{n}_{\|} = n_{\|} + \mathrm{i}k_{\|}$) and the extraordinary complex index of refraction ($\perp$, perpendicular to the surface plane of the film; $\tilde{n}_{\perp} = n_{\perp} + \mathrm{i}k_{\perp}$). n_i is the refractive index and k_i is the extinction coefficient ($i = \|, \perp$), respectively. The absorption coefficient α_i is related to the extinction coefficient through $\alpha_i = 4\pi k_i/\lambda$ (λ; wavelength of the light). One of the few techniques to address both optical properties and morphology of thin films is variable-angle spectroscopic ellipsometry (VASE). VASE in reflection is based on measuring the change in polarization of polarized light reflected from a sample at oblique incidence [13]. The actual sample characteristics is then coupled to the measured VASE data through an optical model in which parameters, describing the thin film morphology, film thickness, and complex index of refraction of the sample for each wavelength is fitted to the experimental data in a nonlinear regression data analysis [14].

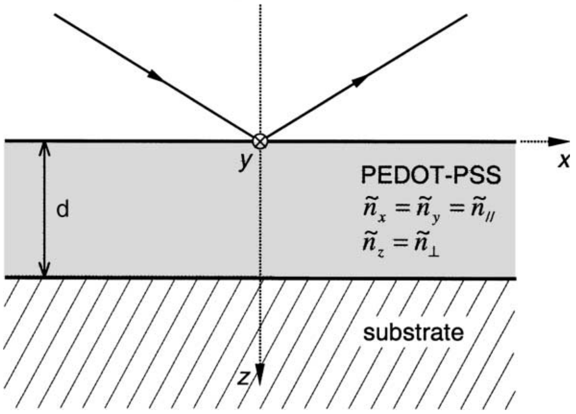

Fig. 2. Schematic figure showing a uniaxial anisotropic thin film of PEDOT–PSS with the optic axis parallel to the z-axis on a substrate. The xz plane is the plane of incidence. The optical response is described by an ordinary complex index of refraction parallel to the surface plane (xy plane) as given by $\tilde{n}_x = \tilde{n}_y = \tilde{n}_{\|} = n_{\|} + \mathrm{i}k_{\|}$ and an extraordinary complex index of refraction and perpendicular to the surface plane as $\tilde{n}_z = \tilde{n}_{\perp} = n_{\perp} + \mathrm{i}k_{\perp}$.

We have previously reported optical and structural studies of thin films of PEDOT doped with the small anion toluenesulfonate prepared by chemical polymerization [10,15]. In the chemical polymerization route thin films are prepared from spin-coating solutions of the monomer (EDOT) on a substrate to be polymerized [16]. In these layers we obtained an electrical conductivity up to 500 S/cm [17]. Chemically prepared PEDOT doped with toluenesulfonate were found to be very anisotropic and in a paracrystalline state. However, in the case of PEDOT–PSS the situation is expected to be different. The conjugated polymer is doped with a large polymeric anion and the thin films are spin-coated from an aqueous dispersion of PEDOT–PSS. In these layers, typical conductivity at room temperature of 0.1–10 S/cm is obtained [18]. By adding polyols such as glycerol or sorbitol to the dispersion before spin-coating, followed by heat treatment of the film, an increase in conductivity of about two orders of magnitude is possible to obtain [17].

Even though PEDOT–PSS has been used in many optoelectronic applications there have been no systematic investigation of its optical dielectric response. In this work, the main objective is the study of the linear optical response in terms of the anisotropic optical constants spectrum of spin-coated thin films of PEDOT–PSS. The complex indices of refraction were determined by analysis of VASE data and polarized intensity transmission data together with absorption spectroscopy.

2. Experimental details

Thin films of PEDOT–PSS were prepared from an aqueous dispersion (Baytron P) obtained from Bayer AG (Germany). In the PEDOT–PSS the polymeric counteranion PSS is in excess with respect to the positively charged PEDOT chain with a molar ratio of the monomer units of PEDOT and PSS of 0.8. For sample preparation the PEDOT–PSS dispersion was filtered using a one micrometer pore size borosilicate glass fiber filter (Gelman Sciences) to remove larger particles. Thin films of PEDOT–PSS were spin-coated onto silicon substrates with various thickness of the silicon oxide (from native to 100 nm) and on fused silica substrates. After spin-coating, the samples were heated to 120 °C during 2 min in order to increase the conductivity and remove any water in the layer. Using spinner speeds in the range from 1500 to 4000 rpm resulted in layers of a thickness from 180 to 84 nm as obtained from the ellipsometry data analysis and complementary thickness measurements with a Sloan Dektak 3030 profilometer for comparison. The electrical DC conductivity of the films was acquired by using four-point probe measurements at room temperature. The measured electrical conductivity in the surface plane of the films was 0.94 S/cm.

PEDOT–PSS films with a higher electrical conductivity were also prepared from the aqueous dispersion containing 65% sorbitol by weight to PEDOT–PSS solid. The spin-coated layers were heated to 175 °C during 1 min resulting in an electrical conductivity of 56 S/cm, i.e., about sixty times higher conductivity as compared to the as-bought PEDOT–PSS dispersion. The material of PEDOT–PSS prepared from the dispersion with sorbitol will be denoted PEDOT–PSS-(s) for clarity.

Ellipsometry data and polarized intensity transmission data for analysis were acquired from 200 to 1700 nm (by 5 nm) using a J.A. Woollam Co. VASE® instrument. This rotating analyzer system was equipped with an autoretarder input unit. For all samples VASE data were acquired at multiple angles of incidence in the range from 55° to 85° and polarized intensity transmission data were acquired at normal incidence. The procedure for analysis of VASE data and polarized transmission data of uniaxial anisotropic polymer thin films is described elsewhere [9,10].

Transmittance spectra of thin films of PEDOT–PSS spin-coated onto quartz-glass substrates were recorded with a Perkin–Elmer Lambda-9 UV/VIS/NIR spectrophotometer in the spectral range from 185 to 3200 nm.

3. Experimental results and discussion

By measuring the transmittance at normal incidence of linearly polarized light for a number of different polarizer azimuths the PEDOT–PSS layers were found to be symmetric with respect to rotation about the surface normal. Thus, absorbance data at normal incidence of thin films of PEDOT–PSS and PEDOT–PSS-(s) of equal thickness (110 nm) in Fig. 3 represents the absorbance for the ordinary component of the light, i.e., parallel (||) to the surface plane (*xy* plane). It should be pointed out that using equal spinner speeds does not result in equal thickness for PEDOT–PSS and PEDOT–PSS-(s) due to difference in viscosity of the two aqueous systems. In the inset of Fig. 3 the absorbance of the PEDOT–PSS layer and a layer of PSS is shown. The absorbance

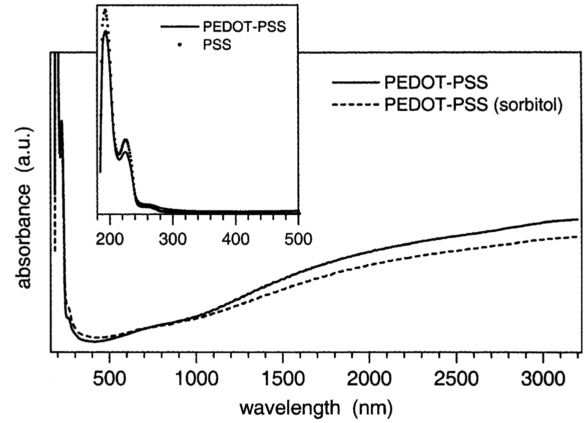

Fig. 3. Absorbance at normal incidence of thin films of PEDOT–PSS and a PEDOT–PSS (sorbitol) of equal thickness (110 nm) in the spectral range from 185 to 3200 nm. In the inset, absorbance of PEDOT–PSS and PSS in the spectral range from 185 to 500 nm.

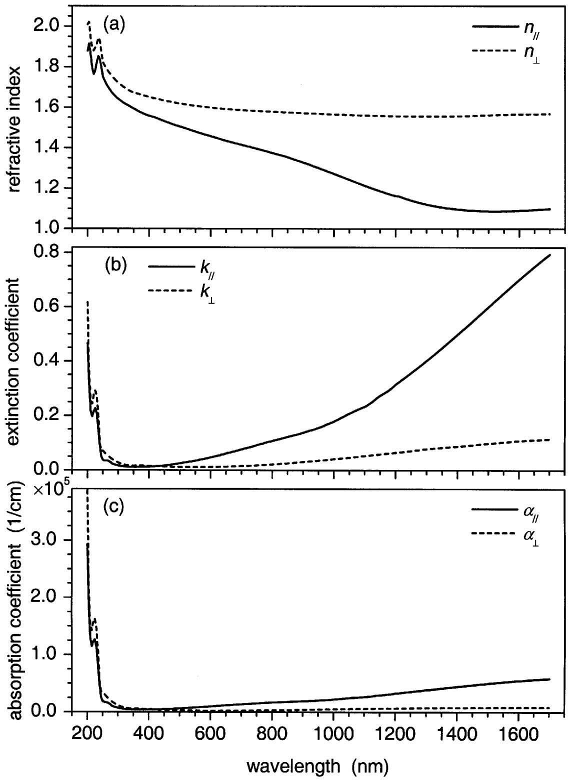

Fig. 4. Uniaxial anisotropic complex indices of refraction $\tilde{n}_i = n_i + ik_i$, $(i = \|, \perp)$ and the absorption coefficient $\alpha_i = 4\pi k_i/\lambda$ parallel (ordinary) and perpendicular (extraordinary) to the surface plane of thin films of PEDOT–PSS in the spectral range 200–1700 nm. (a) The refractive index, (b) the extinction coefficient and (c) the absorption coefficient.

spectra consist of a broad feature above 400 nm increasing all the way up to 3200 nm, which can be interpreted as a free charge contribution to the absorption. However, an alternative interpretation to this long wavelength absorption is that the broad feature is associated with mid-gap states (polaron or bipolaron states). At shorter wavelengths there are two pronounced absorbance peaks at 193 and 225 nm and a broader shoulder at slightly longer wavelengths (250–280 nm), which can be attributed to the π–π* transitions of the benzene rings of PSS as seen in the inset of Fig. 3. Moreover, the absorbance for the more conductive PEDOT–PSS-(s) is lower above 720 nm.

The first order assumption in the VASE data analysis was that the PEDOT–PSS layers were isotropic and for that reason an isotropic model was applied. However, this model was not possible to fit the experimental data. Therefore, in order to relate the measured VASE data to the actual sample characteristics a multi-layer model was employed including a uniaxial anisotropic layer with the optic axis parallel to the surface normal for the PEDOT–PSS. In Fig. 4 anisotropic complex indices of refraction parallel ($\|$, ordinary) and perpendicular ($\perp$, extraordinary) to the surface plane of PEDOT–PSS in the spectral range 200–1700 nm are shown as obtained in multiple sample analysis of the VASE data [9,10]. In addition to the complex indices the absorption coefficients are also shown for PEDOT–PSS. There is a strong anisotropy with a much higher extinction coefficient and thereby absorption in the surface plane compared to perpendicular to it. The higher extinction coefficient is also accompanied by a lower refractive index over the whole spectrum. At shorter wavelengths the contribution from the PSS in form of the peak at 225 nm and the broader shoulder is also seen. As indicated by the higher absorption and the symmetry with respect to rotation about the surface normal, the main part of the polymer chains have their backbone randomly oriented but parallel to the surface plane. This orientation of the polymer chain along the film surface may be caused by the high rate of spinning of the viscous solutions PEDOT–PSS. This result is in good agreement with the optical and structural studies of the chemically polymerized PEDOT doped with toluenesulfonate [10,15]. Errors of the determined optical parameters were at every wavelength estimated from experimental uncertainties and 90% confidence limits that were obtained in the analysis of ellipsometry data. Errors in refractive index and extinction coefficient parallel to the surface plane were less than 0.002 below 900 nm and between 0.002 and 0.03 in the range from 900 to 1700 nm. In the case of refractive index and extinction coefficient perpendicular to the surface plane the errors were less than 0.005 below 500 nm, between 0.005 and 0.01 in the range from 500 to 1000 nm, and between 0.01 and 0.02 from 1000 to 1700 nm. In both cases estimated errors were largest at the longest wavelengths.

By adding sorbitol to the dispersion, sixty times higher conductivity was obtained in the PEDOT–PSS-(s) layers, as mentioned in the experimental section. Analysis of VASE data measured of PEDOT–PSS-(s) was performed, in order to study the increased conductivity and its influence on the optical response. In Fig. 5, the extinction coefficients for PEDOT–PSS and PEDOT–PSS-(s) are shown. A higher conductivity is expected to be accompanying an increase in the extinction coefficient. However, this is not the case as seen in the surface plane absorption of thin films of PEDOT–PSS and PEDOT–PSS-(s) in Fig. 1 and in the optical functions as obtained from data analysis of VASE in Fig. 5. The extinction coefficient parallel to the surface plane is 15–20% larger (above 1000 nm) for the thin films of PEDOT–PSS prepared without sorbitol as compared to those prepared with sorbitol. An explanation to the decrease of the extinction coefficient with increase of the conductivity could be that the long wavelength absorbance is the result of mid-gap states. In this case, the higher conductivity but lower absorbance for PEDOT–PSS-(s) in comparison to the PEDOT–PSS is associated with a red shift of the absorbance maximum.

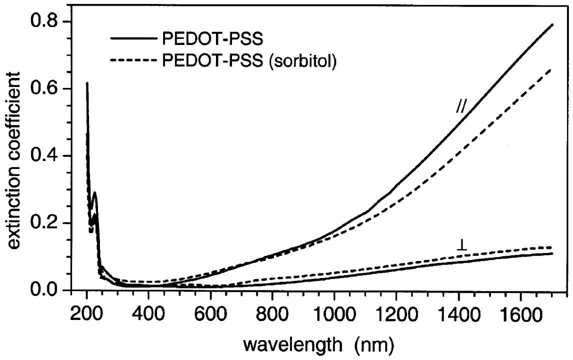

Fig. 5. Extinction coefficients for thin films of PEDOT–PSS and PEDOT–PSS-(s).

The decrease in anisotropy of the PEDOT–PSS-(s) films after the heat treatment, reveals orientational relaxation of the polymer chains. Sorbitol seems to interact strongly with the PEDOT–PSS through hydrogen bonding with the bridging oxygen atoms of the PEDOT monomer unit or with the sulphonate group of PSS. This allows the sorbitol to act as a plasticiser, decreasing the interchain interactions in the PEDOT–PSS-(s) film and hence, the activation barrier for the reorientation of the polymer chains. On heating, therefore, the orientational relaxation occurs more readily in the sorbitol containing film. The accompanied increase in the conductivity seems paradoxical, but may be explained considering the fact that the chemically prepared PEDOT-tosylate films show anisotropy and paracrystallinity. That is, in absence of activation barrier, there is local order in PEDOT system, indicating inter-chain interactions. On heating the sorbitol containing films, the PEDOT–PSS chains may reorient with more favorable inter-chain interaction between the PEDOT units, which in turn decreases the activation energy for charge transfer, increasing the conductivity. Indeed, this explanation is supported by observation that the heat-treated PEDOT–PSS-(s) films become insoluble in water and adheres more strongly with the substrate, than the PEDOT–PSS films, showing the formation of the physical cross-linking.

VASE data from thin films prepared from the PEDOT–PSS-(s) were also acquired before and after heat treatment. Thickness decreases of 63–68% were obtained for all thin films in the data analysis, values that are in good agreement to the weight fraction of sorbitol to PEDOT–PSS (65%) in the dispersion. Thus, the sorbitol is removed from the thin films in the heat treatment. The high conductivity of the material cannot solely be explained by conduction along the chain, also a large inter-chain conduction must be present. Structural studies of the chemically polymerized PEDOT doped with toluenesulfonate showed that there was a very short inter-chain distance (3.4 Å) compared to other poly(thiophene) systems [15]. The short inter-chain distance is presumably related to a high inter-chain conductivity. In the case of preparing PEDOT–PSS from dispersions containing sorbitol, the higher conductivity could be the result of giving the PEDOT molecules more time to get into a more favorable position.

We wish to point out that the extracted indices of refraction are the macroscopic optical response of the material, which correspond to the macroscopic average orientation of the PEDOT molecules.

4. Summary and conclusions

In summary, thin films of PEDOT–PSS were found to be uniaxial anisotropic with the optic axis parallel to the surface normal. The absorption coefficient in the surface plane is much higher than perpendicular to the surface plane indicating that the main part of the PEDOT polymer chains have their backbone randomly oriented but parallel to the surface plane. This anisotropy was the same as previously obtained from thin films of chemically polymerized PEDOT. The process of spin-coating of the films presumably causes the anisotropy.

Thin films of PEDOT–PSS with a higher conductivity were obtained by adding sorbitol to the PEDOT–PSS dispersion before spin-coating and then heat treating the polymer film. This is also accompanied by a decrease in the anisotropy in the polymeric material. This is explained by plasticisation of the PEDOT–PSS-(s) films by sorbitol, which enables reorientation of the polymers chains to more macroscopically random state but which allows more inter-chain interaction between the conducting polymers.

Also, the optical anisotropy is an important aspect to consider when using PEDOT–PSS layers in polymer light-emitting devices and photovoltaic devices.

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