

# On the determination of anisotropy in polymer thin films: A comparative study of optical techniques

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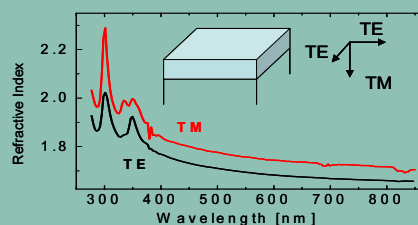
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We have used seven different techniques to measure the anisotropic refractive index of poly(vinylcarbazole) films. These techniques are: two types of variable angle spectroscopic ellipsometry (VASE) with multiple sample analysis, Interference enhanced VASE, Transmittance combined with VASE, Polarised Reflectance, beta-scan VASE, and prism coupling. We have found the average ordinary and extraordinary indices at 633 nm to be  $n_o = n_{TE} = 1.675 \pm 0.008$ , and  $n_e = n_{TM} = 1.722 \pm 0.018$ , respectively, consistent amongst methods and conclusive on the magnitude of  $\Delta n$  in polymer films.



Average refractive indices for PVK from three techniques.

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**1 Introduction** Optical anisotropy ( $\Delta n = |n_o - n_e| = |n_{TE} - n_{TM}|$ ) in cast polymeric thin films arises from a preferential alignment of the macromolecules parallel to the substrate where they are deposited [1-3]. Films are then uniaxial, with the optic axis perpendicular to the plane of the substrate. The existence of this birefringence has strong effects on the optical and electronic properties of devices based on polymer thin films. Applications such as organic light emitting diodes (OLEDs), organic field effect transistors (OFETs) or organic solar cells would all benefit from a better understanding of molecular alignment, which, on the other hand, starts by the determination of the optical anisotropy. However, there are a wide number of discrepan-

cies in the actual values assigned to the anisotropy of this kind of films. In the case of films made of light emitting MEH-PPV, for instance,  $\Delta n(520 \text{ nm})$  values ranging from 0.008 to 0.7 have been reported [4, 5]. In order to decorrelate differences derived from fabrication-related issues and differences in the techniques employed to extract  $\Delta n$ , we have established an international collaboration among six European institutions to address the determination of  $\Delta n$ . We have chosen poly(vinylcarbazole) (PVK) as a model material system since systematic studies of the anisotropy in this material are available [2] and serve as a reference. Since the dipole moment lays perpendicular to the chain axis,  $n_e > n_o$  for PVK films [2].

First, the fabrication of thin PVK films was optimized in order to obtain reproducible properties in terms of thickness, surface roughness, film quality and lateral homogeneity. Then, a series of samples were fabricated in one lab (Mainz) and shipped to the different partners to investigate them using seven different techniques (or variations/combination of more basic techniques). These techniques include: polarized reflectance and transmittance, prism coupling waveguide technique, variable angle spectroscopic ellipsometry (VASE) with multiple sample analysis (either different polymer thicknesses or different SiO<sub>2</sub>/Si substrates), combined reflection ellipsometry and transmittance, beta-scan ellipsometry and Interference Enhancement VASE (IEVASE). Here we show our preliminary results which indicate that these techniques lead to consistent results within the accuracy of the experiments for the ordinary index ( $\sim 0.008$  in  $n$ ), while the standard deviation is greater for the extraordinary index ( $\sim 0.02$ ) for most techniques. This suggests, however, that an important part of the inconsistencies found in the literature regarding the magnitude of  $\Delta n$  is related to different fabrication conditions, e.g. different material suppliers, processing factors, lack of sample reproducibility, etc.

## 2 Experimental

**2.1 Sample fabrication** Poly(N-vinylcarbazole) (PVK) was purchased from Aldrich Chem. ( $M_w = 1,100,000$ ,  $T_g = 200$  °C) and used as received. Thin films were prepared by spin coating from freshly prepared and filtered (0.5 or 1  $\mu\text{m}$  syringe filters) chlorobenzene solutions at ambient atmosphere under a laminar flow hood to minimize dust particles as described in detail recently [4, 6]. We used freshly cleaned fused silica substrates for the UV/Vis/NIR range and silicon wafers with typical substrate sizes of 25 x 35 x 1 mm<sup>3</sup>. We varied concentration by weight and spinning speed to control the film thickness.

The films were placed subsequently in a vacuum oven at  $T = 50$  °C for about 6 hours to remove residual solvent. The thickness  $d$  and the average surface roughness of the films were measured with a Tencor Model P10 profilometer. In order to increase the precision, we have measured the film thickness for each film at several step profiles (typically 8) in the region where the optical experiments were performed and used the average value of these measurements. We have used films with thickness  $d = 40, 65$  and 90 nm for spectroscopic studies and thicker films (1000 nm) for optical waveguides.

**2.2 Techniques to extract optical constants** We have used seven different techniques to characterise the optical anisotropy of PVK. Here we briefly describe them and provide a set of references for full details. All experiments were performed in air at room temperature.

Transmission and reflection (TR) spectra of thin films on fused silica substrates were measured with a spectrophotometer (Perkin Elmer Model Lambda 900). Intrinsic absorption coefficients  $\alpha$  were evaluated from transmission

spectra after correction of reflection losses at film/air- and film/substrate-interfaces as described in earlier works [6, 7]. The spectra of  $n_o = n_{TE}(\lambda)$  were obtained by reflectometry at nearly perpendicular incidence and were evaluated by means of Fresnel's equations [6, 7].

The refractive indices of PVK waveguides (i.e. thick 1000 nm films) for both TE and TM polarizations were determined by prism coupling (PC) using the m-line technique [8] as described earlier [9]. We were able to excite 3 modes at both polarizations at 633 nm and 488 nm laser wavelengths and use these modes to evaluate  $n_{TE}$  and  $n_{TM}$  with high precision.

For Multiple Sample Analysis with Different Polymer thickness (MSA-DPT), ellipsometric data were obtained by means of a J. A. Woollam rotating analyser ellipsometer (RAE) in spectral region from 1.2 to 5.0 eV in steps of 0.02 eV. The spectral resolution was 3 nm (0.01 eV at 2.0 eV). The measurements were performed at several angles of incidence in the range of 60-75 deg. Three samples with slightly different thicknesses were analysed simultaneously [10]. The fitted anisotropic function was then equalised to the dielectric function ( $\epsilon$ ) of the sample with the mean thickness. It is assumed then that the obtained  $\epsilon$  corresponds to the "mean"  $\epsilon$  of the samples.

The  $\beta$ -scan method (BSM) and VASE was also used to obtain the anisotropy of thin PVK films. The ellipsometric data were taken at different azimuth Euler angle  $\beta$  values and/or different (fixed) analyser settings [11] using a SOPRA rotating polariser ellipsometer. A generalised complex reflectance ratio  $\rho$  is used which is related to the experimental  $\tan\Psi$  and  $\cos\Delta$  as well as extrinsic experimental setup parameters. Intrinsic sample properties such as the components of the dielectric tensor of the material and orientation of principal axes can then be deduced.

Interference enhancement VASE (IEVASE) [5] was carried out using a SOPRA rotating polariser ellipsometer, at a minimum of three incidence angles over a 250-850 nm spectral range. The polymer films for this technique were deposited on a Si substrate covered with a thick (1 micron) SiO<sub>2</sub> layer, which allows for an interference pattern to be observed in the ellipsometric angles. This helps to decouple the fitting parameters of the anisotropic optical constants of the polymer film [5]. The data were analysed using the Standard Critical Point (excitonic) model for  $\epsilon$  [12].

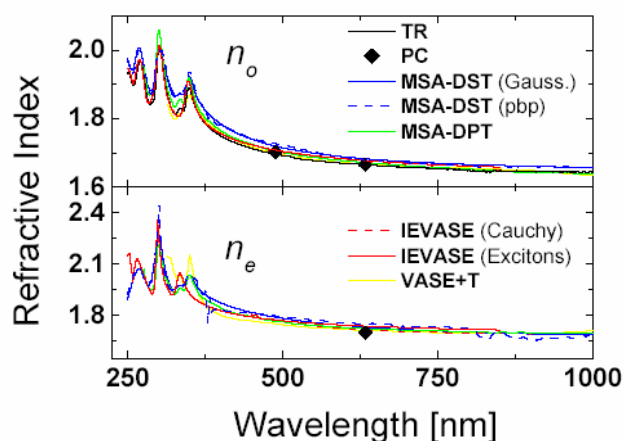
For Multiple Sample Analysis with Different SiO<sub>2</sub> thickness (MSA-DST), VASE was collected using a J. A. Woollam ellipsometer. The data for three samples with a fixed polymer thickness and varying SiO<sub>2</sub> layer thickness were analysed simultaneously. A Cauchy law in the transparent region was first used to obtain the polymer thickness. This was then used for a point by point calculation. Parametric fitting of the data was also performed using Gaussian lineshapes.

Finally, ellipsometry and transmittance data (VASE+T) for PVK samples were also measured and the data analysed simultaneously [13]. The VASE spectra

were collected at 5 nm steps in this case. Point by point analysis was used.

**3 Results and discussion** Figure 1 (top panel) shows the ordinary (in-plane) refractive index ( $n_o$ ) of PVK deduced using six different techniques and eight types of analysis (note that the experiments were performed in six different samples prepared in the same lab).

As it can be seen, the agreement between the different techniques and types of analysis is relatively good. Table 1 summarises the values of  $n_o$  at 633 nm for an easier comparison. At this wavelength, we obtain an average value  $1.675 \pm 0.008$ . The values derived from the different techniques lay within the error bars of the average, which are typical experimental errors in ellipsometry (0.008). These results are also in agreement with previous systematic studies by Prest and Luca [2] on the same material.



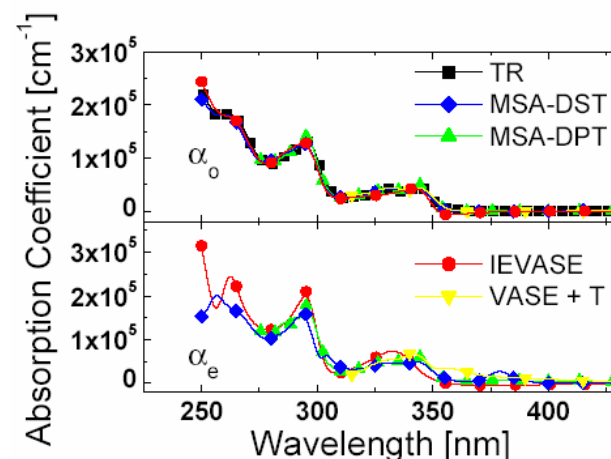
**Figure 1** Ordinary (top panel) and extraordinary (bottom panel) refractive indices for PVK films deduced using 6 techniques and 8 types of analysis as described in the text.

Given the good agreement between the ordinary indices obtained for thick films (1000 nm thick) using the prism coupling method, and those for the other spectroscopic techniques (40–90 nm thick) we can conclude that over these range of thicknesses, the optical constants of PVK do not strongly depend on the film thickness for this molecular weight [4, 10].

The agreement between the different techniques is certainly lower for the extraordinary (out-of-plane) index (see bottom panel in Fig. 1, and Table 1). An average value of  $n_e = 1.722 \pm 0.018$  was obtained, with the standard deviation being twice as large as the ordinary case. This points out the difficulty of measuring the out of plane optical constants in thin films, which was, in the first place, the reason why we have chosen modifications of the more conventional VASE experiment [5, 10, 13].

Interestingly, there are also substantial differences in the refractive index deduced from the same experimental data but using different types of analysis. The analysis of

the MSA-DST experiments using a point by point calculation yields relatively (non-physically) noisy optical constants, since the experimental noise directly transforms in abrupt variations in  $n_o$  and  $n_e$ . The same experimental data fitted with a parametric model (collection of Gaussian oscillators) resulted in much smoother curves, and values typically closer to what was obtained with other techniques. Another example is the modelling of the IEVASE data using exciton lineshapes [12] for the full spectra or just a simple Cauchy law to account for the transparent region. As it can be seen in Table 1, the values obtained with these two fits are quite different (especially for the extraordinary index). It is worth noting that exciton lineshapes (i.e. asymmetric Lorentzian) have been found to yield the smallest standard deviations during the fitting of ellipsometric data of glassy conjugated polymers [12, 14]. This type of lineshape is also the most appropriate since it properly describes the localised nature of the electronic excitations as well as phenomenologically accounting for the electron-phonon coupling. Additional sources of deviations in the deduced values might be small differences in the optical constants used for the substrates (quartz, Si, and SiO<sub>2</sub>). A more detailed analysis is being carried out to address this issue.



**Figure 2** Ordinary (top panel) and extraordinary (bottom panel) extinction coefficients for PVK films deduced using 5 techniques as described in the text.

Figure 2 shows the deduced ordinary and extraordinary absorption coefficients, respectively. Similarly to the case of the refractive index, the agreement is much better for the ordinary than for the extraordinary case. In particular, fitting artefacts can be seen for the extraordinary index for wavelengths greater than the absorption edge in two cases (point by point analysis). Table 1 summarises the absorption maximum for the lower energy peak (around 344 nm). The average values of the different techniques are very representative of the degree of agreement:  $\alpha_o(344 \text{ nm}) = 46000 \pm 3000 \text{ cm}^{-1}$  and  $\alpha_e(344 \text{ nm}) = 62000 \pm 10000 \text{ cm}^{-1}$ .

**Table 1** Summary of results.

Group	Technique	$n_o(633 \text{ nm})$	$n_e(633 \text{ nm})$	$\alpha_o(344 \text{ nm}) [\text{cm}^{-1}]$	$\alpha_e(344 \text{ nm}) [\text{cm}^{-1}]$
Ilmenau	MSA, different polymer thicknesses	$1.672 \pm 0.010$	$1.724 \pm 0.050$	$49600 \pm 1500$	$59600 \pm 5000$
Mainz	Reflectance on thin (<50 nm films)	$1.666 \pm 0.01$	N.A.	$46000 \pm 500$	N.A.
Mainz	Prism coupling waveguide technique on thick films ( $\sim \mu\text{m}$ )	$1.6658 \pm 0.0006$	$1.7003 \pm 0.0010$	N.A.	N.A.
London	IEVASE, film on a Si/SiO <sub>2</sub> ( $\mu\text{m}$ thick) Exciton lineshape analysis	$1.678 \pm 0.009$	$1.738 \pm 0.015$	$43600 \pm 2000$	$73800 \pm 5000$
London	IEVASE, film on a Si/SiO <sub>2</sub> ( $\mu\text{m}$ thick) Cauchy analysis	$1.6733 \pm 0.007$	$1.7181 \pm 0.009$	N.A.	N.A.
Barcelona	VASE with different azimuth angles for the sample	$1.688 \pm 0.006$	$1.702 \pm 0.005$	--	--
Linköping	VASE in reflection coupled to transmittance	$1.666 \pm 0.005$	$1.714 \pm 0.005$	$48000 \pm 2000$	$65000 \pm 5000$
Durham	MSA, 3 different SiO <sub>2</sub> thicknesses for each polymer thickness (point by point analysis)	$1.681 \pm 0.017$	$1.752 \pm 0.018$	$43500 \pm 800$	$50400 \pm 800$
Durham	MSA, 3 different SiO <sub>2</sub> thicknesses for each polymer thickness (Gaussian lineshape analysis)	$1.682 \pm 0.020$	$1.730 \pm 0.020$	--	--
Average		$1.675 \pm 0.008$	$1.722 \pm 0.018$	$46000 \pm 3000$	$62000 \pm 10000$

**4 Conclusion** In this contribution we have presented the anisotropic refractive index of poly(vinylcarbazole) films deduced from seven different techniques and with several types of analysis. These techniques are: two types of VASE with multiple sample analysis, Interference enhanced VASE, Transmittance combined with VASE, Polarised Reflectance and Transmittance, beta-scan method, and prism coupling waveguiding. We found average ordinary and extraordinary indices at 633 nm equal to  $n_o = 1.675 \pm 0.008$ , and  $n_e = 1.722 \pm 0.018$ , respectively. The average absorption coefficients at the 344 nm peak were calculated to be  $\alpha_o(344 \text{ nm}) = 46000 \pm 3000 \text{ cm}^{-1}$  and  $\alpha_e(344 \text{ nm}) = 62000 \pm 10000 \text{ cm}^{-1}$ . The derived optical constants for the out-of-plane direction are less consistent for the different techniques than the in-plane, as the standard deviations indicate. The observed deviations are, however, much smaller than the discrepancies found in the literature for polymer films, suggesting that material synthesis and sample fabrication are central sources of inconsistencies.

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