

Optical absorbance of oriented thin films

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Abstract

We report that the optical absorbance of oriented thin films of *para*-hexaphenyl (PHP), produced by vacuum deposition, shows strong anisotropy effects. An explanation for the orientation dependence of optical absorption of PHP is proposed, using first principles dielectric tensor calculations. The lack of the π - π^* absorption band in the normal UV-Vis absorption spectrum is consistent with theoretical predictions for an orthorhombic thin PHP film with oligomer chains oriented near normal to the substrate surface.

Keywords: Optical absorbance; Films

1. Introduction

It has recently been reported that the oligomers of poly(*para*-phenylene) (PPP) polymer materials are suitable as electro-optically active materials [1]. The six-unit oligomer, *para*-hexaphenyl (PHP), shows some interesting properties when incorporated into optical devices, such as blue-light electroluminescence emission. The PPP structure consists of a linear chain of linked benzene (phenyl) rings showing strong π bond delocalization in the direction of the chains, leading to a typical band structure of a semiconductor with a bandgap (≈ 3 eV). It has recently been possible to produce well-oriented films from organic systems such as PPP oligomers [1], or in oligothiophene-derivative thin films [2–4] that show similar optical properties.

2. Experimental

PHP thin-film samples were produced by vacuum deposition from a quartz evaporation cell. The film thickness was monitored by a quartz crystal balance, and the resulting film thicknesses ranged between 150 and 600 nm. The ordered thin films were produced by depositing on a quartz substrate heated to 250 °C, while films deposited on room-temperature quartz were characterized as being polycrystalline in nature. This effect of substrate temperature on the ordering of PPP and polythiophene oligomer films has also been shown elsewhere [5]. Optical absorption spectra were taken on the PHP samples using a Perkin-Elmer Lambda 9 spectrometer at nor-

mal incidence. In addition to normal transmission spectra, near-normal reflectance was also measured, in order to allow calculations of refractive indices and absorption coefficients by iterative Fresnel equation methods.

3. Theoretical methods

The band structure of crystalline PPP, with chains running parallel to each other, was calculated using the linearized augmented plane wave (LAPW) method within density functional theory [6,7]. An orthorhombic space group with two chains per unit cell was assumed, taking the Z direction as parallel to the chains. From these results, complex dielectric tensor coefficients could be calculated in each of the three primary orthogonal space group directions (X,Y,Z).

The band structure of PHP can be assumed to be very similar to that of PPP, but, due to a shorter chain length, the chain relaxation leads to a lower energy gap. This blue shift was determined to be 0.36 eV calculated from UV-Vis spectra of dissolved oligomers of PPP, where the π - π^* peak was observed to shift linearly with the inverse chain length ($1/n$) of the oligomers. This linear function could also be extrapolated to larger oligomers and to an infinite PPP chain polymer (Fig. 1) to show good agreement with measured UV-Vis spectra of a PPP film [8,9]. Starting from the LAPW results for PPP by taking into account the larger energy gap in PHP the frequency-dependent complex dielectric tensor for PHP was determined. The calculated real part of the dielectric tensor is illustrated for PHP in Fig. 2(a); the imagi-

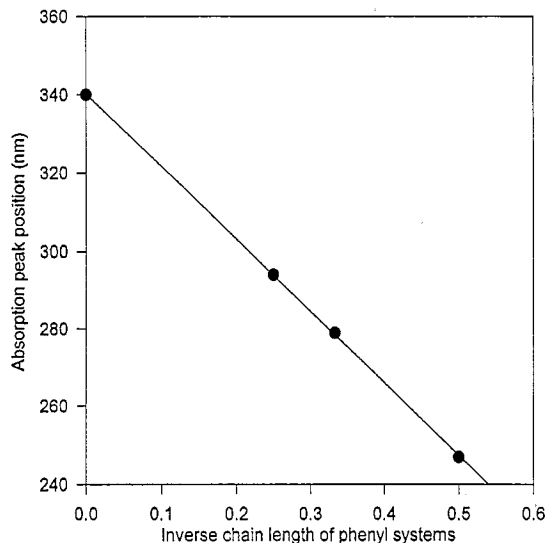


Fig. 1. Oligomer absorption peak dependence on chain length.

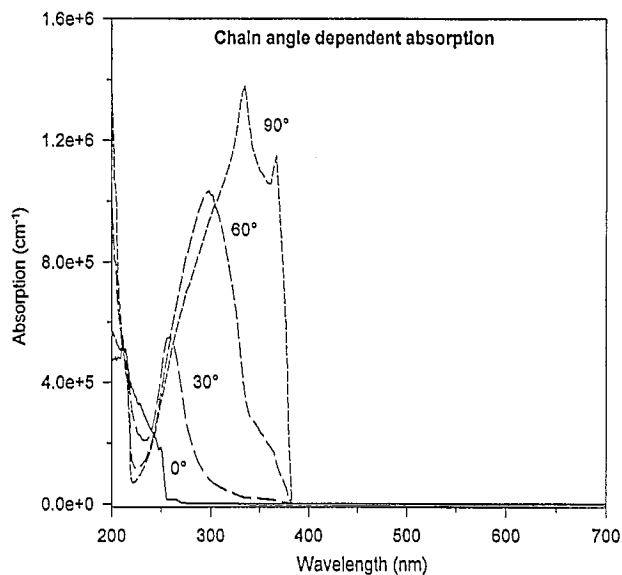


Fig. 3. Variation of optical absorption with PHP orientation.

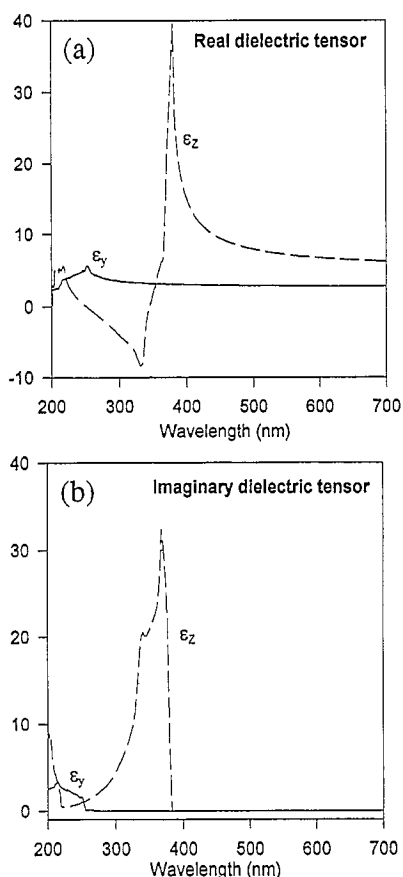


Fig. 2. Calculated real part (a) and imaginary part (b) of the dielectric tensor for PHP.

nary part of the dielectric tensor is shown in Fig. 2(b). The calculations predict a strong anisotropy between the dielectric coefficients parallel and perpendicular to the chain direction. The major difference is the existence of a wide absorption band in the Z direction, when observing the imaginary dielectric components, with a peak at 380 nm, while absorption in this region is negligible in the X,Y directions. This band is attributed to the $\pi-\pi^*$ transition in the Z direction. Differ-

ences between X and Y components are marginal; hence, only the Y and Z components are illustrated in Fig. 2. The band structure calculations indicate that a strong anisotropy of the optical absorption of a crystalline PHP film occurs, when different chain orientations are considered. Radiation of wavelengths near to 380 nm, interacting with the PHP material will only be strongly absorbed when polarized parallel to the chain direction.

From the theoretical dielectric tensor, effective refractive indices were calculated for a thin crystalline film with a given orientation of PHP chains, in order to describe optical absorption of a thin film on a substrate. This was achieved making use of Fresnel equations [10,11], and the resulting refractive indices show strong anisotropic behaviour. A calculation of chain-orientation-dependent optical absorption of normally incident radiation was performed from the refractive index. The results are illustrated in Fig. 3 and show the variation of polarized absorption in the plane of PHP chains as the angles of chains are rotated between the parallel to the deposition surface (90°), and the vertical on the substrate surface (0°). The plotted curves show that the $\pi-\pi^*$ absorption band does not appear with chains oriented vertically on the substrate surface, but a significant absorption arises as the chain angle flattens on the substrate. The calculated peak absorption undergoes a red shift as the angle to the surface normal is increased, and a maximum magnitude of about $1.4 \times 10^6 \text{ cm}^{-1}$ is achieved when chains lie flat on the substrate surface.

4. Results and discussion

Fig. 4 shows the absorption spectra (optical density) for two types of PHP thin films, which illustrate the difference between the ordered and polycrystalline films. The absorption spectrum for an oriented film shows very low absorption in the wavelength range 280–400 nm compared to the polycrystalline film. Only a relatively small peak at 280 nm can

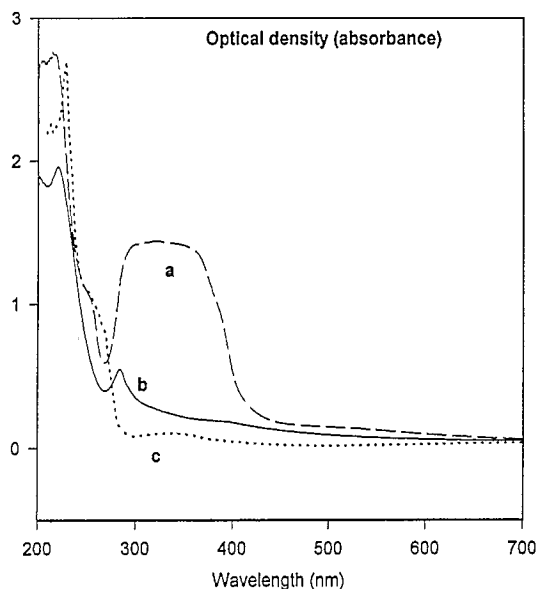


Fig. 4. Measured and calculated optical density for PHP: (a) polycrystalline film (experiment); (b) oriented film (experiment); (c) oriented film (theory).

be seen, whose origin is at present being investigated. The polycrystalline film shows similar absorption to the ordered film in the 200–250 nm region, but has a wide absorption band centred at 320 nm. Electroluminescence and photoluminescence spectra do not reveal major differences between oriented and unoriented samples.

By comparing the measured absorption spectra to the theoretical absorbances for ordered films of PHP, excellent agreement can be found with PHP chains oriented near to the vertical on the surface of the quartz substrate, as any absorption in the 280–400 nm range arises from an interaction between the E.M. wave and the Z component of the dielectric tensor. Curve (c) in Fig. 4 shows the theoretical normal absorbance for vertically oriented PHP chains in a crystalline film, which compares favourably with the measured spectra

in curve (b). For the polycrystalline film, multiple orientations of the chain direction are expected; hence, the Z component of the chains plays a role in the resulting absorption spectrum. By observing the absorption curves in Fig. 3, it can be seen that a distribution of chain orientations will sum to produce a wide absorption band similar in shape to the polycrystalline film (curve (a) in Fig. 4). Thus, by simply changing the growth procedure, it is possible to tune the optical absorption of PHP thin films.

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