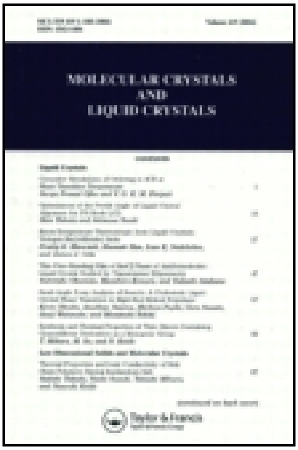

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MAKERFRINGE METHOD FOR MEASURING OPTICAL ANISOTROPY IN THIN POLY-(P-PHENYLENE-VINYLENE) FILMS

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Abstract Third harmonic generation with p-polarized light was used to probe the optical anisotropy in thin poly-(p-phenylene-vinylene) (PPV) films. As a result we have obtained that the chain segments of the conjugated polymer are almost all in plane of the substrate.

INTRODUCTION

Frequency tripling Makerfringe experiments for nonlinear organic polymer films are usually carried out in s-polarization configuration: the electric field of the fundamental wave is oriented parallel to the rotation axis (y-direction). By performing measurements with field orientation perpendicular to the rotation axis (p-polarization) other tensor components than $\chi^{(3)}_{yyyy}$ have to be taken into account and the experiments become sensitive to the anisotropy of $\chi^{(1)}$ and $\chi^{(3)}$ of the investigated films. Here we present experiments on thin PPV films with different polarization configurations.

DATA ANALYSIS

Makerfringes of multilayer systems are often analyzed by a formula that considers only bound waves of $b1$-type, which mix from 3 forward propagating fundamental waves: $E^{b1}_{it} \propto (E^{\omega}_{it})^3$ [2]. In thin films there are furthermore reflected fundamental waves, which can interfere with the transmitted ones. This gives additional possibilities for creation of bound waves: For example there are the so-called $b2$-type waves which are mixtures of two forward and one backward propagating fundamental waves: $E^{b2}_{it} \propto 3(E^{\omega}_{it})^2 E^{\omega}_{ir}$ [3]. Though the influence of these type of waves is often neglected, it is known that especially in thin films they can lead to an error of a factor 4 in the determination of susceptibilities by makerfringe methods[1]. In case of

PPV these waves are non-negligible compared to $b1$-waves. In fact they can become even larger than the $b1$-type waves because of the large refractive index of approximately 2 for a fundamental at $1.0\mu m$. We therefore took care of the interference effect between the fundamental waves and between the free and all types of bound waves (type $b1$, $b2$, $-b2$) in the nonlinear optical film. For the thick substrate layer, interference of counterpropagating waves is possible only for small incidence angles because of the finite transversal dimension of the ray. For this reason we neglected the interference effect in the substrate. We also included absorption of the third harmonic wave. Linear and nonlinear anisotropy of the film as well as absorption of the third harmonic wave was taken into account with limitation to cases where the main axis of the linear susceptibility tensor coincides with the sample coordinate system. This simplifies the treatment because no double refraction occurs and enables us to apply a 2×2-matrix formalism to the nonlinear boundary value problem of the multi layer system[16]. Otherwise an extension to a 4×4-formalism would be neccessary.

It was found that the interference effect in the thin film is crucial not only for the determination of modulus and phase of $\chi^{(3)}$, but also for the envelopes of the fringes.

MODELS FOR THE SUSCEPTIBILITIES

In the conjugated polymer PPV the linear and nonlinear optical properties originate mainly from one dimensional chain segments with a 1d segment linear susceptibility $\chi^{(1)}_{\xi\xi}$ and a 1d cubic susceptibility $\chi^{(3)}_{\xi\xi\xi\xi}$. Measurable tensor components of the susceptibilities are obtained by oriental averaging over those segments. If the chain segments are randomly oriented in three dimensions the linear and nonlinear optical properties are isotropic. For the linear susceptibility one gets $\chi^{(1)}_{ij} = \frac{1}{3}\chi^{(1)}_{\xi\xi}\delta_{ij}$. The cubic susceptibility for this case is $\chi^{(3)}_{xxxx} = \chi^{(3)}_{yyyy} = \chi^{(3)}_{zzzz} = \frac{1}{5}\chi^{(3)}_{\xi\xi\xi\xi}$

Isotropic 2d segment distribution:

The chain segments are isotropic oriented in the substrate plane with a Gaussian distribution of the angle ϑ between the chain segment axis and the normal vector of the film:

$$f(\vartheta) = \frac{2}{\sqrt{\pi\Delta\vartheta}} e^{\left(\frac{\vartheta-\pi/2}{\Delta\vartheta}\right)^2} \tag{1}$$

The linear susceptibility then becomes:

$$\begin{array}{lllll} \chi^{(1)}_{xx} & = & (n^o)^2 - 1 & = & \frac{1}{4}[1 + e^{-\Delta\vartheta^2}]\chi^{(1)}_{\xi\xi} \overset{\Delta\vartheta\to 0}{=} \frac{1}{2}\chi^{(1)}_{\xi\xi} \quad \text{ordinary} \\ \chi^{(1)}_{zz} & = & (n^e)^2 - 1 & = & \frac{1}{4}[1 - e^{-\Delta\vartheta^2}]\chi^{(1)}_{\xi\xi} \overset{\Delta\vartheta\to 0}{=} 0 \qquad \text{extraordinary} \end{array}$$

As a result the film shows an uniaxial optic anisotropy of negative character ($n^e < n^o$) with an extraordinary refractive index n^e and an ordinary in plane refractive index n^o. For s-polarized waves and for arbitrary polarized waves at normal incidence the ordinary index is valid and for waves with p-polarization an effective refractive index $\tilde{n}^e(\Theta)$, which depends now on the incidence angle Θ, has to be taken. The linear anisotropy is more pronounced at large incidence angles. For the limiting case $\Delta\vartheta \to 0$, where all segments are in the substrate plane, one gets a vanishing susceptibility $\chi^{(1)}_{zz}$ which corresponds to the vacuum refractive index of 1. This model could be improved if one splits up the susceptibility into two parts: an isotropic contribution of the σ-bonds and an anisotropic one of pure π-bonds as done by McBranch[4].

For the nonlinear optical properties, however, the dominant contribution originates mainly from these π-bonds. For s-polarization only one tensor component $\chi^{(3)}_{yyyy}$ contributes to the nonlinear polarization P^{NL}. For p-polarization the following tensor components have to be taken into account:

$$\begin{array}{lll} \chi^{(3)}_{xxxx} & = & \frac{3}{64}\left[3[1 + e^{-\Delta\vartheta^2}] + e^{-\Delta\vartheta^2}[1 + e^{-3\Delta\vartheta^2}]\right]\chi^{(3)}_{\xi\xi\xi\xi} \overset{\Delta\vartheta\to 0}{=} \frac{3}{8}\chi^{(3)}_{\xi\xi\xi\xi} \\ \chi^{(3)}_{xxzz} & = & \frac{3}{16}\left[[1 + e^{-\Delta\vartheta^2}] - e^{-\Delta\vartheta^2}[1 + e^{-3\Delta\vartheta^2}]\right]\chi^{(3)}_{\xi\xi\xi\xi} \overset{\Delta\vartheta\to 0}{=} 0 \\ \chi^{(3)}_{zzzz} & = & \frac{3}{64}\left[3[1 - e^{-\Delta\vartheta^2}] + e^{-\Delta\vartheta^2}[1 - e^{-3\Delta\vartheta^2}]\right]\chi^{(3)}_{\xi\xi\xi\xi} \overset{\Delta\vartheta\to 0}{=} 0 \end{array}$$

The direction $\hat{p}^b$ of the nonlinear polarization for a bound wave of type b in an anisotropic medium is given by:

$$\hat{p}^b = \begin{pmatrix} \alpha\chi^{(3)}_{xxxx}((\frac{\tilde{n}^e(\omega,\Theta)}{n^o})^2\cos\Theta)^3 + \beta\chi^{(3)}_{xxzz}((\frac{\tilde{n}^e(\omega,\Theta)}{n^e})^2\sin\Theta)^2(\frac{\tilde{n}^e(\omega,\Theta)}{n^o})^2\cos\Theta \\ 0 \\ -\chi^{(3)}_{zzzz}((\frac{\tilde{n}^e(\omega,\Theta)}{n^e})^2\sin\Theta)^3 + \gamma\chi^{(3)}_{zxxz}((\frac{\tilde{n}^e(\omega,\Theta)}{n^o})^2\cos\Theta)^2(\frac{\tilde{n}^e(\omega,\Theta)}{n^e})^2\sin\Theta \end{pmatrix} \frac{1}{\chi^{(3)}_{xxxx}} \tag{2}$$

where (α, β, γ) is $(1, 3, -3)$ for a $b1$-type bound wave and $(-1, 1, 1)$ for a $b2$-type one. In the limit $\Delta\vartheta \rightarrow 0$ the z-component vanishes and the envelope of the Makerfringes becomes narrower.

EXPERIMENTAL RESULT

The experimental setup was a standard Makerfringe experiment with a rotation stage in a vacuum cell. As laser source we used raman shifted pulses of an Excimer laser pumped Dye-Laser operating at $700nm$. The pulse energy we used for the experiment was $200 - 400\mu J$ at $987.1nm$. The fundamental ray was focussed onto the sample by means of a lense with a focal length of $200mm$.

The samples were PPV thin films created by spin coating of diluted precursor solutions. The elimination was done for 2.5 hours in Ar gas atmosphere at a temperature of 160^oC. The film thickness was measured with a profilometer to $(6.4 \pm 1)nm$. The ordinary complex refractive index $\tilde{n}^o = n^o + i\kappa^o$ was determined by a simultaneous R/T measurement at $\theta = 0^o$ in combination with a Kramers Kronig transformation of the absorption spectrum[7]. We performed 4 different measurement configurations. The Makerfringe data and the applied fits are shown in figure 1. In a first pass the 5 parameters $\chi^{(3)}$, $\phi^{(3)}$, substrate thickness, intensity of the fundamental and $\Delta\vartheta$ were fitted simultaneously to both s-measurements. Therefore we were able to determine the phase $\phi^{(3)}$ of $\chi^{(3)}$. $\phi^{(3)} = 320^o$ indicates a three photon resonance. In a second pass we determined the missing parameters $\Delta\vartheta$, $n^e(3\omega)$ and $n^e(\omega)$ from the p-measurements by applying the Gaussian model for the chain segment distribution orientation. κ^e was set to 0. The width of the Gaussian distribution was determined to $\Delta\vartheta = 9.2\,\text{deg}$. This indicates that chain segments are oriented predominantly parallel to the substrate. An isotropic segment distribution would lead to p-Makerfringes with too high amplitude at angles greater

	n^o	n^e	κ^o	$\chi^{(3)}$:
ω	$1.92 \pm .05$	$1.2 \pm .2$	$.00 \pm .02$	$\chi^{(3)} = (2.85 \pm 0.5) \times 10^{-11} esu$
3ω	$1.40 \pm .05$	$1.2 \pm .2$	$.64 \pm .02$	$\phi^{(3)} = 320^o \pm 20^o$

Table 1: Evaluation of the experimental data from 1:

30 deg. By considering pure $b1$-waves, it would be misleading to accept a stronger anisotropy $\Delta\vartheta = 0$ and a higher $\chi^{(3)}$-value. Only by consideration of all bound waves we were able to find a consistent parameter set for all four measurements. The increasing intensity with increasing incidence angle in the measurement with s-polarization and film on the backside of the substrate ("s,Back" of Fig. 1) is a result of the contribution of these waves.

The sharp peaks near zero incidence angle are due to multiple reflection in the film and the substrate (microcavity). For this situation a full 2×2-matrix formalism including the substrate is neccesary. With larger angles this effect gets smaller.

CONCLUSION

The analysis proposed, shows that in thin PPV films the 1d chain segments are predominantly in the substrate plane with a narrow Gaussian orientation distribution of the chain segments out of the plane. Optical anisotropy in PPV films was also demonstrated with linear optical methods by R. Burzynski et. al.[5] and D. McBranch et. al.[4]. For the data analysis all types of bound waves in the thin film have to be taken into account. Because of the high sensitivity of the method to the orientation of the 1d chains we think that Makerfringe experiments with p-polarized light are from value to determine the orientation of 1d chains in polymer films or crystals.

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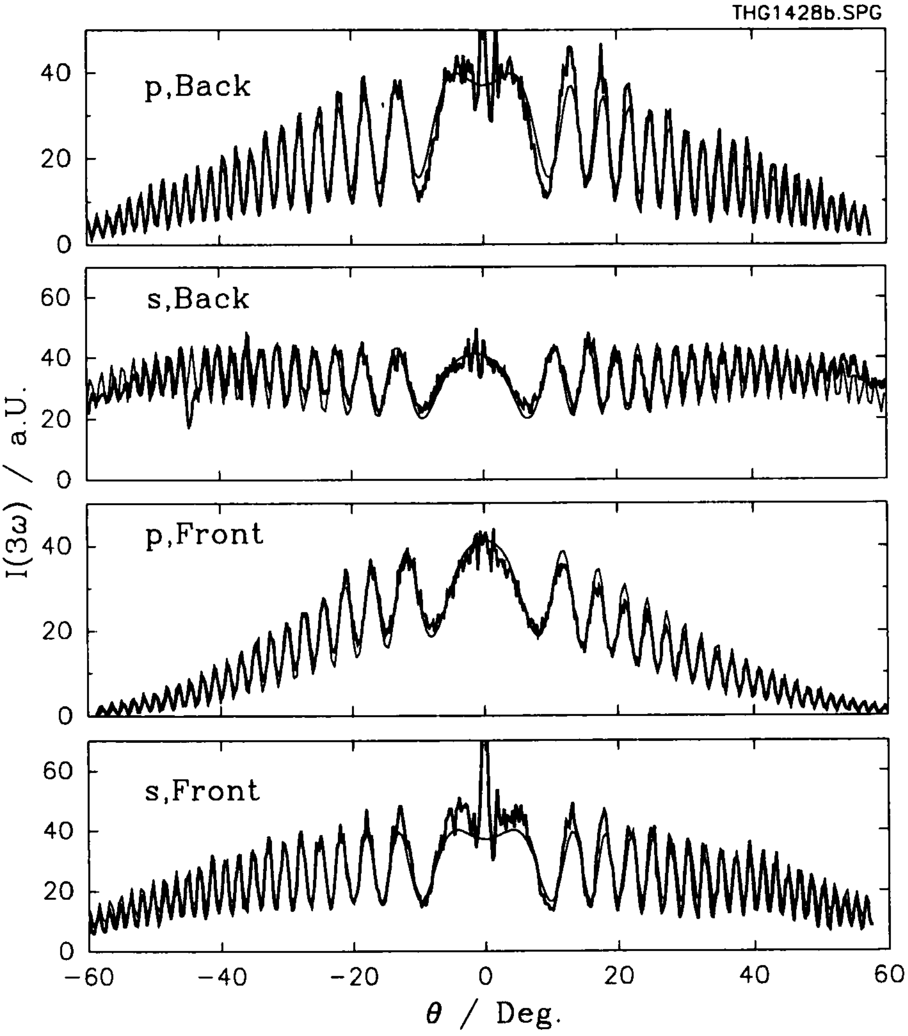

Figure 1: **Makerfringes in a 6.4nm thin Layer of PPV for different experimental conditions: "s/p" denotes polarization of the fundamental, whereas "Back" refers to the film on the backside of the substrate (in respect of the incident fundamental) and "Front" to the film on the frontside; thin lines indicate best simultaneous fits to all 4 curves, the scale is the same in each figure;**