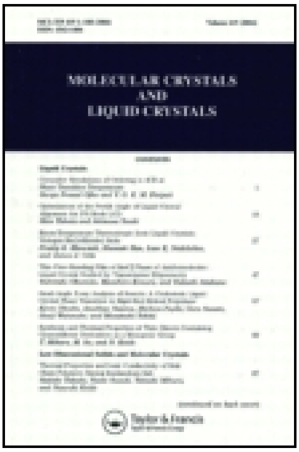

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COPLANAR-ELECTRODE MEASUREMENT OF ELECTRO-OPTIC COEFFICIENTS IN POLED POLYMER THIN FILMS

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Abstract A coplanar electrode structure is introduced to measure the linear electro-optic (EO) effect of poled polymer thin films. The coplanar structure has advantages over the parallel plate structure in removing artifacts such as piezoelectric effect and electrostrictions. Optical geometry of coplanar electrode thin film setup is analyzed to find a relationship between the measured modulated intensity and microscopic molecular parameters.

1. Introduction

Polymeric materials received a wide attention as electro-optic (EO) materials for their high processability and compatibility with current microelectronic techniques as well as for the intrinsic high-bandwidth response of organic molecules.[1][2] EO effect, one of the second-order nonlinear optical processes, can exist in materials lacking the centrosymmetry. In EO polymers, the centrosymmetry of polymer thin films is removed by a dc electric field poling to achieve a macroscopic polar alignment of nonlinear optical (NLO) chromophores. In thin film samples, two configurations of electrodes are commonly adopted for the electric field poling, parallel and coplanar. In the parallel-plate configuration, EO polymer is sandwiched between two thin electrode plates on top of a substrate (glass or silicon). In the coplanar electrode structure, on the other hand, two thin separate electrodes with a narrow gap in between them are deposited on top of a substrate, and then the EO polymer film is spin-coated. When compared with the commonly adopted parallel-plate configuration, the coplanar-electrode configuration has some advantages. First, the piezoelectricity and electrostriction effects present in parallel plate electret samples do not exist in coplanar electrode samples[3], because the electrodes evaporated onto the optical substrates do not undergo any mechanical deformation even in the presence of a strong electric field between two electrodes. While the electrostriction effect shows up as a second harmonics of the modulation frequency, the piezoelectric effect is of the fundamental frequency. In a simple reflection measurement[4], it's hard to distinguish the linear EO effect from the piezoelectric effect unless the modulation frequency is varied in a wide range. In the case of electrostrictions, the second harmonics of modulation frequency is indistinguishable from the quadratic EO effect.[5] Secondly, the parallel-plate thin film configuration cannot be employed for certain NLO polymers where NLO active chromophores are attached to the polymer backbone as side chains. π-electrons residing on the backbone but not participating in the NLO response due to the symmetry restriction can cause a strong absorption at the probing laser light wavelength. In this case the high reflectivity at the front surface of thin film makes most of the incident light intensity reflected without experiencing the modulations induced by the linear EO effect of the poled thin film. When this happens, the modulation depth is so low that it is very hard to observe the linear EO effect. Thirdly, the sample preparation is simpler for the coplanar electrode configuration compared to the parallel plate configuration. Once a coplanar-electrode with a fixed spacing gap is patterned on optical substrates, thin polymer film can be spin-coated directly on top of the patterned electrodes. It is particularly useful for thermoset polymers where a further thermal or UV curing steps are required to obtain the proper material properties.[6][7] In this paper we analyze the coplanar-electrode configuration for the linear EO measurement of poled polymer thin films.

2. Index Ellipsoid and Linear EO Coefficient

The orientational distribution of NLO chromophore of thermally cured polymer film is isotropic. Hence, the index ellipsoid of cured polymer film is a sphere. The electric field poling process, however, breaks the isotropy of orientational distribution, leading to a uniaxial 'crystal'. The poled polymer thin film, then, possesses $C_{\infty v}$ point group symmetry with the infinite-fold symmetry z (optic) axis (the direction of electric field poling). (See Figure 1.) Taking the direction across the metal gap as z axis, the equation of refractive index ellipsoid is

$$\frac{x^2}{n_o^2} + \frac{y^2}{n_o^2} + \frac{z^2}{n_e^2} = 1 \tag{1}$$

with n_o and n_e the refractive indices of the ordinary- and extraordinary-wave components.

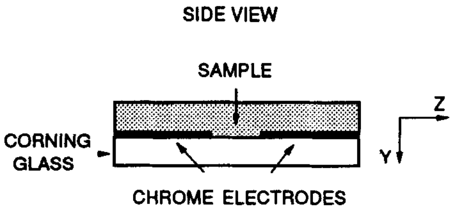

Figure 1. Sample geometry is shown. Chrome electrodes are patterned on top of optical substrate. NLO polymer is spin-coated onto the patterned electrode. After the electric field poling, the polymer film possesses the point group $C_{\infty v}$ with Z axis as infinite-fold symmetry axis.

When an external modulation electric field is applied, the linear EO effect induces a change of refractive indices, resulting in the modulation of index ellipsoid. In a medium belonging to the point group $C_{\infty v}$, the change in the coefficients is represented as[8]

$$\begin{aligned}\Delta(\frac{1}{n^2})_i &= \sum_{j=1}^{3} r_{ij}E_j \\ &= \begin{vmatrix} 0 & 0 & r_{13} \\ 0 & 0 & r_{23} \\ 0 & 0 & r_{33} \\ 0 & r_{42} & 0 \\ r_{51} & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \begin{vmatrix} E_1 \\ E_2 \\ E_3 \end{vmatrix}\end{aligned} \tag{2}$$

with

$$r_{13} = r_{23}, \qquad r_{42} = r_{51}$$

where r_{ij} are the linear EO coefficients and E_j is the modulating external field with 1, 2, and 3 corresponding to x, y, and z. When the external field is applied in the z direction, the same direction as the dc poling field, i.e., $E = E_3$, the principal axes remain unchanged, and the changed refractive indices satisfy the index ellipsoid equation the same as Eq.(1), only the refractive indices varied.[9][10]

$$\begin{aligned}\frac{x^2}{n_o'^2} + \frac{y^2}{n_o'^2} + \frac{x^2}{n_e'^2} &= 1 \\ \begin{pmatrix} n_o' &= n_o + \Delta n_o \\ n_e' &= n_e + \Delta n_e \end{pmatrix}\end{aligned} \tag{3}$$

From Eq.(2) and Eq.(3) with the approximation $\Delta n_e \ll n_e$ and $\Delta n_o \ll n_o$, Δn_e and Δn_o can be expressed in terms of the linear EO coefficients.

$$\begin{aligned} \Delta n_e &= \frac{1}{2} n_e^3 r_{33} E \\ \Delta n_o &= \frac{1}{2} n_o^3 r_{13} E \end{aligned} \tag{4}$$

In Figure 2, the index ellipsoid is illustrated for an isotropic unpoled thin film (solid curve), the poled thin film (dashed curve), and the poled thin film with a dc modulation voltage applied (dotted curve).

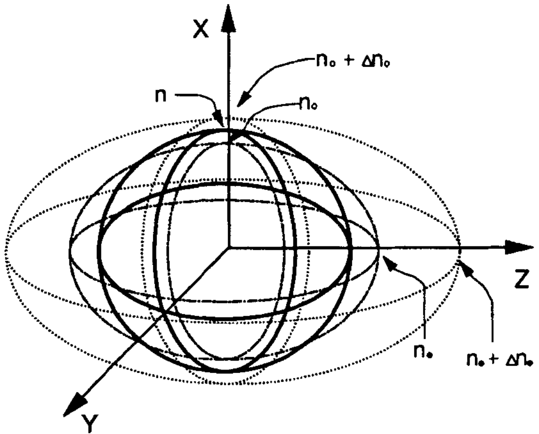

Figure 2. Index ellipsoid of polymer film is shown. The solid (spherical) and the dashed (prolate) curves correspond to the cured and the poled polymer film respectively. The dotted (prolate) curve represents the index change resulting from the electro-optic modulation.

Now let's look at how the EO modulation intensity is related to the linear optical parameters. The detailed experimental set-up for measuring the change of refractive index ellipsoid is shown in Figure 3. The polarizer in front of the detector is set to a cross-polarization position to allow only the polarization component perpendicular to the polarization plane of incident beam to pass through. Total retardation is the sum of the retardation due to the quarter-wave plate and the poled polymer, thus the output beam intensity I_o is

$$I_o = 2 I_c \sin^2\left(\frac{\Gamma_{eo} + \Psi_{eo}(\theta)}{2}\right) \tag{5}$$

where Γ_{eo} and $\Psi_{eo}(\theta)$ are the retardations due to the quarter-wave plate and the poled polymer with external electric field respectively. Here I_c is the half of the maximum output beam intensity, and θ denotes the angle between the incident beam polarization plane and the poling field direction.

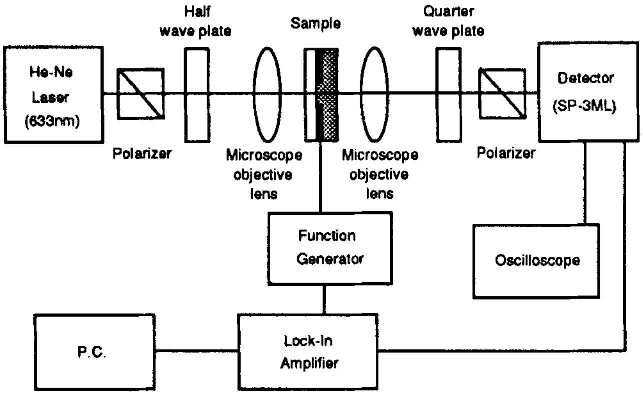

Figure 3. Schematic diagram of the experimental setup is shown.

The net phase shift Δ between the ordinary- and extraordinary-waves caused by the linear EO effect in the polymer thin film can be obtained by considering the functional form of $\Psi_{eo}(\theta)$.

$$\Delta = \frac{\pi l}{\lambda} n^3 (r_{33} - r_{13}) \frac{V_m}{d} \sin \omega_m t \tag{6}$$

where d is the distance between two electrodes along the direction of the applied field, that is, metal gap dimension in the sample, and $V_m \sin \omega_m t$ is the modulation voltage. After summing the components of the ordinary- and extraordinary-wave projected along the orthogonal direction of the polarizer, we obtain the final equation relating the output modulation intensity I_{mo} and the other optical parameters.

$$I_{mo} = I_c \frac{\pi l}{\lambda} n^3 (r_{33} - r_{13}) \frac{V_m}{d} \sin \Gamma_{eo} \sin 2\theta \tag{7}$$

We find that the modulation amplitude depends on the optical bias determined by the retardation Γ_{eo} introduced by the quarter-wave plate and the angle θ of the incident light polarization plane relative to the optic axis.

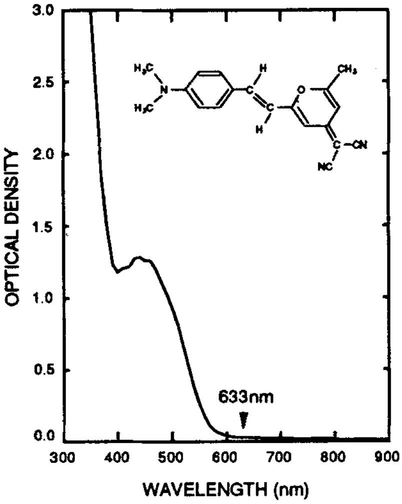

Figure 4. The linear absorption spectrum of DCM/PIQ-2200 thin film after curing at 250° is shown. Also shown is the chemical structure of the NLO chromophore, DCM.

3. Experimental Measurement of Linear EO Coefficient

Liquid solution of guest/host system is prepared by stirring 4- (dicyanomethylene) - 2- methyl -6- (*p*- dimethylaminostyryl- 4*H*- pyran (DCM) chromophores (guest) into *Hitachi Chemical Co.* LQ-2200 polyamic acid (host) (6 % weight concentration). A $10\mu m$ gap coplanar electrode structure was patterned on top of a Corning 7057 glass slide (low ionic concentration) by the thermal evaporation of chrome and a subsequent photo-resist mask patterning process. On the substrate the chrome layer thickness is measured to be approximately $0.2\mu m$. Thin polymer film is prepared by spin-coating DCM/LQ2200 (guest/host) solution onto the substrate at 800 RPM for 20 seconds and 2000 RPM for 10 seconds. The DCM/LQ2200 thin film was cured inside a temperature controlled oven. Temperature was increased with the ramp rate of 3°C/min. and the imidization process was completed by curing at 250°C for 1 hour. The linear absorption spectrum of cured film is shown in Figure 4. The absorption peak around $450nm$ is characteristic of the stilbene dye π electrons. We note that the linear absorption is not significant at the He-Ne laser wavelength $633nm$. For the electric field poling, wires are bonded to both sides of separated chrome layers with silver paste. The glass transition temperature T_g of cured DCM/LQ2200 polymer film is reported to be about 210°C.[11] Therefore the electric field poling is performed at 220°C for 5 minutes after temperature increase with the ramp rate of 7°C/min. With the external electric field applied, the sample is cooled down, and the electric field was disconnected upon reaching 50°C.

The experimental layout for the measurement of linear EO effect is shown in Figure 3. Between two crossed-polarizers, thin film sample was positioned with two microscope objective lens to focus the laser beam onto the clear gap. The half-wave and quarter-wave plates are to control the polarization plane of incident beam. Function generator (131 Hz) supplies the modulation voltage to the electrodes. A PIN photodiode (SP-3ML) was used as a detector. At the detector DC light intensity I_c appearing in Eq.(5) is monitored by an oscilloscope and the modulated light intensity I_{mo} appearing in Eq.(7) is monitored by a lock-in amplifier. The modulation voltage applied to the electrodes is varied and the signal at the lock-in amplifier is measured. According to Eq.(7) we expect a linear relationship between the modulated light intensity I_{mo} and the modulation voltage V_m. for the linear EO effect. Figure 5 shows the experimental data and the linear fit.

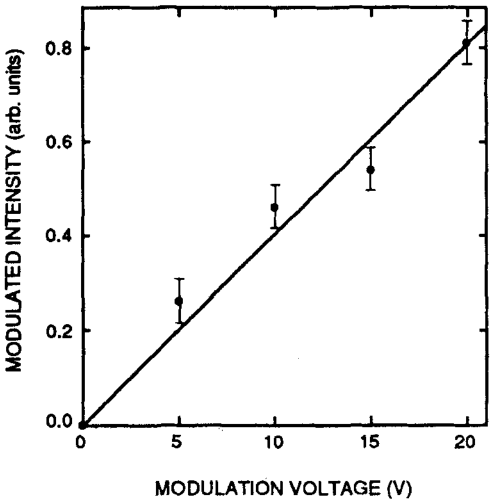

Figure 5. The modulated intensity is plotted as a function of the modulation voltage. The straight line is the least square fit, confirming that the measured signal is from the linear EO effect.

4. Linear EO Effect as a Function of Poling Field Strength

Now the linear EO effect measurement of poled polymer thin film in a coplanar electrode configuration is analyzed, it's interesting to apply this measurement method to the understanding of the order parameter determining the macroscopic linear EO response. In a poled polymer the linear EO effect originates from the microscopic molecular hyperpolarizability $\beta(-\omega;\omega,0)$ of guest chromophores. The observed linear EO effect, however, is related to the statistical average of the orientational distribution of guest chromophores, $f(\theta)$. In a Boltzmann distribution, $f(\theta)$ can be expanded in terms of the Legendre polynomials.[10]

$$f(\theta) \;=\; \sum_{n=0}^{\infty}\frac{2n+1}{2}\frac{i_n(x)}{i_o(x)}P_n(\cos\theta) \qquad (8)$$

with

$$x = \frac{\mu E_o}{kT}$$

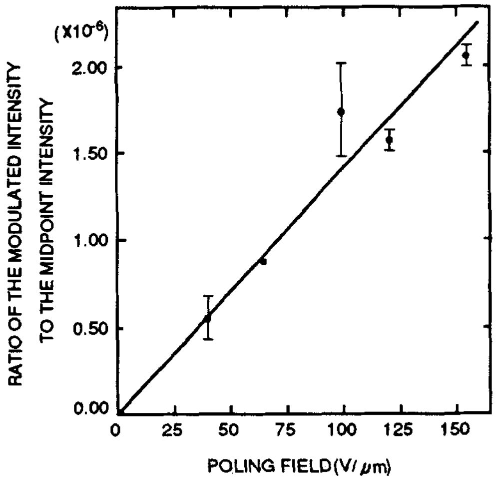

Figure 6. The ratio of the modulated intensity to the midpoint intensity is shown as a function of the poling field magnitude. The distribution function $f(\theta)$ is a linear function of $\mu E_o/kT$ at a low poling field strength. The solid line is from the theory.

The linear EO coefficient r and the second order nonlinear susceptibility $\chi^{(2)}_{IJK}$ are related as follows.

$$\begin{aligned} \chi^{(2)}_{ZZZ}(-\omega;\omega,0) &= -\frac{1}{8\pi}[n^2(0)n^2(\omega)]r_{33}(-\omega;\omega,0) \\ \chi^{(2)}_{XXZ}(-\omega;\omega,0) &= -\frac{1}{8\pi}[n^2(0)n^2(\omega)]r_{13}(-\omega;\omega,0) \end{aligned} \tag{9}$$

Substitution of Eq.(9) and (10) into Eq.(7) yields the expression of the measured EO signal in terms of the order parameter. For $\mu E_o/kT << 1$, a linear relationship is expected between the EO signal and the poling field strength E_o. Figure 6 shows the experimental data and the least square fit, confirming that the Boltzmann distribution describes the orientational distribution of NLO chromophores appropriately.

5. Conclusion

The index of ellipsoid of poled polymer thin film in a coplanar-electrode structure is analyzed to relate the change of refactive indices with the linear EO modulation. In a cross-polarizer setup, the phase modulation from linear EO response is converted to the intensity modulation. The linear optical parameters determining the magnitude of EO modulated intensity is theoretically investigated. Experimentally, EO modulated intensity is studied as a function of the dc modulation voltage and the poling field strength. Experimental results agrees well with the theoretical analysis.

Acknowledgement

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