Anisotropy and dispersion of quadratic nonlinear properties of electrooptic azo-polymer thin films

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Different components (iiz) of the $\chi^{(2)}(-\omega;\omega,0)$ and $\chi^{(2)}(-2\omega;\omega,\omega)$ nonlinear quadratic susceptibilities tensors of a nonlinear optical polymer are both measured independently using a Fabry-Pérot interferometric technique and the second harmonic Maker fringes method. Electro-optic dispersion is obtained from visible wavelengths up to 1.55µm while second harmonic generation measurements are performed at 1.32µm. These techniques agree with a wavelength independent $\chi^{(2)}_{zzz} / \chi^{(2)}_{xxz}$ ratio close to 5 for the copolymer Poly(methyl methacrylate)-Dispersed Red 1 (PMMA-DR1) and close to 3 for the guest-host PMMA-DR1 blend, thus designating the interaction of the chromophores with their environment as an important feature in electro-optic device design.

Keywords : nonlinear quadratic susceptibilities, Fabry-Pérot interferometric technique, electrooptic polymer

1. Introduction

Organic nonlinear optical (NLO) materials have emerged over the last decade as appealing candidates towards integrated optics technology in view of some of their specific advantages as compared to inorganic materials. The low-cost and relatively easy processability of NLO polymers exhibiting large nonlinearities have allowed the demonstration of very performing active integrated organic optical components with impressive figures of merit [1]. Accurate measurement of nonlinear quadratic susceptibilities $\chi^{(2)}(-\omega;\omega,0)$ and $\chi^{(2)}(-2\omega;\omega,\omega)$ which respectively pertain to electro-optic modulation and second harmonic generation is a prerequisite step towards subsequent design of devices for light modulation and all-optical signal processing [2].

Several methods have been developed for the determination of the electro-optic related tensor coefficient and related NLO susceptibility. First, reflection techniques have been developed for determining the electro-optic coefficient r_{33} of poled polymers based on a weak field cylindrical symmetry imposed r_{33} / r_{13} ratio set at a fixed value of 3 [3,4]. Uchiki and Kobayashi have proposed a Fabry-Pérot interferometric technique to measure the coefficient r_{13} by varying the light beam wavelength [5]. Moreover, an attenuated total reflection technique allows to evaluate both r_{13} and r_{33} coefficients independently [6]. However, this technique requires the knowledge of the metallic layers thickness with a high level of accuracy.

In this paper, we used two techniques to measure independently nonlinear quadratic susceptibilities of a PMMA-DR1 copolymer from the visible up to the 1.55µm telecom window. The r_{33} and r_{13} electro-optic coefficients are evaluated using a Fabry-Pérot interferometric technique that has been initially introduced by Meyrueix and coworkers [7,8]. The second order nonlinear coefficients d_{33} and d_{31} are then determined by second harmonic measurements following the Maker fringes envelope method. The $\chi^{(2)}_{zzz} / \chi^{(2)}_{xxz}$ ratio obtained with theses techniques is then compared to the theoretical values predicted by various models.

2. Experimental

The nonlinear co-polymer was synthesized at Ecole Nationale Supérieure de Chimie de Montpellier. The chromophore tethered to the backbone of the PMMA polymeric matrix is the azo-dye Disperse Red 1 from Aldrich. The experimental molar composition MMA/MMADR1 = 76/24. The same polymeric matrix and chromophore are used to prepare a 10% weight doped PMMA. Linear optical properties, namely refractive index and linear absorption of these materials were characterized using tranditional spectroscopic ellipsometry and spectrophotometry.

Electrooptic measurements are achieved with thin film Fabry-Pérot cavities while second-harmonic measurements are performed using a thin film spin coated on a glass substrate. Fabry-Pérot thin film processing starts with the semi-transparent aluminium bottom electrode deposition by sputtering on a glass substrate. Then, the active organic material, a concentrated solution of 10% weight nonlinear optical polymer in 1,1,2 trichloroethan, is filtered through a 0.2 µm Teflon filter and spun coated onto the bottom aluminium electrode. The film is then dried at 120°C for two hours. Finally, the upper semi-transparent aluminium electrode is sputtered. Electric wire bonding is ensured by gluing onto the two electrodes coated with a silver contact layer. Initially, the active polymer in the cavity is centrosymmetric which precludes quadratic nonlinear effects. Thermo-assisted electric field poling is subsequently used to induce noncentrosymmetry.

3. Electrooptic Measurements

Electro-optic measurements were obtained using the Fabry-Pérot under oblique incidence set-up. The poled Fabry-Pérot cavity is placed on a motorized rotating stage and a quasi-static field (30 V peak to peak at Ω = 1 kHz) supplied by an AC generator is applied onto the electrodes of the cavity. Angular transmission spectra, $T_S(\theta)$ and $T_P(\theta)$ at zero frequency, and $T_S^{EO}(\theta)$ and $T_P^{EO}(\theta)$ at Ω frequency, are simultaneously measured at a discrete set of wavelengths using different laser diodes operating respectively at 675, 785, 1064, 1330 and 1550 nm. Modulated spectra $T_S^{EO}(\theta)$ and $T_P^{EO}(\theta)$ are recorded with a lock-in amplifier. Experimental data at 1.55µm for S and P polarization are presented in Figs. 1 for the co-polymer (dotted curves).

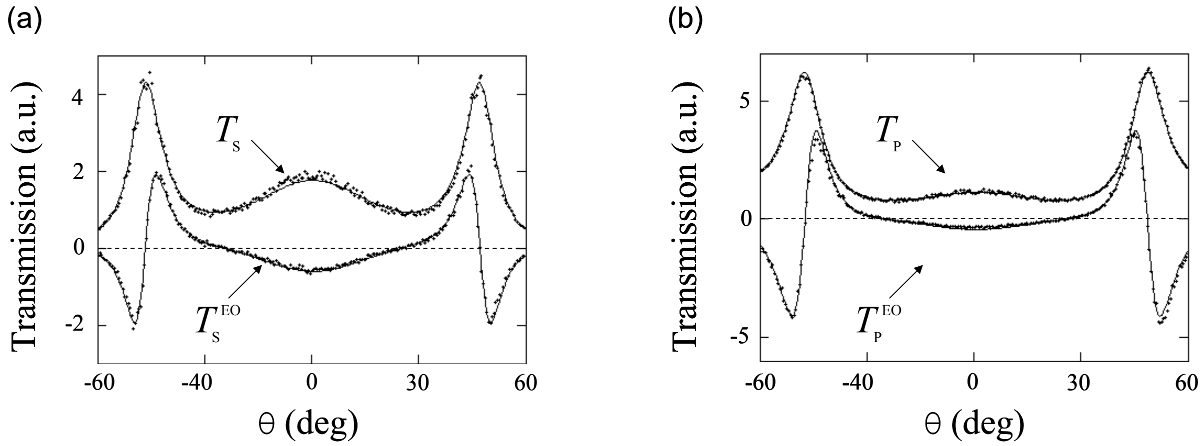

Figure 1 : Direct transmission ($T_{S,P}$) and modulated transmission ($T_{S,P}^{EO}$) at λ = 1.55µm. The polymer thickness is L=3.5 µm and the poling field Ep = 63 V/µm. (a) S-polarization; (b) P-polarization.

Electro-optic coefficients r_{13} and r_{33} are obtained from experimental data fits (solid lines) using standard matrix propagation method. First, the fits of $T_S(\theta)$ and $T_P(\theta)$ allow the determination of polymer thin film and aluminium electrodes thicknesses. Then, r_{13} (respectively r_{33}) is inferred from $T_S^{EO}(\theta)$ (respectively $T_P^{EO}(\theta)$ and the value of r_{13} deduced previously). Fig. 2 (a) and (b) summarize respectively the results for r_{13} (dots) and r_{33} (squares) at different wavelengths with the same sample.

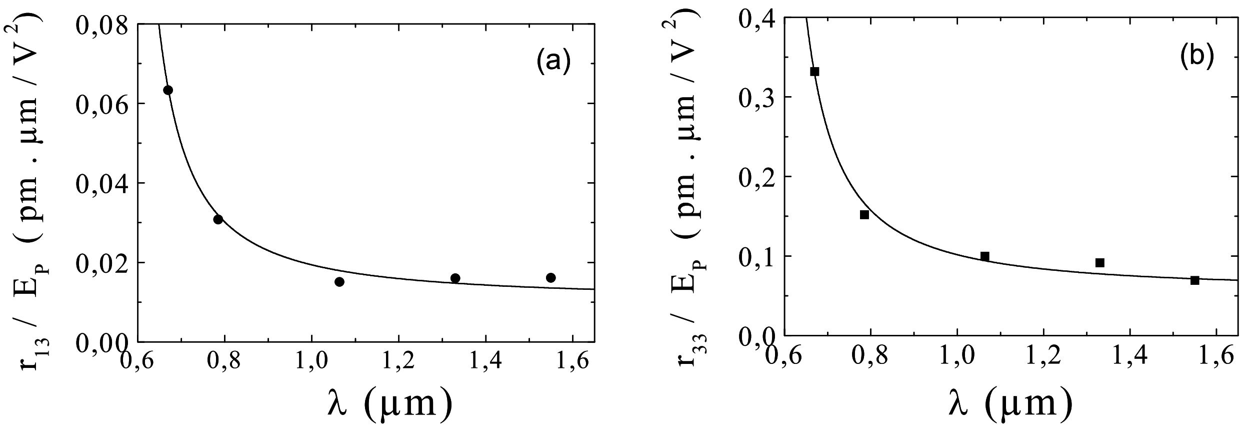

Figure 2 : Electro-optic dispersion normalized to the poling field Ep. (a) r13 coefficient; (b) r33 coefficient. (a) and (b) are fitted using a two level model with λ_0 = 532nm and λ_0 = 530nm respectively.

In first approximation, the dispersion of electro-optic coefficients, $r_{13}(\lambda)$ and $r_{33}(\lambda)$, is fitted by the two level model and rather good agreement is obtained. We found a ratio $r_{33}/r_{13} \approx 5$ which is almost constant over the investigated wavelength range. This ratio is greater than the theoretical value 3 predicted by the Langevin model in the limit of small field which points out that chromophores interact with their environment. The Van der Vorst – Picken model based on the Maier-Saupe theory, which takes into account the dipole interaction with their environment, gives much better results, even if the predicted r_{33} / r_{13} ratio is smaller than measured [9]. The wavelength independence confirms the intrinsic structural character of the underlying physical mechanism. As expected, a ratio $r_{33}/r_{13} \approx 3$ is obtained with DR1 dye-doped PMMA guest-host system, where the chromophores interaction with their environment is expected to be much weaker.

4. Second harmonic measurements

Second harmonic generation measurements are performed on a polymer thin film spun coated on a glass substrate. The sample is placed on a motorized rotating stage and is poled in situ by a 6 kV Corona needle set-up. A Q-switched nanosecond Nd3+YAG laser operating at 1.32µm was used. Envelope fringes corresponding to the second harmonic signal in function of the incidence angle, $I_{2\omega}(\theta)$, are detected using a photomultiplier linked to a boxcar integrator for different polarization configurations. Fig. 3a and 3b present the $I_{2\omega}^{polymer}(\theta)$ (dotted curves) and $I_{2\omega}^{quartz}(\theta)$ (solid curves) for a S and P polarized fundamental incident beam.

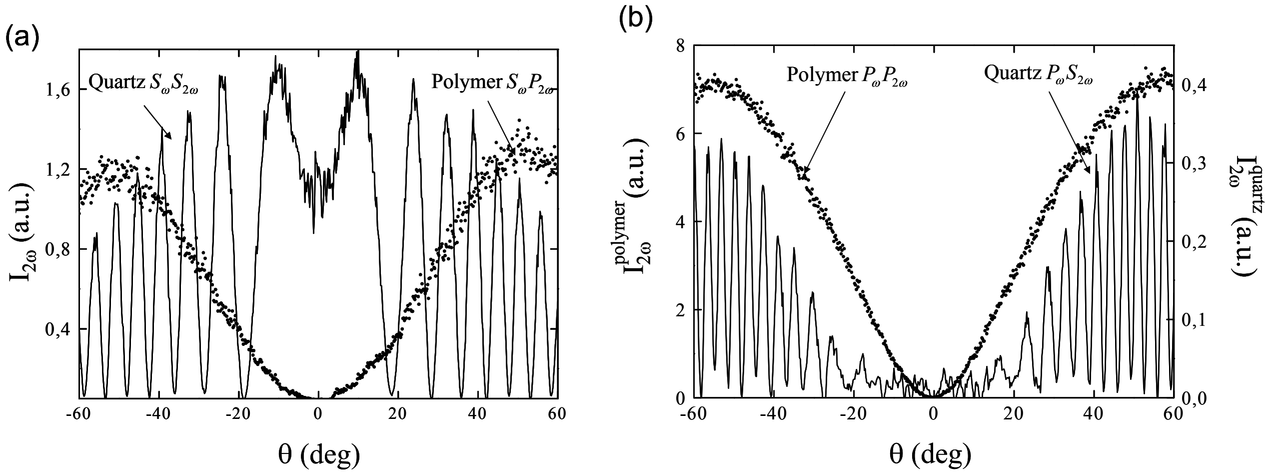

Figure 3 : Maker fringes for the polymer thin film and the quartz crystal. (a) S-polarized fundamental incident beam. (b) P-polarized fundamental incident beam

The thickness of the polymer being less than the coherence length, no fringing is observed in contrast with the thicker 2mm-quartz, for which many coherence lengths are seen throughout the angular variation. In these figures, notation $X_\omega Y_{2\omega}$ refers to X-polarized fundamental incident beam and detection of Y-polarized second harmonic field. The components of the nonlinear quadratic susceptibility tensor, $2d_{13} = \chi^{(2)}_{xxz}(-2\omega;\omega,\omega)$ and $2d_{33} = \chi^{(2)}_{zzz}(-2\omega;\omega,\omega)$, are evaluated comparing results obtained with polymer thin film with those obtained from 2mm-thick quartz crystal for which d_{11} = 0.5 pm/V at 1.32 µm. First, d_{13} is evaluated from a $P_\omega S_{2\omega}$ polymer configuration. Then, the $P_\omega P_{2\omega}$ configuration allows for the determination of d_{33}. We found a ratio $d_{33}/d_{13} \approx 5$, that confirms previous results obtained from electro-optic measurements.

Conclusion

In conclusion, Fabry-Pérot interferometric technique and second harmonic measurement were used to determinate independently the components of nonlinear quadratic susceptibilities tensors from the visible up to 1.55µm, allowing to determine the dispersion of the electro-optic coefficients was measured. A constant $\chi^{(2)}_{zzz} / \chi^{(2)}_{xxz}$ ratio over the investigated wavelength range is greater than the theoretical value 3 predicted by the weak field independent molecule Langevin model. This points out the interaction of the chromophores with their environment which is further confirmed by the second harmonic generation measurements.

[1] M. Lee, H.E. Katz, C. Erben, D.M. Gill, P. Gopalan, J.D. Heber and D.J. McGee, *Science*, **Vol. 298**, 2002.
[2] A. Donval, E. Toussaere, R.Hierle and J. Zyss, *J. Appl. Phys.*, **Vol. 87**, N° 7, 2000.
[3] C. C. Teng and H. T. Man, *Applied Physics Letter*, **Vol. 56**, pp.1734-1736, 1990.
[4] J. S. Schildkraut, *Applied Optics*, **Vol. 29**, N° 19, pp. 2839-2841, 1990.
[5] H. Uchiki and T. Kobayashi, *J. Appl. Phys.*, **Vol. 64**, N° 5, 1988.
[6] M. Dumont and Y. Lévy, *Nonlinear Optics of Organics and Semiconductors*, **Vol. 36**, 1989.
[7] R. Meyrueix, M. Dickens, O.Lemonnier, J.Lecomte and G. Tapolsky, *Optics Communications*, **Vol. 110**, 445-455, 1994.
[8] R. Meyrueix, J.Lecomte and G. Tapolsky, *Nonlinear Optics*, **Vol. 1**, pp. 201-211, 1991.
[9] C. P. J. M. van der Vorst and S. J. Picken, *J. Opt. Soc. Am. B*, **Vol. 7**, N°3, pp 320-325, 1990.