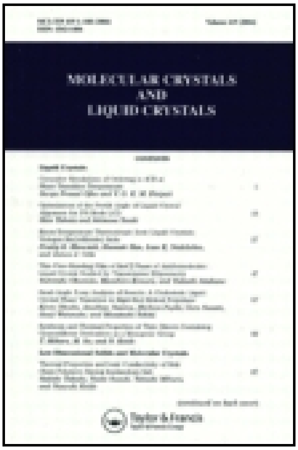

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Spectroscopic Linear and Nonlinear Optical Characterizations of Azopolymer Gratings Inscribed on p(DR1M) Thin Films

F. Lagugné-Labarthet [a] , J. L. Bruneel [a] & C. Sourisseau [a]

[a] LPCM, UMR 5803-CNRS, Université de Bordeaux 1, Talence Cedex, France

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F. Lagugné-Labarthet
J. L. Bruneel
C. Sourisseau
LPCM, UMR 5803-CNRS, Université de Bordeaux 1,
Talence Cedex, France

In this study we have investigated the electrical poling effects in a p(DR1M) azopolymer thin film and in related diffraction gratings inscribed on other films. Their optical properties were determined using polarization measurements in UV-visible spectroscopy, in confocal Raman micro-spectrometry and in second harmonic generation (SHG) in the transmission mode. Near-field scanning optical microscopy (NSOM) experiments together with SHG responses in reflection were also performed in order to retrieve simultaneously the topography and the SHG contrasts of the surface gratings. This multitechnique approach led to the determination of the first even and odd parity Legendre polynomials, from $\langle P_1\rangle$ *up to* $\langle P_4\rangle$*, allowing the establishment of precise chromophore orientational distribution functions.*

In particular, from SHG near-field scanning optical microscopy (NSOM) experiments we have evidenced that poled gratings with large diffraction efficiencies and $\chi^{(2)}$ *nonlinear susceptibilities exhibit new sub-structures with puzzling differences from their topographical AFM images. A combination of all the linear and nonlinear results allows us, for the first time, to explain the peculiar orientational and mechanical properties in the peak areas of the surface relief modulations, at near each half-period grating* ($\Lambda/2 \approx 0.7\ \mu m$)*. An efficient poling of the azobenzene dye groups in such gratings thus leads to new interesting properties.*

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Address correspondence to C. Sourisseau, LPCM, UMR 5803-CNRS, Université de Bordeaux 1, 351 cours de la Libération, 33405 Talence Cedex, France. E-mail: c.sourisseau@lpcm.u-bordeaux1.fr

Keywords: diffraction gratings; distribution functions; DR1 azobenzene; electrical poling; far-field Raman microscopy; near-field second harmonic generation; nonlinear optical property; order parameters

INTRODUCTION

The distribution of molecular orientations in a material has generally a great influence on its microscopic and macroscopic physical properties and, in particular, mesostructured systems with large optical nonlinearities may exhibit many potential photonics applications. In this respect, $\chi^{(2)}$ gratings inscribed on polymer thin films are important and attractive components allowing the generation and separation (over distinct diffracted orders) of the second harmonic wave from the fundamental one: they represent excellent alternatives to inorganic materials in terms of processability, reliability and low cost [1–3].

From both the fundamental and practical points of view, it is also very important to characterize the molecular orientations of active nonlinear optical (NLO) chromophores embedded in a polymer film and oriented upon poling. Using a high dc electric field, a direct corona- or wire-electrical poling process is generally thermally assisted by heating the film up to the polymer glass transition temperature and, then, by slowly cooling it down to room temperature while keeping the field on. So, a main challenge is to determine how long the polar molecular orientations are maintained in a noncentrosymmetric arrangment.

For this purpose we have thus made use of linear and nonlinear optical measurements, in order to estimate the first even and odd Legendre polynomials or order paremeters, including $\langle P_1 \rangle$ up to $\langle P_4 \rangle$, and to establish the related chromophore orientational distribution functions. This has been accomplished for a simple polymer thin film, just after poling and after several periods of relaxation, as well as for an already poled holographic grating inscribed on another film. Actually, we have combined the results of various polarization experiments in UV-visible, in far-field confocal Raman microscopy, in transmission second harmonic generation (SHG) spectroscopy, and in near-field SHG scanning optical microscopy (SHG-NSOM).

This work completes previous theoretical [4–5] and experimental studies, in Raman [6] and SHG-NSOM [7], all performed for efficiently poled homopolymer thin films and for nonlinear gratings inscribed on various p(DR1M) films. It establishes for the first time a direct comparison of the most probable orientational distribution functions associated with the azobenzene photochromes in these two kinds of anisotropic polymer thin films.

EXPERIMENTAL

Thin films of a covalently bonded azobenzene derivative, namely of the p(DR1M) homopolymer or [poly(4′-((2(methacryloyloxy)ethyl)-ethylamino)4-nitro-azobenzene)], were prepared by spin casting (1500 rpm) a solution of p(DR1M) in chloroform (5% by weight) onto clean microscope slides. The thickness of the films was controlled by atomic force microscopy (AFM) in contact mode and was found equal to ~290 nm for the simple poled films and to ~400 ± 10 nm for grating inscriptions, respectively. Several gratings with a period spacing of ~1.40 μm, displaying medium ($\eta = 12\%$) and high ($\eta = 25\%$) diffraction efficiencies, and surface relief modulations equal to 250 nm and 410 nm respectively, were prepared using two horizontally polarized (p + p) interfering laser beams (~ 50 mW/cm^2). Once the gratings were fabricated, the electrical poling was performed (at 90°C using 3 kV during 1 or 2 hour) using a home-made wire poling scheme. More details about the holographic setup for grating inscriptions, the beam intensity recordings of the various diffracted orders, the poling and relaxation (in the dark) processes, the far-field UV-visible, the polarized Raman confocal microscopy and the SHG transmission experiments and, finally, the near-field polarized SHG-NSOM measurements have been already published and can be found elsewhere [5–7].

THEORY AND BASIC FORMALISM

Here, we recall only some important theoretical expressions to derive the orientational distribution functions by using either the expansion series of Legendre polynomials or the Information entropy model and, to construct the most probable functions using a “modified entropy method.” The orientation distribution function $f(\theta, \phi, \psi)$ for any uniaxial system containing cylindrically symmetric azobenzene chromophores is completely defined by the polar angle (θ) between the unique long symmetry axis of the dye and a local laboratory vertical axis. In that case the distribution function $f(\theta)$ can be developed on the basis of the Legendre polynomials:

$$f(\theta) = \sum_{i=0}^{\infty} \left(i + \frac{1}{2}\right) \langle P_i \rangle \, P_i(\cos\theta) \tag{1}$$

where only even order polynomials are contributing in a centrosymmetric system, but both sets of odd and even parameters can be effective in a noncentrosymmetric polar sample; the order parameters or coefficients $\langle P_i \rangle$ are given by:

$$\langle P_i \rangle = \int_0^{\pi} P_i(\cos\theta)\, f(\theta)\sin(\theta)d\theta \tag{2}$$

with

$$\langle P_0 \rangle = 1.0; \quad \langle P_1 \rangle = \langle \cos\theta \rangle; \quad \langle P_2 \rangle = \frac{1}{2}\left(3\langle \cos^2\theta \rangle - 1\right);$$
$$\langle P_3 \rangle = \frac{1}{2}\left(5\langle \cos^3\theta \rangle - 3\langle \cos\theta \rangle\right) \text{ and } \langle P_4 \rangle = \frac{1}{8}\left(35\langle \cos^4\theta \rangle - 30\langle \cos^2\theta \rangle + 3\right) \tag{3}$$

The development in Eq. (1) is generally restricted to the first known $\langle P_i \rangle$ values and, obviously, it is not mandatory that the series is converging. As already discussed in the literature [4,5], it is more accurate to determine the equilibrium and most probable orientational distribution function $f(\theta)$ by maximazing the information entropy (S) of the distribution,

$$\mathrm{S}(f(\theta)) = -\int_0^{\pi} f(\theta) ln[f(\theta)] sin(\theta) d\theta \tag{4}$$

Using the Lagrange method of undetermined multipliers, λ_i (i = 1 to 4), this leads to the physically meaningful in any spatial region and most probable (*mp*) normalized function:

$$f_{mp}(\theta) = \frac{\exp[\lambda_1 P_1(\cos\theta) + \lambda_2 P_2(\cos\theta) + \lambda_3 P_3(\cos\theta) + \lambda_4 P_4(\cos\theta)]}{\oint_{-1}^{+1} \exp[\lambda_1 P_1(\cos\theta) + \lambda_2 P_2(\cos\theta) + \lambda_3 P_3(\cos\theta) + \lambda_4 P_4(\cos\theta)] d(\cos\theta)} \tag{5}$$

Actually, this powerful method can only be applied when several $\langle P_i \rangle$ parameters are well known. In this study, $\langle P_1 \rangle$ and $\langle P_3 \rangle$ were determined from SHG transmittance measurements using the "pp" and "sp" polarization setups ("p" and "s" mean in-plane and out-of-plane polarization, respectively),

$$\langle P_1 \rangle = \frac{2(d_{33} + 2d_{31})}{N\beta^*_{zzz}} \text{ and } \langle P_3 \rangle = \frac{2(d_{33} - 3d_{31})}{N\beta^*_{zzz}} \tag{6}$$

where d_{ij} are the nonlinear coefficients and $N\beta^*_{zzz}$ is the local field corrected hyper- polarizability component ($N\beta_{zzz} \approx 586.0\,\mathrm{pm/V}$ at 1064 nm). Furthermore, $\langle P_2 \rangle$ and $\langle P_4 \rangle$ were estimated in different surface regions of the gratings from results of polarized Raman microscopy data. However, in the simple poled films the $\langle P_2 \rangle$ parameter value was only known either from the UV-visible spectra,

$$\langle P_2 \rangle = 1 - \frac{A_\perp}{A_0} = \frac{A_{//} - A_\perp}{A_{//} + 2A_\perp} \tag{7}$$

where the symbols parallel (//) and perpendicular ($\perp$) are defined with respect to the poling direction, respectively, or from our complete treatments of the SHG data which were including the one photon anisotropic absorption contributions at the harmonic frequency ($2\omega = 532\,\text{nm}$). So, during the fitting procedures we have adjusted the $\langle P_4 \rangle$ value in order to satisfy Eqs. (4)–(5) and also to obtain a best fit agreement between the function stemmed from the series truncated at the fourth order (Eq. (1)) with that adjusted using the general information entropy model (Eq. (5)): This process was referred as "modified maximum entropy approach" and appeared to be rapidly converging, leading always to practical results with reasonable values for all the parameters [5,6].

RESULTS AND DISCUSSION

The main results concerning the values of the nonlinear coefficients (d_{33} and d_{31}) and of the best fit values of the order parameters (from $\langle P_1 \rangle$ up to $\langle P_4 \rangle$) in an efficiently poled thin film and in a poled grating are summarized in Table 1; the corresponding shapes of the most probable distribution functions are reported in Figures 1 and 2, respectively.

TABLE 1 Values of the Nonlinear Coefficients (dij) and the Four Legendre Polynomials or Order Parameters ($\langle P_1 \rangle$ to $\langle P_4 \rangle$) in a p(DR1M) Thin Film and in a Diffraction Grating after an Electrical Poling Process, and Main Properties of the Related Chromophore Orientation Distribution Functions

	d_{33} pm/V	d_{31} pm/V	$\langle P_1 \rangle$	$\langle P_2 \rangle$	$\langle P_3 \rangle$	$\langle P_4 \rangle$	Function type
Poled thin film							
After 1 hour	437	~78	0.188	0.494	0.064	0.164	Oblate Max. at 0°
After 1 day	204	~45	0.129	0.286	0.030	0.063	Oblate Max. at 0°
After 42 days	117	~21	0.070	0.197	0.024	0.035	Oblate Max. at 0°
Poled grating							
Bottoms	15.7	~4.4	0.085	0.228	0.004	–0.067	Asymm. Max. ± 34°
Intermediates	62.1	~9.2	0.277	0.251	0.121	–0.153	Asymm. Max. ± 35°
Tops	44.4	~7.2	0.201	0.266	0.072	–0.230	Asymm. Max. ± 35°

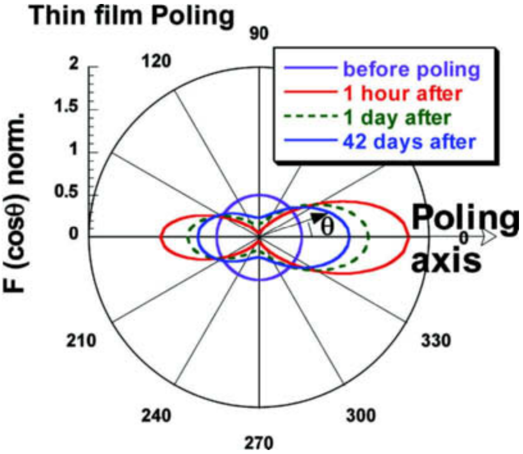

FIGURE 1 Most probable normalized distribution functions calculated by using the four $\langle P_1\rangle, \langle P_2\rangle, \langle P_3\rangle$ and $\langle P_4\rangle$ order parameters in a p(DR1M) polymer thin film before poling (isotropic case, circle), after a two hours poling and several relaxation periods (1 hour, 1 day and 42 days, respectively) in the dark; the length of any vector from the origin to a curve represents the magnitude of the distribution in that direction.

First, in the polymer thin film it is remarkable that the wire process has led to a huge value of the d_{33} coefficient as large as ~440 pm/V at 1064 nm (with respect to quartz with $d_{11} = 0.30$ pm/V) just one hour after poling; also, a relatively slow decay of the second harmonic power is observed over time, even after a 42 day period of relaxation in

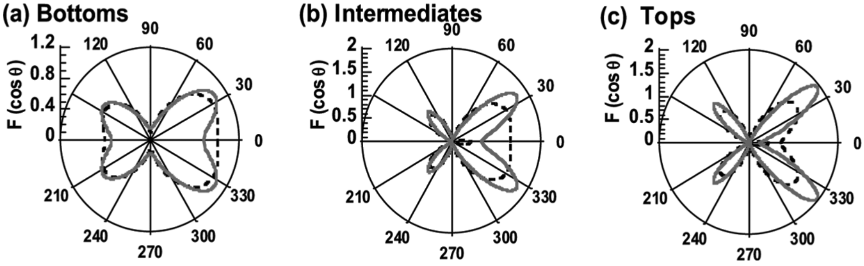

FIGURE 2 Most probable normalized distribution functions (solid lines) estimated from the four $\langle P_1\rangle, \langle P_2\rangle, \langle P_3\rangle$ and $\langle P_4\rangle$ parameter values in various regions of the surface relief of a p(DR1M) diffraction grating after 1 hour electrical poling at 90°C; the dashed curves represent the corresponding functions calculated by using the limited polynomial series.

the dark. A strong polar ordering of the chromophores has been established under high field conditions and is persistent in the film. This is confirmed by the relatively large and positive values of the $\langle P_1 \rangle$ and $\langle P_2 \rangle$ parameters, whereas the $\langle P_3 \rangle$ polynomial displays weaker values. Using the "modified maximum entropy method" the $\langle P_4 \rangle$ values have been fitted and the whole data have thus allowed us to construct the related orientational functions. As shown on Figure 1, they give rise to two-leaved oblate type curves exhibiting a very intense maximum at 0° and a weaker one at 180°.

The strong polar ordering of the chromophores can then be rationalized by the area ratios of the two-leaved curves which demonstrate that the proportion of field-oriented molecules remains significant, and only decreases from 74% down to 54% after 42 days.

The experimental results for the studied poled gratings were by far more complex since, as above mentioned, the orientation functions are now dependent on the diffraction efficiency, on the amplitude of surface relief modulation and on the surface spatial region, namely in the bottom, intermediate or top position, respectively. We thus report in Table 1 only the results obtained in the various surface regions of a 25% diffraction efficiency grating with a large surface relief modulation of ~410 nm. In that case, after a thermal dc poling at 90°C during 1 h, polarized near-field SHG-NSOM experiments have provided clear evidences for the existence of persistent new half-period substructures in contrast with topography images [6,7]. So, relatively large and positive $\langle P_1 \rangle$ and $\langle P_3 \rangle$ parameter values in agreement with strong polar asymmetric distributions are observed in the intermediate and top grating regions, while very weak values are effective in the bottom positions, suggesting a polar but less anisotropic distribution (Table 1). In contrast, the even order parameters determined from confocal Raman microscopic measurements show slight variations on the large and positive $\langle P_2 \rangle$ values, but pronounced variations on the $\langle P_4 \rangle$ coefficients which become more and more negative on going from bottom, to intermediate, and top positions. Consequently, because of the $\langle P_4 \rangle$ variations and as shown on Figure 2 (solid lines), the final orientation functions calculated using the maximum entropy method look like bimodal asymmetric polar distributions, which are in the same ordering more sharply peaked at ±35°. It is noteworthy that the introduction of the same four parameter values into the series expansion of Eq. (1) would lead in general to broader distributions and, in particular, meaningless negative distributions at near 90° and 180° in the intermediate and top surface grating positions (Fig. 2 dashed lines).

This justifies our used theoretical approach and allows us to definitely conclude, in a good agreement with the new bumps observed in near-field SHG-NSOM experiments, to a deficiency in the chromophore density and in the uniaxial polar ordering at the exact top or half-period positions. The shapes of these final distributions may also suggest the persistence of antiparallel interacting chromophores in these restricted stiffer areas, the viscoelastic properties of which are surely modified during the grating formation because of the photoisomerization cycles and the diffusion processes from the higher irradiation intensity regions (wells) to the lower intensity ones (ridges).

As a conclusion, in this spectroscopic and theoretical study we have focussed our attention on the orientation properties of azobenzene chromophores in a poled polymer thin film and in various regions of an electrically poled grating inscribed on another film. We have clearly emphasized that complementary experimental techniques, such as nonlinear polarized SHG-NSOM and linear polarized Raman confocal microscopies, which are sensitive to the first odd and even orientational order parameters, respectively, are particularly well adapted for the investigation of the dye distribution functions in these noncentrosymmetric polymer systems. The both non-destructive techniques can afford new consistent information at the molecular level and at a sub-micronic spatial resolution, provided that the polarized data treatments are carefully examined and that physically meaningful related orientational distribution functions are properly constructed.

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