

Monitoring molecular orientational order in NLO push–pull based polymeric films via photoacoustic measurements

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ABSTRACT

The pulsed-laser photoacoustic-technique (PLPA) was implemented to characterize molecular orientational order and anisotropy in push–pull poled polymeric films as function of temperature and laser polarization. Traditionally, photoacoustic signals are considered to be directly proportional to the linear optical absorption in amorphous media. In this work, however, it is shown that photoacoustic signals can also be highly sensitive to the material anisotropy when convenient polarization dependent photoacoustic analyses are performed. Thus, variation of the molecular orientation in organic films, comprising rod-like polar chromophores, can be unambiguously monitored via rms-analyses performed on the amplitude of the generated opto-acoustical PLPA-signals as function of the incident laser polarization. This result can be useful for the characterization of organic-based nonlinear optical (NLO) poled films and, in general, in studies of anisotropic materials. In fact, in this work we were able to accurately determine the molecular order parameter (ϕ) of a NLO-active spin-coated polymeric film containing optically active push–pull chromophores. These molecules, previously oriented via an electrical-poling procedure, are capable to exhibit strong second harmonic generation (SHG) effects. The PLPA-measurements were systematically compared to the linear UV–vis optical absorbance spectra while heating the poled film sample in order to monitor the thermally induced molecular disorder, so that the order parameter may be photo-acoustically evaluated via the PLPA-signals generated from the poled to the unpoled film phase. These PLPA-experiments were performed taking into account the UV–vis reference spectra for calibration and comparison purposes in the evaluation of the order parameter. A significant advantage of the PLPA-technique over commonly used optical spectral methodologies is its convenient applicability in samples exhibiting poor or null optical transmission.

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1. Introduction

In recent years, interest in the development and applications of oriented push–pull organic films has increased considerably. As this trend grows, so does the need for accurate and reliable techniques for the measurement and determination of the molecular orientational properties. For instance, in the field of nonlinear optics, the fabrication and characterization of highly aligned rod-like and push–pull dipolar compounds are crucial factors for the improvement of ferroelectric functional materials, such as anisotropic organic films specifically designed for quadratic nonlinear optical NLO-applications (for instance SHG) and other regarding phenomena [1–3]. In the dipolar regime, these systems should exhibit high molecular alignment and polar order (if possible, in an infinite-fold rotational axis: $C_{\infty v}$ symmetry), which is equivalent to a non-centrosymmetric crystalline arrangement [4]. Moreover, there is a variety of other phenomena, which also demand stable molecular orientation and

non-centrosymmetric structural properties [5]; for example, pyroelectric and piezoelectric activity can also be present in organic materials such as polyvinylidene fluoride (PVDF) poled films, which are commonly used in sensor and battery applications [6,7].

Traditionally, the molecular orientational distribution (usually defined and quantified as the order parameter, ϕ) in poled organic films has been determined from UV–vis absorbance spectral measurements [8], or others methodologies based on NLO-phenomena where the intensity of the transmitted SHG-beam measured from a semi-transparent, oriented probe sample, is compared to the SHG-signal produced by a well known reference sample. This procedure allows the relative evaluation of the order parameter [9]. However, investigations concerning molecular ordering in nonstandard, dispersive, or even in highly opaque polymeric films may become a difficult task when implementing these standard methodologies. This is due to experimental limitations in the acquisition and analysis of weak transmitted linear or nonlinear optical signals. In this work, a novel approach based on photoacoustic measurements to specify molecular ordering in electrically poled push–pull polymeric films, is proposed. This method is based on the PLPA-analysis of the opto-acoustical signals generated within the sample via its optical

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absorptive properties. In fact, we show in this article that the PLPA-technique is capable of resolving molecular ordering given that the PLPA-signals are directly related to the linear optical absorption, which depend, on the other hand, on the structural molecular arrangements of the sample [10]. Indeed, in-situ variation of the molecular orientation of a representative organic film comprising polar chromophores can be unambiguously monitored in polarization and temperature-dependent PLPA-experiments via an adequate rms-analysis of the amplitude of these opto-acoustical signals.

2. Basic concepts and theory

2.1. Fundamentals of the pulsed laser photoacoustic technique (PLPA)

The PLPA-technique takes advantage of the electronic de-excitation induced in a material after applying a high-intensity pulsed laser beam. This photophysical interaction produces, among other physical effects, acoustic waves traveling within the material lattice. The generated acoustic signals (in the ultrasonic regime) are primarily generated within the excited material volume due to fast thermal processes taking place as a non-radiative response to the absorbed light. Since the amplitude of the photoacoustic waves are proportional to the laser excitation intensity and to sample's optical absorptive properties, the PLPA-technique offers the advantages and simplicity of the UV-vis absorbance based spectroscopic detection, with a high sensitivity comparable to other optical transmission techniques [9]. In a typical PLPA-experiment, the acoustic waves travel at the characteristic speed of sound of the excited material to reach a coupled piezoelectric detector/microphone; this allows the mechanical-electrical experimental interface to collect the PLPA-data from the sample on a digital oscilloscope for further analyses (usually performed via numerical algorithms). The experimental simplicity to obtain photoacoustic signals has led to the development of several PLPA-based measurement devices, which are commonly used for the accurate evaluation of thermal and optical material properties (for instance, thermodynamic phase transitions [11] or absorption coefficients [12]) of different materials such as: crystals, semiconductors and polymers [13]. In summary, several physical and structural material characteristics can be efficiently studied by means of diverse PLPA-based techniques and the adequate data analysis thereof.

2.2. Molecular alignment and UV-vis spectroscopic determination of the order parameter

The molecular design and synthesis of novel chemical compounds for NLO-applications has traditionally been dominated by molecular templates consisting of electron-donor and electron-acceptor groups (*D*- and *A*-groups, respectively). These moieties are usually bonded to complex molecular structures rich in delocalized-quantum electrons (π -electrons) such as aromatic compounds. These kinds of *D*- π -*A* antenna-like compounds generally form dipolar molecules with a C_n or C_{nv} symmetry and rod-like appearance and are commonly known as push-pull compounds. Unfortunately, most of these compounds reorganize or crystallize in centrosymmetric space groups due to electrical self-organization and mutually cancellation of their dipolar moments [3], which is totally inappropriate to exhibit strong pyro- or piezo-electricity effects, as well as quadratic NLO-activity within the dipolar regime. As a practical alternative, these push-pull molecules are frequently deposited onto ITO-coated¹ glass substrates and then electrically

poled in order to achieve a macroscopically oriented molecular film structure. In this way, these molecules can exhibit stable and efficient quadratic NLO-activity such as SHG due to their non-centrosymmetric molecular organization. To this end, so called "wet deposition techniques" (such as spin coating, dip coating or spray coating-deposition, among other methodologies) are generally implemented. At this first deposition stage, the optical chromophores are randomly distributed within the film geometry showing a macroscopic centrosymmetric and quasi-isotropic structure. Afterwards, a high intensity DC-electric field can be applied in order to align the respective chromophores. This poling procedure should be performed at a suitable temperature conditions (typically around the glass transition temperature T_g of the organic compound) for a convenient period of time. The T_g -value defines the thermodynamic state in which the organic compound presents its highest molecular mobility, still preserving its chemical and physical properties (i.e. just before the onset of the compound degradation stage). Depending on the thermal and structural properties of the compound, the poling-procedure may take from 30 min to 3 h in order to achieve an optimal molecular orientation. After this electrical poling process, the sample is cooled down to room conditions (T_0), keeping the DC-field on in order to avoid molecular disalignment. Thereafter, the poled organic film is ready for spectral-, NLO- and PLPA-characterizations in order to investigate the electrically induced molecular alignment, film symmetry and variations on the thermally induced molecular disorder.

It should be remarked that the applied DC-electric field, acting perpendicularly to film's plane, induces an optically uniaxial symmetry after molecular poling; thus, the ordinary refractive index (n_o) axis of the organic film is parallel to the direction of the electric field; whereas the extraordinary one (n_e) lies along the in-plane film direction (perpendicular to the poling electric field). In the case of spin-coated films, just before electrical poling, n_o is only slightly smaller than n_e (with $n_e - n_o \sim 0.0001$). The poling procedure drastically modifies this situation, increasing the material anisotropy and inducing a large optical birefringence (with $n_e - n_o \sim 0.05$) [14]. The connection between the change in the linear optical parameters as a consequence of the induced molecular alignment and order parameter has been thoroughly studied; we summarize in the following points the three main results of these investigations [15,16]:

- (1) Due to the electrically induced molecular orientation, the characteristic optical absorbance band of an organic film decreases. This effect can be optimally detected at normal optical incidence conditions. In this case, the ratio between the absorbance spectral variations (ΔA) induced by the poling process and the original absorbance spectra (A_0 : absorbance peak value measured before molecular poling), is proportional to the average orientational distribution [$3 \langle \cos^3 \theta \rangle - 1$]/2, and is usually defined as the order parameter ϕ . Since the difference in the peak intensity values of the optical absorbance (ΔA : measured before and after performing the poling process), and the initial absorption (A_0), are traditionally detected via UV-vis optical spectroscopic methods, this parameter is commonly defined as the molecular order parameter, we define this coefficient as ϕ_{OPT} for the purposes of this work:

$$\phi_{OPT} = \frac{\Delta A}{A_0} \cong \frac{3 \langle \cos^3 \theta \rangle - 1}{2}. \quad (1)$$

It is clear that the ϕ_{OPT} parameter is limited within the 0–1 range; where $\phi_{OPT}=0$ represents a fully disordered molecular phase, whereas $\phi_{OPT}=1$ corresponds to an optimally aligned molecular phase. θ represents the angle between the chromophore dipole moment (for polar compounds) and the direction

¹ ITO (Indium Tin-Oxide) electro-conductive coatings are deposited onto glass substrates and are commonly implemented as electrical contacts in opto-electronic and electro-optical applications. This material is deposited as a thin film and may present any desired electrical resistivity conserving an adequate optical transparency.

of the poling DC-field (parallel to substrate's normal vector). Experimentally, the best reported values for electrically poled push-pull based polymer films are in the order of $\phi_{OPT}=0.5-0.6$ [17].

- (2) Compared to the polymer backbone, the large electronic polarizabilities of the chromophores immersed within the organic structure, induce a general increase of the refractive indices n_o and n_e . Thus, after electrical poling, the film acquires outstanding birefringent properties (with $n_e - n_o > 0$), which is strongly related to the induced chromophore orientation [14]. In this case, the optical order parameter can also be associated with the intrinsic birefringence as follows:

$$\phi_{OPT} = \frac{n_e^2 - n_o^2}{n_e^2 + 2n_o^2}. \quad (2)$$

- (3) Additionally, according to several soft-matter molecular phase models [14–16], the order parameter can also be written as a function of other physical parameters, which are directly related to the implemented poling field. The main parameters in such techniques are the local poling field E_{poling}^l and the poling temperature T_{poling} ; thus, the optical order parameter can also be written as

$$\phi_{OPT} = \frac{1}{15} \left[\frac{\mu E_{poling}^l}{kT_{poling}} \right]^2, \quad (3)$$

where μ represents the molecular dipole moment and k is the Boltzmann constant.

Thus, it is evident that a simple UV–vis spectral analysis of the studied sample can allow the determination of several physical parameters, such as the optical order parameter, birefringent properties and the local poling electric field. In the present work, it is our main objective to show that the PLPA experimental technique can be directly used as an alternative methodology to determine the molecular structuring and orientational optical properties of push-pull based NLO-active films. One important aspect to be considered in typical optical absorbance spectroscopic measurements is the fact that these measurements are actually affected by two physical phenomena, namely the molecular optical absorption and the light scattering effects. These effects strongly depend on the microscopic molecular organization of a given material (*i.e.* on the isotropic or anisotropic molecular organization and on their respective absorption and scattering cross-sections), as well as on the nature of the excitation source (*i.e.* on the polarization state of the light source).

3. Experimental details

3.1. Polymer film preparation and electrical poling procedure

The implemented polymer was a Poly(hexa-2,4-diynylene-1,6-dioxy)benzoate polymer (named here PB-DR19) containing the Disperse-Red 19 push-pull molecule (DR19: 2,2'-[[3-methyl-4-[(4-nitrophenyl)azo]phenyl]imino]bisethanol) as optical chromophore. The DR19 reddish molecules consist of electron-donor and electron-acceptor functional groups linked to its molecular rod-like structure (see Fig. 1); here, the well-known and efficient withdrawing nitro-group (NO_2) has been selected in the synthesis of this compound. These functional groups are connected through an azobenzene chain acting as a bridge for π -electrons in their base and excited states, which gives rise to a D– π –A polar structure. In previous works, the synthesis and second-order NLO-properties of this polymer have been reported [18,19].

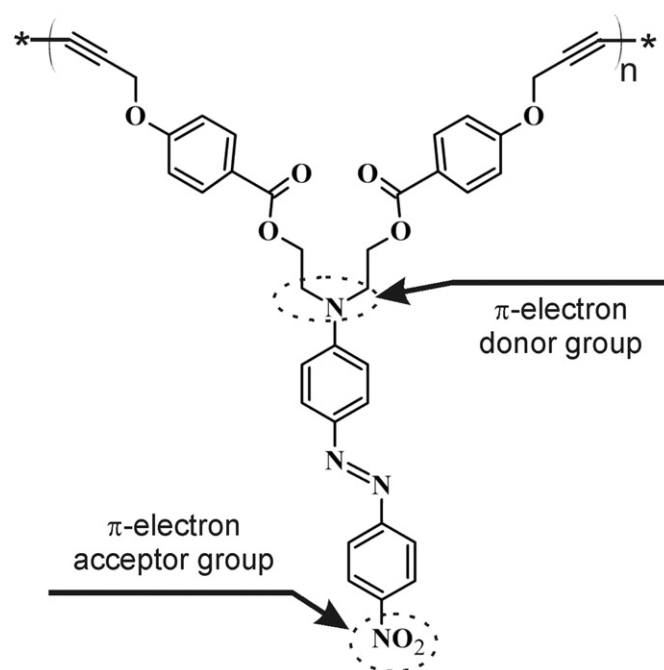


Fig. 1. Molecular structure of the Poly(hexa-2,4-diynylene-1,6-dioxy)benzoate (PB-DR19) polymer containing the optical chromophore Disperse Red 19 (DR19). This push-pull compound was implemented to monitor, via PLPA-measurements, the average chromophore orientation in spin-coated films after performing molecular electrical-poling and heating/cooling thermal processes.

For spin-coated film fabrication, 2.5 mg of the PB-DR19 probe polymer were dissolved in 4 mL of tetrahydrofuran (THF). With the aim of obtaining high quality films avoiding any molecular cluster formation, the saturated solution was ultrasonically mixed (10 min) and filtered through Teflon membrane filters (pore diameter: $\varnothing=0.22 \mu\text{m}$); this process assures a homogeneous solution to be used in spin-coating deposition procedures. Thereafter, the deposition of 2 mL of this solution was carried out onto ITO-coated glass substrates according to the following methodology: film deposition was performed in two steps; each layer was deposited with 1 mL (the spin-coating system was programmed to deposit one layer at 100 rpm for 15 s). Each bi-layered film was slowly dried at room temperature for one day. According to these conditions, deposited samples showed homogeneous structural properties and good optical and mechanical qualities; the film thickness of the obtained samples was $1.05 \mu\text{m}$ (measured with the AFM step-height measurement technique). Since the obtained films possess an average amorphous structure with only poor in-plane chromophore orientation due to spin-coating centrifugal forces, it was necessary to induce a significant molecular ordering perpendicularly to the substrate plane. In this way, a macroscopic non-centrosymmetric polar order within the film volume can be induced, as required for quadratic NLO-effects. A well established methodology developed to optimally achieve this objective is the “corona poling procedure”; this technique implements an open temperature controlled oven equipped with a vertical non-oxidizable iron needle acting as the anode, while the ITO-substrate layer of the sample acts as the cathode [15,20]. By a proper implementation of this technique, the poling conditions for convenient chromophore alignment of our samples were set as follows: the T_g -value of the polymer was $\sim 146^\circ\text{C}$, thus the sample temperature was raised from room conditions to the T_g -temperature range in order to allow high molecular mobility ($T_{poling} \sim 150^\circ\text{C}$); then the applied voltage was set to +5.00 kV at a needle-film gap distance of $\sim 10 \text{ mm}$; these conditions were kept for at least 40 min. Subsequently, film samples were slowly cooled down to

room temperature, the applied DC-field was kept on to preserve the induced molecular alignment while cooling. At this point, prepared film samples were ready for PLPA-, SHG- and spectroscopic-characterizations.

3.2. Photoacoustic and UV-vis absorption spectroscopic detection

In Fig. 2 the experimental set-up implemented for the simultaneous detection of the PLPA-signals and the UV-vis optical absorbance spectra is schematically presented. The film sample is illuminated with a *P*-polarized Q-switched frequency-doubled Nd:YAG laser system (Minilite II, from Continuum, USA) along the *z*-direction at an optical incidence of 45° (see reference axes in Fig. 2); the laser source generates light pulses of $\tau \approx 7$ ns and operates at a repetition rate of 10 Hz with maximum output energy of ~ 5.0 mJ/pulse (@ 532 nm). The spatial mode of the laser is close to a Gaussian TEM₀₀ mode (with a laser spot diameter of $\varnothing \approx 5.3$ mm); the laser beam was not focused in order to avoid either lateral diffusion of heat or photo-bleaching damage on the sample. Thus, an incident laser fluence of ~ 226.6 J/m² on the film sample allows the excitation of a large number of chromophores within the large laser spot, this experimental condition guarantees a representative and non-local acquisition of PLPA-signals arising from the excited organic chromophores. A fast photodiode detector (Thorlabs Inc., FDS010, rise time: $\tau_{\text{Rise}} < 1$ ns) is implemented after a beam-splitter to trigger a digital oscilloscope (Tektroniks, TDS5040). The organic film is mounted on a home-made oven stage consisting of a copper box of $10 \times 5 \times 5$ mm³, which is connected to a couple of electrical resistances in order to supply the heating/cooling temperature ramps via a digital control board. As acoustical detector, a 500 KHz PZT cylindrical piezoelectric transducer (PZT: Lead-Zirconate-Titanate, 10.0 mm in diameter) is attached to the center of the substrate (on the opposite side to the deposited film). The PZT-microphone transforms the generated acoustic wave signals to electronic ones, which are then averaged, visualized, stored and partially analyzed in the 500 MHz digital oscilloscope. Registered PLPA-signals are then processed in a personal computer via rms-numerical processes encoded in MatLab to single out relevant physical information of the photophysical interaction.

On the other hand, a Xenon lamp (Oriel, 66,023) equipped with a universal power supply of 400–1000 W (Oriel, 6882) is used to simultaneously illuminate the sample at normal optical incidence (along the *x*-reference axis). The purely transmitted beam is captured by a multi-modal quartz optical fiber (600 μ m core aperture) in order to evaluate the optical absorption of the sample within the 400–1000 nm spectral range by means of an optical spectrometer (Ocean Optics, HR4000CG UV-NIR). In this way, in-situ

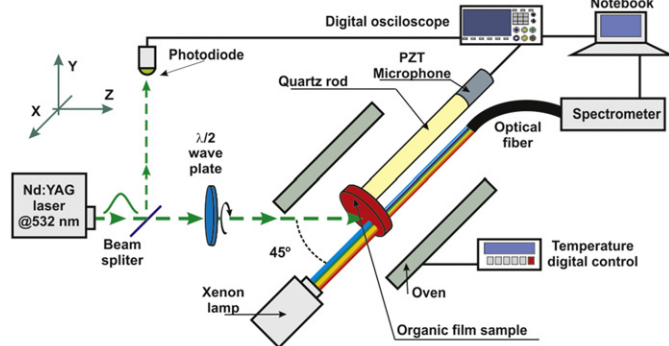


Fig. 2. Schematic representation of the PLPA-experimental set-up implemented for the monitoring of the molecular orientational ordering in the PB-DR19-based poled organic film as function of temperature. In this device it is possible to perform the simultaneous detection of the photoacoustic and optical transmission data.

PLPA- and absorbance-measurements can be simultaneously monitored during experiments as different thermal treatments are applied to the probe sample.

Additionally, in order to verify the efficiency of the electrically induced chromophore alignment, SHG-transmission signals (@ $\lambda_{2\omega} = 532$ nm) were independently measured on the probe sample at different temperatures in a separate experimental set-up. Briefly, the SHG-device consists of a Nd:YAG laser system with fundamental excitation @ $\lambda_{\omega} = 1064$ nm. SHG-data was obtained according to the well established Maker fringes method; details on the implemented experimental set-up are given in the recent literature [2,21].

4. Results and discussion

4.1. UV-vis absorbance spectra and nonlinear SHG-measurements

Fig. 3 shows the absorbance spectra of a poled PB-DR19-based organic film obtained at contrasting temperature conditions ($T_0 = 23^\circ\text{C}$ and $T_g = 146^\circ\text{C}$, respectively). The UV-vis reference spectrum of an ITO-coated glass substrate is also shown in this figure; this material exhibits high transparency within the whole visible spectral region at the implemented temperature working range. By contrast, as temperature is increased in the PB-DR19-based poled film, a clear increment of its characteristic absorbance band is detected. During this process, no significant band shifts or deformations were detected; hence, no evident chemical modifications (e.g. sample degradation or oxidation processes) can be confirmed. Indeed, in an ideal organic poled film, the oriented rod-like chromophores (orthogonally aligned to the substrate plane), tend to transmit more incident light than unpoled film samples (this effect strictly applies at normal optical incidence conditions). On the other hand, given that UV-vis spectroscopy measures the optical attenuation (or optical absorbance, which consists of the sum of both the pure molecular optical absorption and optical scattering along the optical path using Beer's law), it is then expected that as the chromophores lose their collective alignment with increasing temperature, they present different optical interaction cross-sections (*i.e.* absorption

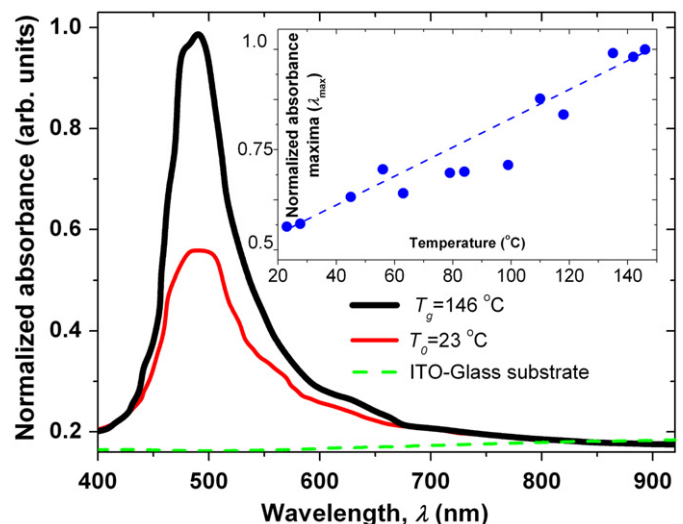


Fig. 3. Normalized temperature dependent UV-vis absorbance spectral features obtained from the studied PB-DR19-based spin-coated poled film. The probe film exhibits a strong and characteristic absorbance band within the visible range, which is highly sensitive to molecular ordering. The inset in this figure shows the variations on the absorbance peak as the sample temperature is increased within the T_0 - T_g range.

and scattering cross-sections). Hence, light beams traveling within such disordered media experience higher absorption and/or scattering effects, which may reduce the number of transmitted photons arriving at the photo-detector. In this way, the increment of the absorbance band intensity detected in our sample when implementing an unpolarized and incoherent Xenon lamp excitation (at normal incidence conditions), is in principle due to an increase of both optical absorption and scattering effects arising as a consequence of the thermally induced chromophore disorder. In fact, the absorbed energy causes an increment of the dipolar electronic vibrations and optical transitions, which can be transformed in derived re-emitted and scattered photons, but it can also induce strong energy dissipation in non-radiative phenomena such as heat diffusion and photo-acoustically (PA) induced mechanical vibrations through the material lattice (phonons). The inset in Fig. 3 shows the increment of the peak absorbance intensities (on heating) registered as the sample temperature increases from T_0 to T_g . Spectral analyses for temperatures beyond T_g are nonsense since organic samples undergoes irreversible degradation after their characteristic T_g values.

It is worth noting that the characteristic absorbance band of the film sample is located within the 450–550 nm visible spectral range. Thus, this band can be identified as the characteristic absorption band typically found in azobenzene based compounds exhibiting high conjugated π -electron activity [2]. Within this optical region, the light absorption of the DR19 chromophores is considerably larger than that observed for the ITO-glass substrate; hence, the photoacoustic signals generated from the organic film are expected to be significantly stronger. Indeed, the laser excitation emission line (at 532 nm) implemented in PLPA-experiments is located within the full width at half maximum (FWHM) of chromophore's absorbance band; thus, suitable resonant absorptive conditions are guaranteed. This fact offers an excellent opportunity for the easy detection of high amplitude photoacoustic signals via PLPA-experiments. It is important to point out that within the UV-vis spectral detection; no special absorbance peaks or adjoined absorptive bands produced by scattered laser light at 532 nm were detected for our probe film.

By applying Ec. 1 to the absorbance peak intensities measured from the PB-DR19-based film at both T_0 and T_g poled/unpoled states, an optical order parameter of $\phi_{OPT} \approx 0.40$ is obtained. This value denotes a good contrast ratio between the ordered and disordered molecular phases induced within the film sample by electrical poling and thermal relaxation processes, respectively. On the other hand, since the Xenon lamp is located far away from the probe sample and its characteristic spectral emissions occur in a continuous mode, the respective peak intensities are considered to be negligible compared to those produced by a monochromatic and coherent laser source. Thus, additional photoacoustic signals due to the Xenon lamp can be considered as negligible during simultaneous spectroscopic and laser excitation experiments. Furthermore, no sample temperature increase due to the Xenon lamp irradiation, capable of inducing substantial molecular disorder, was detected.

Finally in this section, Fig. 4 shows the variations on the SHG-signals measured from the poled probe film as function of increasing temperature. These reference SHG-measurements were performed in order to verify the efficiency of the corona-poling procedure, the convenient structuring of collective molecular ordering, the induced polar-order and the macroscopically arranged non-centrosymmetric organization. It is shown in Fig. 4, as in the case of UV-vis spectroscopic measurements, that the NLO/SHG-properties of the polymeric film are drastically affected by the induced temperature variations. In this case, maximal SHG-signals are obtained at room temperature (T_0), indicating a

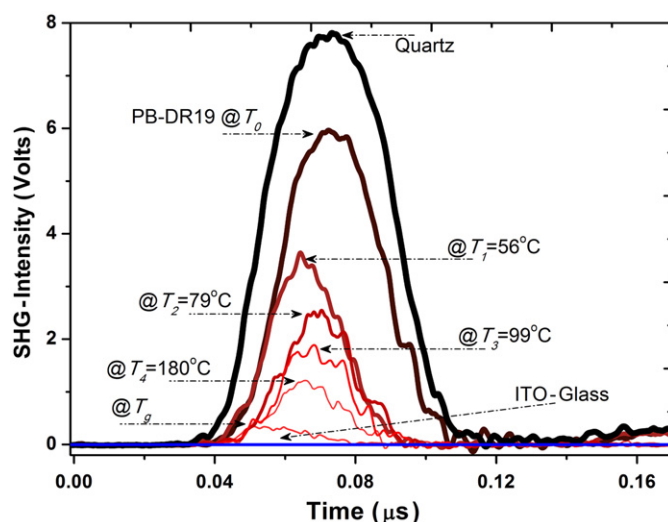


Fig. 4. Comparative temperature dependent SHG-signals recorded from the PB-DR19-based spin-coated poled film. Measurements were carried out within the T_0 – T_g temperature range at optimal SHG-conversion efficiency ($\theta_i \approx 45^\circ$).

successful molecular alignment (after poling). Conversely, as the film temperature increases, the SHG-activity decrease until the T_g -temperature range is reached, and the SHG-signals consequently disappear due to the loss of the collective polar ordering. As a matter of fact, the thermally induced molecular disorder completely destroys the macroscopic non-centrosymmetric molecular arrangements of the poled film, giving rise to an amorphous and isotropic film structure where quadratic NLO/SHG-phenomena are strictly forbidden (under the dipolar regime). The obtained SHG-signals were recorded within the characteristic SHG Maker fringe patterns measured for our probe film; particularly, the SHG-signals shown in Fig. 4 were directly recorded at an optical laser incidence of $\sim 45^\circ$, which corresponds to best possible phase-matchable conditions in our sample. At such conditions, highest possible SHG-intensities can be observed during Maker fringe recording. On the other hand, the SHG-signal obtained from an α -quartz crystalline sample (commonly implemented as standard NLO-reference material in SHG-calibration measurements) is also presented for comparison purposes only. Considering the tiny thickness of our organic film, it is concluded that the SHG-signals obtained from the PB-DR19-based film sample are relatively strong, which also verifies an adequate molecular alignment obtained via the corona-poling method.

4.2. Polarization dependent PLPA-photoacoustic measurements

Poled organic films give rise to birefringent anisotropic systems due to their inherent homogeneous rod-like chromophore alignment. Indeed, these films form linear dichroic structures after electrical poling, which can act as effective linear polarizers under convenient excitation. For this reason, poled films are suitable for polarization-dependent linear and nonlinear optical studies such as NLO/SHG and molecular birefringence characterizations, as in the case of nematic or smectic liquid crystalline materials confined in electro-optical (EO) cells [22,23]. In such investigations, input **P**- and **S**-polarized laser beams are typically implemented as excitation sources. Analogously, we have performed polarization-dependent opto-acoustical measurements in our PB-DR19-based poled organic films at different temperatures in order to investigate their molecular orientational properties by means of the PLPA-technique. First of all, we show in Fig. 5 two typical examples of unprocessed PLPA-signals obtained from the poled film under **P**-polarized laser irradiation

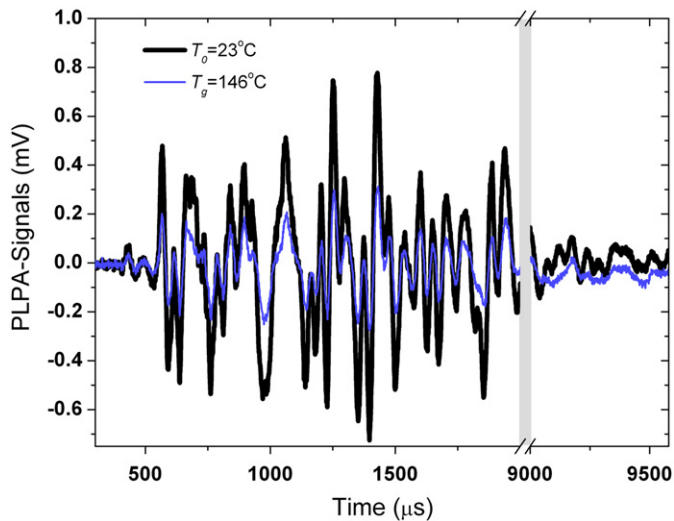


Fig. 5. Typical unprocessed PLPA-signals directly recorded from the oscilloscope screen for the poled organic film at T_0 and T_g thermodynamic states. These signals correspond to the minimal and maximal optical absorbance registered in the sample for the poled and thermally unpoled phases, respectively. PLPA signal frequency and phase changes are negligible, only the PLPA relative amplitude variations and the signal decrement/damping (in time) are of relevance in photophysical analyses (implemented PLPA averaging: 130 samples at each temperature step).

at meaningful and contrasting thermal conditions ($T_0 = 23^\circ\text{C}$ and $T_g = 146^\circ\text{C}$). These PLPA-signals were directly recorded in the oscilloscope with an averaging of 130 PLPA-signal samples (one sample per laser pulse) at each selected temperature. The obtained PLPA-signals correspond to opposite optical absorbance conditions (as measured with the unpolarized Xenon lamp) corresponding to the poled and unpoled film states (*i.e.* minimal and maximal optical absorbance, respectively). Again, under these experimental conditions, a clear difference in the averaged amplitude of the PLPA-signals can be unambiguously observed. In this case, however, the strongest PLPA-signal (in amplitude) is obtained from the electrically poled film sample (exhibiting lower optical absorbance at T_0 with the unpolarized Xenon lamp), whereas the weaker PLPA-signal is obtained from the heated sample (exhibiting higher optical absorbance at T_g with the Xenon lamp excitation). This significant result indicates the importance of performing polarization-dependent photoacoustic studies in anisotropic media to further understand the physical information generated via PLPA-measurements in such systems; thus, the derived opto-acoustical data can be better analyzed to reveal additional information in material characterizations and measurement technology.

As previously mentioned, the photoacoustic signal detection has been traditionally thought to be directly proportional to the optical sample absorption, *i.e.*, the higher the optical absorption, the stronger the induced photoacoustic signals. This condition is indeed strictly valid for amorphous isotropic materials [24,25]. However, by analyzing the effect of both *P*- and *S*-laser polarized beams on the induced PA-signals generated from highly anisotropic and absorptive organic materials (see below), it is concluded that a polarization-dependent PLPA-analysis may play an important role in the characterization of structured materials. In our case, the obtained PLPA-signals, as recorded from the oscilloscope screen, are typically composed of several oscillations with different amplitudes. These signals slowly decay in time as the acoustic-waves lose energy while traveling within the material lattice. Differences between the relative phases and frequency components of the PLPA-signals measured in the poled and thermally unpoled sample phases are not detected. In general, the amplitude

variations observed on the PLPA-signals are directly related to the optical absorptive properties of the sample, while phase and frequency variations are primarily connected to the optical reemission and optical impedance of the material at the selected wavelength [10]. Consequently, a polarization-dependent systematic study of the PLPA-signals within the meaningful 23–146 °C temperature range may reveal fundamental information regarding the loss of structural orientation and anisotropy of our PB-DR19-based probe film. In fact, such studies, if feasible, may give rise to alternative photo-acoustical based calibration and experimental test procedures in materials characterizations, which could be very useful for the research of non-transparent media and materials systems with $C_{\infty v}$ or similar symmetries.

Fig. 6 shows the amplitude rms-analyses of the temperature dependent PLPA-signals obtained under *P*- and *S*-incident polarized excitations in the PB-DR19-based film. These experimental data provide information concerning the averaged amplitude of the PLPA-signals obtained at different temperatures. As temperature increases from T_0 to T_g , both *P*- and *S*-induced PLPA-signals (as shown in Fig. 5) exhibit a drastic decrease in their average amplitudes, which is clearly evidenced via the amplitude rms-analyses as a monotonically decrement of the obtained PLPA processed data (see Fig. 6). This effect is evidently attributed to the thermally induced molecular disorder, which simultaneously induces drastic changes on the respective absorptive and impedance material properties. However, in contrast to the spectroscopic measurements performed with the unpolarized Xenon lamp at normal optical incidence, it should be remarked that optimal PLPA-signal detection and maximal contrast (see Eq. (4)) between the *P*- and *S*-induced PA-waves can be only obtained at an optical laser incidence of $\sim 45^\circ$. Indeed, in an ideal collective chromophore orientation (vertically aligned to substrate's plane), most favorable optical molecular excitation (particularly under incident *P*-polarized light) can be achieved at $\theta_i \approx 45^\circ$. This is due to the strongest photophysical interaction occurring between the molecular long-axis and the *P*-polarized laser beam at this particular incidence angle. In other words, under this excitation geometry, an optimal light-matter interaction takes place due to the larger molecular and optical interaction cross-sections. In case of the *S*-polarized laser state, lower optical interaction and consequently weaker PLPA-signals are expected; this is

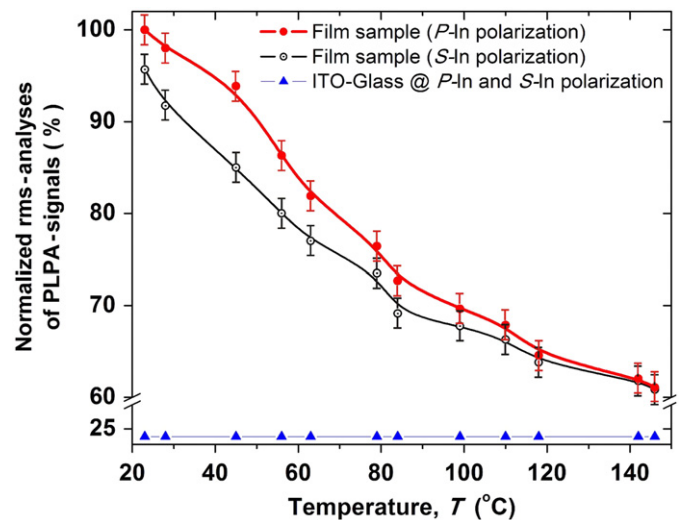


Fig. 6. Temperature dependent rms-amplitude analyses performed to the averaged PLPA-signals obtained from the electrically poled PB-DR19-based organic film at *P*- and *S*-incident laser beam polarizations. An estimated experimental error below 7% (error-bars) is also considered for the rms-analyses of the PLPA-data. The continuous lines are only drawn as guides to the eyes.

understandable for this excitation geometry due to the smaller optically-active molecular cross-section (corresponding to the short rod-like molecular-axis). These photophysical interactions are analogous to those observed in commercial organic polarizer films; in such cases, the molecular long-axis (typically comprising aligned polymeric chains) lies over the substrate plane. Thus, best possible optical incidence conditions to observe linearly polarized optical effects are at normal incidence. In the case of our poled organic PB-DR19-based probe film, comprising NLO/SHG-active push-pull molecules, sample excitations at optical incidence angles of $\sim 45^\circ$ can also deliver strongest NLO/SHG-emissions. This was in fact verified via NLO Maker fringes measurements (see Fig. 4).

The photophysical interpretation of the temperature-dependent photoacoustic signal decrease, as observed in Fig. 6 via the PLPA-signal amplitude rms-analyses, is in general related to the increment of acoustical scattering occurring within the organic medium, which gives rise to an increase of the acoustical impedance as the sample temperature increases. This is indeed provoked by the dynamical molecular reorganization attributed to the temperature increment of the sample. In fact, in the low temperature poled state (T_0), most of the DR19 chromophores are regularly aligned; hence, the generated photo-acoustical vibrations can be straightforwardly transmitted from one azo-compound to another as a continuous low-impedance acoustical transmission line. In other words, coherent acoustical transmission across the film thickness and throughout the collectively aligned chromophores takes place. The aligned chromophores acting as point sources favor the coherent sum of the acoustical waves within this more homogeneous medium. Thus, constructive wave addition provokes easier acoustical transmission from the film sample to the transducer surface and, as a consequence, stronger PLPA-signals can be recorded at the detector plane when using either **S**- or **P**-polarized laser excitations. In fact, due to quasi-constructive acoustical wave addition, the average amplitude of the PLPA-signals is not drastically affected as these photoacoustic-waves travel across the low-impedance structured film. Moreover, the PLPA-measurements are sensitive enough to permit the discrimination of either **S**- or **P**-induced PLPA-signals within the poled molecular phase.

By contrast, this condition cannot be achieved at higher temperatures (e.g. T_g) due to the thermally induced molecular disorder (unpoled phase). Indeed, around T_g , the PA-signals induced by laser excitations either due to **P**- or **S**-polarization states are nearly equal; this is in fact due to the random molecular organization typical of isotropic materials. In such conditions, the chromophores offer equivalent optical cross-sections to both **P**- and **S**-polarized laser beams, which generate PA-signals of nearly the same amplitude. In this case, the PA-waves are not coherently added to a large extent, thus producing a drastic decrease in the average amplitude of the detected PLPA-signals as was registered at the transducer surface. The increment of the acoustical impedance is then provoked by the formation of multiple acoustical pathways giving rise to a significant dissipation and attenuation of the acoustical waves; hence, the PLPA-signals and rms-amplitudes detected at the transducer surface are considerably weakened. This thermal dependent photoacoustic effect occurs whatever the polarization states of the incident laser beam is used, and makes it difficult to distinguish between the PLPA-signals originated either from either **P**- or **S**-polarized laser excitations (see Fig. 6). On the other hand, from the purely optical perspective, considering the optical absorptive properties of the organic film only, a better indication of how the loss of molecular ordering affects the optical absorption when using polarized laser beams is given by the reduction in contrast between the **P**- and **S**-induced PLPA-signals, as is shown in Fig. 6. In fact, at poled

conditions (T_0), molecular alignment offers large optical cross-sections to the incident polarized laser beams (with stronger optical interaction in the case of **P**-polarized beams); this fact also induces stronger PLPA-signals due to optimal energy absorption. By contrast, within the unpoled phase (T_0), the thermally induced molecular disorder provokes all the DR19-chromophores to lie on substrate's surface with a random distribution. Under such conditions, the optical absorption cross-sections are statistically reduced compared to the homogeneously aligned molecular phase. Thus, equal absorption cross-sections to both **P**- and **S**-polarized laser beams generate PLPA-signals of nearly the same amplitude (without any defined contrast) and with weaker intensities in relation to the poled molecular phase.

Taking into account the polarization effect of the laser beam on the induced PLPA-signals and in order to quantify such phenomena, it is observed that at low temperature poled conditions the rms-amplitude of these signals, obtained under **P**-polarized excitation are significantly larger than those obtained under **S**-polarized laser irradiance. This allows the observation of an optimal PLPA-signal contrast at T_0 . However, as temperature increases to T_g , the molecular disorder is stimulated, reducing the collective chromophore alignment and the macroscopic anisotropy. This effect is clearly observed as a monotonic decrease of both **S**- and **P**-based rms output PLPA-signals with increasing temperature. Therefore, PLPA-signal's contrast obtained from the **P**- and **S**-induced PLPA-signals is drastically reduced, until the critical case where these averaged magnitudes exhibit nearly the same rms-amplitude values (at T_g). This fact confirms the anisotropic structuring of the film sample. In order to concretely evaluate the molecular orientational properties of our push-pull organic film, and in analogy to the several spectroscopic optical analyses, we define the signals contrast ratio C between the **P**- and **S**-induced opto-acoustic signals, as follows:

$$C(T_i) = \frac{I_P(T_i) - I_S(T_i)}{I_P(T_i) + I_S(T_i)}, \quad 0 \leq C(T_i) \leq 1, \quad (4)$$

where I_P (I_S) denotes the rms-amplitude of the **P**-polarized (**S**-polarized) PLPA-signals at a given temperature (T_i). Thus, from Fig. 6, the PLPA signal contrast obtained at the poled state ($T_i = T_0$) is on the order of $C = 2.7\%$, whereas at the thermally disordered molecular state ($T_i = T_g$), this parameter decreases to $C = 0.4\%$. This outstanding relative difference obtained for the C -parameter at contrasting temperatures via polarization-dependent PLPA-measurements and the corresponding amplitude rms-analyses, assures an accurate opto-acoustic determination of the molecular orientational properties of poled organic films. Indeed, as in the purely optical case (see Eq. (1)), the opto-acoustical evaluation of a molecular orientational order (ϕ_{PLPA}) from the rms-amplitude analyses of the PLPA-signals, is unambiguously proposed. Indeed, taking into account the fact that the **P**-polarized excitation gives rise to stronger PLPA-signals under convenient molecular excitation, we define the ϕ_{PLPA} parameter, as follows:

$$\phi_{PLPA}(T_i) = 1 - \frac{PA_{MIN}(T_g)}{PA_{MAX}(T_i)}, \quad 0 \leq \phi_{PLPA} \leq 1, \quad (5)$$

where $PA_{MIN}(T_i)$ and $PA_{MAX}(T_g)$ are the minimum and maximum values of the **P**-based (higher contrast C) rms-averaged PLPA-signals obtained from contrasting poled conditions,² respectively. In this way, the opto-acoustically estimated order parameter at the poled molecular state is $\phi_{PLPA}(T_0) = 0.38$. This value is in good agreement with the respective value determined via UV-vis spectroscopic measurements ($\phi_{OPT} \approx 0.40$, see Section 4.1).

² In analogy to the evaluation of the order parameter ϕ_{OPT} , determined via UV-vis optical spectroscopic measurements at contrasting molecular ordering (at $T_i = T_0$ and T_g).

This excellent correspondence reveals the feasibility of performing accurate PLPA-based studies for the determination of molecular orientational properties in organic-based optical materials. At this point and in analogy with the classical UV-vis spectroscopic method, we assume the general applicability of the PLPA-methodology for the determination of the orientational molecular properties in organic-based poled films (composed of polar rod-like functionalized optical chromophores). Indeed, given that the chromophore poling is electrically induced in such materials and this electrical process is fully reversible before sample's electrical damage threshold is reached, then it is reasonable to expect that similar results ($\phi_{PLPA} \approx \phi_{OPT}$) can be consistently obtained for any given material satisfying the previous structural conditions. Besides, one can also evaluate the order parameter at each intermediate temperature (T_i) within the heating process by taking into account only the two corresponding thermal states (at T_i and T_g). However, the signal contrast C becomes smaller for increasing temperatures, until the extreme value of $C \approx 0$ (at T_g) is reached.

On the other hand, since the laser spot size at the film sample and the transducer surface area are comparable, the laser source excites a very large number of chromophores within this region; this fact allows the convenient release of non-local and representative PLPA-signals, which can be appropriately detected in the PZT-microphone. Thus, we can reasonably assume that the measured ϕ_{PLPA} -parameter represents a reliable physical magnitude directly related to the macroscopic properties of the material sample. Under this framework, since the determination of the ordinary refractive index of our oriented organic film was previously performed via ellipsometry measurements at normal optical incidence (with $n_o \approx 1.73$, @ 1064 nm [25]), and given our accurate measurement of the molecular orientational properties of this poled film via PLPA-studies (with $\phi_{PLPA} \approx \phi_{OPT}$, Difference $\leq 5\%$), we argue that other important physical parameters relevant in materials characterizations and for linear and NLO applications can also be evaluated by means of this technique. Thus, since Eq. (2) is suitable for a straightforward evaluation of the extraordinary refractive index of poled films, we estimate this value to $n_e \approx 2.99$. Indeed, from ellipsometry measurements a value of $n_e \approx 2.916$ was experimentally estimated for the extraordinary refractive index of the poled probe film. Thus, the ratio between the photo-acoustically determined n_e -refractive index and the optical value (via ellipsometry) is $n_e(\text{optical})/n_e(\text{PLPA})=0.97$ (congruence: 97%). Again, this fact demonstrates an excellent agreement between traditional optical measurements and the PLPA-based methodology, thus confirming the accuracy of the PLPA-derived data. Complementarily, taking into account the reversibility of the electrical poling process in push-pull based organic films, Eq. (3) was employed to estimate the local poling field acting at the molecular level within the film sample, the obtained results was $E_p^l \approx 5.41 \text{ MV cm}^{-1}$ with a molecular dipole moment $\mu \approx 7.67 \text{ D}$, evaluated via molecular modeling [25]. In this regard, a poling electric field of $E_p^l \approx 4.8 \text{ MV cm}^{-1}$ was estimated for equivalent aligned chromophores (DR1-compounds) via the corona poling methodology with similar experimental poling conditions (needle-film distance: 1–2 cm @ 4–5 kV) [16].

Finally, it is noteworthy that the averaged PLPA-signals generated from the clean ITO-glass substrate are negligible compared to those obtained from the organic film under the same experimental conditions. This is a consequence of its null optical absorption at the implemented laser excitation wavelength (@ 532 nm). These small PLPA-signals are highly stable during the thermal process which is indeed indicative of a lack of structural changes and phase transitions of this material under the implemented experimental conditions. Thus, this kind of ITO-coated glass substrates can be conveniently used as an experimental

reference material and as an appropriate support for optically active organic compounds.

5. Conclusions

Given that classical optical absorbance measurements are frequently obtained from the difference between the incident and transmitted light intensity (via the Beer-Lambert law), traditional optical absorbance measurements cannot be intrinsically considered as direct measurements. Furthermore, these measurements strongly depend on the optical transparency of the sample to deduce some of the light-matter photophysical interactions. Thus, alternative experimental methodologies, not depending on the sample transparency, are highly required to conveniently investigate material absorption effects and their consequences in several light-matter interactions. One of these techniques is based on the photoacoustic effect which can also be considered as an absorption measurement as the measured quantity is strongly related to this optical parameter. Indeed, the photoacoustic effect and derived physical phenomena occur as a direct result of the amount of absorbed light involved in the whole photophysical interaction. Under this framework, the sample heating provoked by the absorbed light and producing opto-acoustical signals, is straightforwardly related to the absorbed electromagnetic energy in non-radiative phenomena. In fact, contrary to conventional transmission spectroscopic measurements, neither scattered nor reflected light considerably alters the PLPA-measurements. The PLPA-technique can then provide a more accurate perspective to the different photophysical processes occurring within the studied material structures at an electronic-lattice level. Indeed, as particularly shown in this work, the good experimental correspondence between the traditional optical absorbance spectroscopic method and the amplitude rms-analysis of the PLPA-signals to determine molecular orientational properties of anisotropic organic films, shows the possibility to precisely identify from the opto-acoustic viewpoint both material symmetries and molecular order parameters in aligned and semi-opaque push-pull polymeric film structures. In this case, the optical transmission data was itself used as control and reference experiment to consistently confirm and validate our PLPA-based results.

The main advantage of the PLPA-based photoacoustic analyses is that this methodology can be simultaneously implemented in the monitoring of molecular anisotropies, orientational order and other desired applications such as the determination of thermally induced structural changes (for instance crystalline phase transitions) in both organic and inorganic compounds having poor or null optical transmission/transparency properties. In general, the PLPA-method is an easy and low-cost technique and the respective data analyses can reveal important and complementary information concerning the macroscopic material structure. The accurate characterization of the absorbance distribution and polarization-dependent photo-acoustic signals performed in the implemented organic material opens new and potential possibilities for the PLPA-method, including for instance, the characterizations of other interesting anisotropic NLO-materials. In particular, in the research of novel materials or even in industrial control processes, the implementation of PLPA-based experimental methodologies and the respective data processing and rms-averaging may provide practical and highly efficient alternatives for the characterization of non-transparent anisotropic materials. These are from our perspective, plausible new application proposed for the PLPA-technique in material sciences and engineering, allowing the determination of preferential/induced material directions and/or macroscopic orientational order distributions within the material network; thus, providing useful experimental data to perform a full optical and morphological

description of novel and interesting materials suitable for photonic applications.

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