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DOMAIN STRUCTURE STUDIES IN PHASES OF BENT-SHAPED MOLECULES BY SPATIALLY RESOLVED SECOND HARMONIC MICROSCOPY

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This article arrived too late to be included in the appropriate section of the ILCC Proceedings, which is Structural Characterization.

Several banana-shaped liquid crystalline molecules have been studied as active media for second harmonic generation (SHG) in their different thermotropic phases [1]. Besides the B_2- and B_7-phases, which exhibit SHG under external applied electric fields, the so-called "blue" B_4-phase exhibits spontaneous SHG without application of any external field [2,3]. Both phases form a complex poly-domain structure which lead us to develop a SHG-Scanning microscope to perform a more detailed study of this complex systems. First experimental 2D-SHG-Scans in this molecules show the possibility to discriminate domains of different polar and NLO-properties, allowing a better understanding and analyses of this structures. A well defined polar structuring by external fields and analyses thereof is a prerequisite for the development of non-linear-optical (NLO)-applications of banana-shaped molecules like quasi-phase-matched (QPM)-waveguiding structures [4,5] or fast NLO switches.

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Keywords: bent shaped liquid crystalline molecules; domain and molecular orientation; nonlinear microscopy; second harmonic generation (SHG)

INTRODUCTION

Second order nonlinear optical processes are of particular interest since they offer several potential applications in photonics and telecommunication. Besides other materials, for instance poled polymers, in the recent past liquid crystals have been intensively investigated regarding their NLO-properties, as for example SHG. Moreover, from a fundamental point of view SHG offers the possibility to determine symmetry properties.

Recently it could be shown that so called banana-shaped molecules possess high hyperpolarisabilities leading to high effective non-linear optical coefficients especially in the smectic B_2-phase when compared to other ferroelectric liquid crystals of rod-like molecules, i.e. in the SmC*-phase [6]. In the B_2-phase the polar order of the achiral molecules in a layered structure together with a tilt of the molecular long axis with respect to the layer normal is leading to a chiral layer structure, either right or left handed [7]. The stacking of single layers results in two principal structures: an alternation of chirality from layer to layer results in racemic whereas stacking of layers with same chirality gives homochiral domains. In the first case the symmetry is C_{2v} whereas in the second case it is D_2. The domains may be distinguished by SHG experiments only while an external electric field is applied, high enough for the switching to noncentrosymmetric states. We therefore performed studies of the topology of this phase at both, zero applied electric field as well as fields with values $E > E_{th}$ (the new ferroelectric phases discovered recently are not present in the molecules studies here).

The solid B_4-phase, having a remarkable blue coloured appearance, always shows a spontaneous chiral resolution and moreover is SHG-active without application of an external electric field. The reason for the spontaneous SHG is up to now under discussion [8–11].

In order to resolve and get a deeper insight into the complex domain structure, a SHG-Scanning microscope has been developed with spatial resolution of 2.5–10 μm, which is high enough to reproduce *2D-SHG*-images from the topology of the different mesophases. The performed experiments enable us to distinguish domains of different chirality and polar order in a micrometer length scale.

INVESTIGATED MATERIALS

It was only since 1993 that Matsunaga and co-workers [12–13] synthesized different banana shaped molecules and reported mesogenic phases for

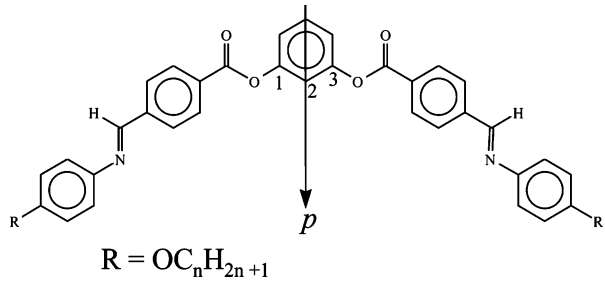

FIGURE 1 Chemical structure of the alkyloxy homologues showing a spontaneous polarization ***p*** along the two fold symmetry axis.

some of these materials, although the very first observation of a nonspecified liquid crystalline phase with strongly bent molecules can be dated back to 1929 by Vorländer [14–15]. Recently, Heppke *et al*. synthesized many alkyl- and alkyloxy-homologous series of banana shaped molecules and described their mesophases [16]. In the present work the domain structure of the B_2- and B_4-phases of some known representatives of the alkyloxy-homologs are investigated with the SHG-Scanning microscope for the first time. The general chemical structure of these compounds is shown in Figure 1.

The banana shape of the molecules results from linking two benzylideneaniline-groups to 1,3-dihydroxy-benzene by an ester linkage. An alkyloxy-chain is connected to each benzylidene-aniline-group. The different phase types and transition temperatures have been determined by polarization microscopy and Differential Scanning Calorimetry (DSC) [1]. A general description of the physical and chemical properties of each mesophase as well as the corresponding nomenclature can be found in more detail in the literature [17,18].

The transition temperatures for the investigated homologues are given in Table I. The B_2-phase which is of special interest here has a broken

TABLE I Temperature Phase Transitions of the Investigated Alkyloxy-Compounds Measured on Heating Process ($\Delta T = 3$ K/min, DSC-Technique)

n: Number of C-atoms	Name of the molecule	Thermotropic phases and temperature phase transitions T [°C] (heating process)										
		n	Cr_1		B_1		B_2		B_3		I	
OC_nH_{2n+1}	$\bar{n}B\bar{n}$	7			•	158.2	•	166.5	•	173.6	•	
n = 7, 9, 12		9	•	106.2	•	154.5			•	174.9	•	
		12	•	107.5	•	149.2			•	171.7	•	

fan shaped texture similar to a SmC phase. Antiferroelectric electro-optical switching with response times under 20 μs and saturation polarization up to 350 nC/cm^2 have been observed within this phase in different compounds [4,17].

On the other hand, the solid B_4 modification occurs in most of the alkyloxy derivatives. It has a slightly blue coloured appearance but is optically clear at the same time, in contrast to the "polycrystalline" B_3 phase. In fact it looks much like a glassy state. The texture of the B_4 phase shows a statistic distribution of different oriented domains and looks very similar to the sanded texture of a smectic C phase, where the point singularities are very small and blurred. The blue coloured appearance was supposed to originate from a Rayleigh-like light scattering superimposed on the self absorption of the chemical compound [17].

On a molecular level the structure of these banana-shaped compounds show a non-centrosymmetric density distribution of the conjugated π-electron-system resulting in a permanent dipole moment $\boldsymbol{p}$ required for SHG.

SHG - SCANNING EXPERIMENTS

Experimental Setup

Figure 2 shows the experimental setup developed for SHG-Scanning microscopy. In this device a commercial diode pumped, passive Q-switched Cr:/Nd:YAG Laser operating at $\lambda_\omega = 1064\,nm$ is coupled to a stereoscopic-polarizing microscope by means of a quartz optical fiber. The laser operates with an adjustable repetition rate between 5–25 KHz and a pulse duration of $\tau = 5\,ns$. Typical pulse powers between 150–350 W are achievable depending on the repetition rate of the laser. The intensity on the sample can be varied between $0.70 - 1.70\,GW/cm^2$ depending on the spot size of the focused beam. To avoid damage of the samples caused by high intensities of strong focused beams, different neutral density filters were used to decrease the effective intensity on the sample to some MW/cm^2 till the required power for SHG-measurements was tuned.

For NLO experiments the LC-samples are filled into commercially available I.T.O.-coated glass cells (Indiumtinoxyde $4 \times 4\,mm$, E.H.C.-Ltd. Corp., Japan) with cell thickness varying from 4 to 10 μm. Some cells are also coated with PI-(polar induced)-layers to induce molecular alignment along the (RU)-rubbing direction. By application of convenient external electric fields the polarity and size of the domain structures can be remarkably influenced.

A Glan-Taylor polarizer and a $\lambda/2$- or $\lambda/4$-Quarz-retarder permits the selection of the polarization of the fundamental laser beam. A second polarizer is used as analyzer allowing the characterization of the SHG-generated light. The LC sample was mounted inside a heating stage (Instec

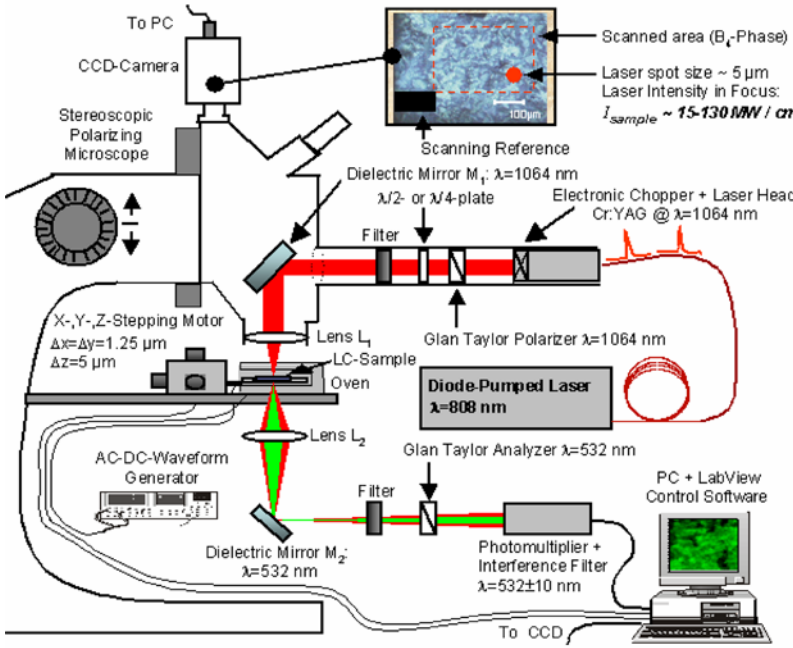

FIGURE 2 Experimental set-up developed for SHG-Scanning microscopy. (See COLOR PLATE XXXX)

HS400, Controller STC200B, $\Delta T = 0.1°C$). A stepping motor system holding the sample mount allows the scanning process in the x-y-plane with maximal spatial resolution of $\Delta x = \Delta y = 1.25\,\mu m$ and $\Delta z = 5\,\mu m$. The resolution is rather given by the spot-size of the laser beam, which was about 5 µm, and the scanning time was limited by the speed of the steeping motors system and DAQ-PC-board; in contrast to others SHG-Microscope systems where the resolution and speed are given by the integration time and the size of the pixel matrix of a CCD-array [19–20]. The second harmonic wave ($\lambda_{2\omega} = 532\,nm$) is detected by an optical photomultiplier behind optical filters to cancel the fundamental wave. A pulse generator and a wide band signal amplifier are used to perturb the sample with different DC-voltages or AC-wave forms.

The photomultiplier is connected to a DAQ-board and a PC or to a digital oscilloscope in order to store and analyze experimental data. A CCD-camera provides real time images of the sample textures while the scanning process is running. Experiments were totally automated with standard software (Lab-View, v. 6.0). The signal/noise ratio was improved with usual sampling techniques and convenient averaging of the input data.

SHG-Scanning Microscopy in the B_4-Phase

The experiments with the SHG-Scanning microscope technique focus on the characterization of active SHG-domain structures. This study allows the determination and control of different parameters like SHG-efficiency, size and orientation of the liquid crystalline domains. The measurements of the SHG-signal -contrary to previously published results [2–3,11,21–22]- have been performed measuring inside carefully selected single domains. Some experiments have been done under the influence of external electric fields. Different waveforms or DC-fields have been applied in both, cooling and heating processes in order to control the orientation as well as the growth rate of domain structures in each sample.

In a first attempt to investigate in detail the molecular orientation and the direction of the spontaneous polarization in single domain structures of the solid crystalline B_4-phase, some measurements using the SHG-Scanning technique have been performed in several members of the alkyloxy-homologous series. In particular, the $\bar{9}B\bar{9}$ -molecule which shows a relative strong and stable SHG-signal in this phase has been investigated between crossed polarizers [2]. Figure 3(a) shows three main active SHG-domain structures of about $100 \times 80\,\mu m$, exited by a y-polarized fundamental wave and analyzed along the x-direction. The parameters of the scanned area were set to $x_0 = y_0 = 0$, $x_{max} = y_{max} = 400\,\mu m$ with spatial resolution of $\Delta x = \Delta y = 10\,\mu m$. E.H.C.-cells without polar induced layers (PI: $\times$) were used in this

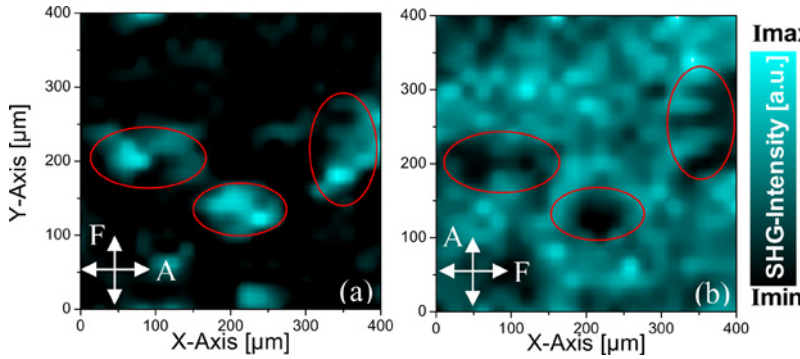

FIGURE 3 (a) Active SHG-domain structures within the B_4-phase of a $\bar{9}B\bar{9}$ - compound exited by a y-polarized fundamental wave and detected in the x-axis. The sample was cooled from the liquid isotropic phase in the presence of an external applied E-field (square-waveform at 1 KHz, $E_{Ext} = 7\,V/\mu m$, 5 µm-cell, PI: $\times$). (b) Scanned SHG-image recorded in the texture of Figure 3(a) excited by a x-polarized fundamental wave and analyzed in the y-axis. The SHG-activity of the single domains is fully cancelled under this geometry. (See COLOR PLATE XXXXI)

experiments, in order to avoid any preferential molecular alignment. A crossed geometry between the polarizer of the fundamental wave (F) and the analyzer (A) was used in both, the x- and y-axis, in order to investigate the image-contrast and variations of the SHG-signal in this simple configuration.

Since the SHG-signal generated by bent shaped molecules appears preferentially parallel to the permanent dipolar moment $\boldsymbol{p}$ for any polarization of the fundamental wave [23], the intense SHG-signal detected in this domain suggest a domain-dipolar moment alignment parallel to the analyzer axis. If the polarizer-analyzer system is now rotated an angle of 90°, the axis of the analyzer should cancel the SHG-wave generated by the selected domain, this is in fact the case as it is illustrated in Figure 3(b), where the SHG-activity of the 3-domain system is completely erased by theanalyzer.

This sample was cooled slowly from the liquid isotropic phase (cooling rate = 3°K/min) in the absence of any external electric field (outside the I.T.O.-layer).

It should be remarked, as mentioned before, that an optical excitation produced by the fundamental wave, polarized either in the x- or y-axis, will produce in any case a SHG-wave (in one case slightly weaker than in the other) polarized always in the direction of the spontaneous polarization $\boldsymbol{p}$ (along the bent direction) [2].

SHG-Scanning Microscopy in the B_2-Phase

The B_2-switchable phase has been also investigated with the SHG-Scanning microscope. First experimental results in this mesophase reveals an efficient and well organized SHG-domain structuring under the influence of external electric fields. Figure 4(a) illustrate a sequence of CCD-microphotographs of the B_2-phase of a $\overline{12}B\overline{12}$-compound, showing the optical modifications of this texture as an applied external electric field is increased. In other words, the modifications optically detected by standard polarizing microscopy occur due to molecular reorientation induced by the external electric field. This effect, photographed between crossed polarizers, makes evident the growth process of uniform electric field aligned domain structures.

In order to investigate the SHG-properties of this high temperature aligned domains, some SHG-scanning measurements were also performed within this phase at different values of an external applied electric field. The scan parameters were set in this case to $x_0 = y_0 = 0$, $x_{max} = y_{max} = 200\,\mu m$ with spatial resolution of $\Delta x = \Delta y = 10\,\mu m$ (see Fig. 4(b)). Due to the antiferroelectric behaviour of the B_2-phase in this material, the first SHG-scanned image corresponds essentially to the structural transition to a ferroelectric state within this phase (*i.e.* to a noncentrosymmetric

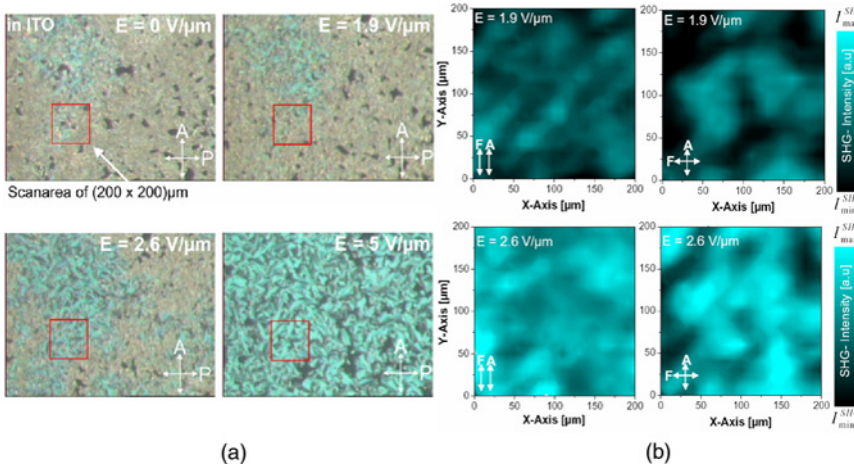

FIGURE 4 Active SHG-Domain structuring induced by an external DC-electric field within the B_2-phase of a $\overline{12}B\overline{12}$ -compound. (a) CCD-Standard polarizing microscopy microphotographs illustrate the domain-growing process, as an external E-field is increased. (b) Scanned SHG-images recorded in the textures of Figure 4(a), excited at $E_{Ext} = 1.9\,V/\mu m$ and $E_{Ext} = 2.6\,V/\mu m$. The SHG-images are analyzed along the y-axis, whereas the fundamental wave is polarized in both directions, in order to investigate local variations of the SHG-signal caused by different molecular optical field perturbations. An E.H.C.-cell with rubbing layers parallel to the x-axis (RU = 0°) was used in this experiments. (See COLOR PLATE XXXXII)

SHG-active structure), this occurs at an electric field threshold of $E_{th} = E_{Ext} = 1.9\,V/\mu m$.

Finally, some SHG-Scanned images have been also obtained from the B_2-phase in the homologous $\bar{9}B\bar{9}$ (9-O-PIMB)-compound. In this case the sample was optically excited by the fundamental wave polarized in both, the x- and y-directions. The SHG-signal was also analyzed along these two axes, in order to investigate the active SHG-domain distribution. Figure 5 shows the corresponding SHG-scanned measurements where the sample, under the influence of an external DC-field ($E_{ext} = 8.4\,V/\mu m$), μm), is induced to the required noncentrosymmetric-ferroelectric state.

As it is shown in Figures 5(a) and 5(d), the molecules are efficiently excited by the fundamental wave in both, the x- and y-directions, generating in either case efficient SHG-signal polarized parallel to the x-axis. These observations suggest again an average dipolar moment alignment favourable to this direction and a uniform molecular orientation (long axis of the molecules) parallel to the y-axis within the active SHG-domain structures of this mesophase.

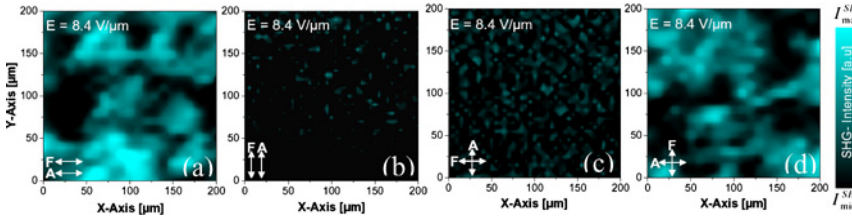

FIGURE 5 Active SHG-Domain structures induced by an external DC-electric field in the B_2-phase of a $\bar{9}B\bar{9}$ compound. (a) Sample optically excited and analyzed along the x-axis, showing high SHG-activity. (b) Sample excited and analyzed along the y-axis, showing a poor SHG-activity. (c) Sample excited and analyzed between a crossed polarizers system, the SHG-activity vanishes as the SHG-wave is analyzed along the y-axis. (d) A 90°-rotation of the crossed polarizers system reveals a permanent dipolar moment alignment parallel to the x-axis, since the SHG-activity increases again as the SHG-wave is analyzed along this direction. (5 µm-cell, PI: ×). (See COLOR PLATE XXXXIII)

It should be noted however, that the nonlinear SHG-scanned images illustrate only the active SHG-domain structures, which are oriented in such way, that irradiate a component of the SHG-wave parallel to the analyzer axis, whereas the CCD-microphotographs obtained by standard polarizing microscopy, show only linear optical properties of the domains within this texture (birefringence).

CONCLUSIONS

First experimental results with the SHG-Scanning Microscope in the B_2- and B_4-phases of some known banana shaped compounds (Alkyloxy-derivatives) have been presented. The experimental technique demonstrates the possibility to study active SHG-domain structures with optical spatial resolution up to 5 µm. On the other hand, the dynamics of the domain structuring induced by external electric fields was investigated into the switchable antiferroelectric B_2-phase. The SHG-scanned images studied in different geometries show the possibility to discriminate molecular and dipolar moment orientations as well as different polar and NLO- properties. Further investigations in the solid B_4-phase will permit a better understanding of the symmetry properties and crystalline structure of this relative unknown phase, as well as the development of methodologies to grow larger SHG-active domain structures, which are required for some NLO-applications. The developed setup will be an important tool for the characterization and study of active SHG-liquid crystalline molecules in new mesophases and gives complementary information as that

obtained by standard linear microscopy to characterize these complex structures.

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