Second-harmonic generation studies in the B_2 and B_4 phases of a banana-shaped liquid crystal

J. Ortega
Departamento de Física Aplicada II, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain

N. Pereda, C. L. Folcia, and J. Etxebarria
Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain

M. B. Ros
Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Zaragoza, 50009 Zaragoza, Spain
(Received 30 May 2000; published 18 December 2000)

Second-harmonic generation (SHG) measurements have been performed in the B_2 phase of the achiral banana-shaped molecule with $n=12$ alkoxy end chains (P-12-O-PIMB). A quantitative value of the nonlinear efficiency has been obtained from SHG curves at oblique incidences, taking into account that the signal is generated by a random orientation of different domains. In the B_4 phase, circular dichroism, optical absorption and SHG studies have been carried out. It has been found that there are no simple helical arrangements giving rise to selective reflection in the visible region of the spectrum. In addition, some unusual features of the SHG behavior are pointed out. It is concluded that the phase is intrinsically inactive for the SHG process. The detected signal is due to the presence of some birefringent inclusions that are created at the B_2 to B_4 transition and slowly disappear while the sample is maintained within the B_4 phase. A structural model for these inclusions is presented.

DOI: 10.1103/PhysRevE.63.011702 PACS number(s): 61.30.Eb, 42.65.Ky, 42.70.Df

INTRODUCTION

Recently [1] it has been experimentally proved that molecular chirality is not a necessary condition for the existence of ferro or antiferroelectricity in liquid crystalline smectic phases. In this kind of materials the constituent units are achiral banana-shaped molecules with $mm2$ symmetry. Within the mesophase the molecules are packed to form a tilted smectic layer with point group 2, which permits the existence of a polar axis parallel to the layer. According to Link *et al.* [2] in the so-called B_2 phase the polarization direction is inverted in alternating layers, and thus the material is antiferroelectric in the absence of applied electric field. Niori *et al.* [1] have observed ferroelectric switching in this phase, with a field-induced transition from antiferroelectric to ferroelectric. The observed saturation values for the spontaneous polarization are high ($P_s \approx 350\,\mathrm{nC/cm^2}$) and, in addition, the nonlinear second-order susceptibility for second harmonic generation (SHG) is very large [3] ($d \approx 10\,\mathrm{pm/V}$). For a recent review see Ref. [4].

This last characteristic is very interesting from the viewpoint of the design of liquid crystals for NLO applications. As is well known, in spite of the synthetic efforts in this field during the last decade, no materials with nonlinear susceptibilities larger than 1 pm/V have been found among the conventional calamitic ferroelectric liquid crystals. The reason for this seems to be the following. In standard liquid crystals the required elongated molecular shape sets a geometric limit for the introduction of functional groups with high hyperpolarizabilities β along the transverse direction (polar axis). However, banana-shaped molecules can present large β values along the polar axis of the mesophase precisely because of the bent shape of the constituent units. This fact has been recently proved by means of β measurements using hyper-Rayleigh scattering [5].

The interest of the NLO properties of these materials is not restricted to the B_2 phase. SHG has also been observed in the so-called B_4 phase [3,6] although the origin of the phenomenon is unknown. In this case, the reported efficiencies are smaller (about 1 pm/V) but the process occurs at room temperature without the necessity of application of electric fields, which may have some interest for technological applications.

In this paper we present a study of the SHG characteristics in the B_2 and B_4 phases of the material 1,3-phenylenebis[4-(4-*n*-dodecyloxyphenyliminomethyl)-benzoate] (P-12-O-PIMB) [7]. The compound was synthesized and satisfactorily characterized in our laboratory and presents the following phase sequence:

$$B4 — B2 — \text{Isotropic phase.}$$

The chemical structure and transition temperatures are shown in Fig. 1. In contrast to previous works on this material, our SHG study has been carried out by taking into account explicitly the random orientation of the different domains that the B_2 phase presents in the currently available samples. In addition, we have analyzed some structural features of the B_4 phase on the basis of measurements of circular dichroism. Finally we present a hypothesis about the origin of the SHG process in this phase.

EXPERIMENT

Commercially available cells (EHC) of a nominal thickness of 4 μm were used to prepare samples of liquid crystals

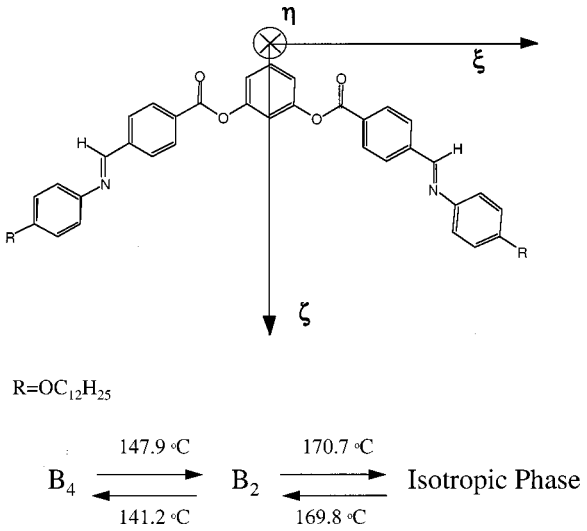

FIG. 1. Chemical structure and phase sequence of the studied material. Transition temperatures were determined from DSC experiments performed at 5 °C/min.

in planar geometry. The cell thickness was determined accurately by means of an interferometric technique. The material was introduced into the cell in the isotropic phase and the cell was placed into a temperature-controlled stage with optical access. Time-dependent electric fields were applied to the sample by means of a function generator.

SHG measurements were carried out using a *Q*-switched Nd^{3+}:YAG laser (wavelength $\lambda=1064$ nm, pulse width 6 ns, pulse frequency 5 Hz). The pulse energy was 0.8 mJ and the intensity at the sample was 6.7 MW/cm^2. The complete experimental setup has been described elsewhere [8].

Measurements of circular dichroism were performed by measuring the differential absorption for dextro and laevo circularly polarized eigenwaves in the sample by using a spectrometer equipped with a photoelastic modulator (PEM). The incident light was linearly polarized and was detected by a photomultiplier after passing through the PEM and the sample. The polarizer axis made an angle of 45° with respect to the PEM axes. The PEM retardation was set to $\lambda/4$. The signal detected consists of a constant component V_0 together with successive harmonics with frequencies f, 2 f, etc., being f the PEM frequency ($f=50$ kHz). The circular dichroism in the case of a nonbirefringent medium is proportional to the ratio V_f/V_0. The light wavelength was selected with a monochromator and the measurements were performed in the range 350–550 nm.

B_2 PHASE

In a first stage of the investigation, the macroscopic textures corresponding to the distinct configurations of the B_2 and B_4 phases were studied by means of polarizing microscopy. Various samples under different conditions of temperature and applied electric fields were used.

The transition temperatures (see Fig. 1) were quite similar to those reported previously by Sekine *et al.* [7] and by Kentischer *et al.* [3]. In agreement with the first order character of the isotropic-B_2 and B_2-B_4 phase transitions, a thermal hysteresis of a few degrees occurred between cooling and heating runs. A fringe pattern was always observed when the sample was cooled from the isotropic into the B_2 phase. According to Link *et al.* [2] this texture is characteristic of a racemic structure in planar alignment (where the smectic planes are perpendicular to the glass plates) and the different fringes correspond to synclinic antiferroelectric regions with opposite tilts. The texture was transformed into a smooth fan-shaped one when a low frequency square-wave electric field of ± 12.5 V/μm was applied to the cell, being this texture exactly the same whatever the polarity of the voltage was [2]. Each domain of the fan-shaped texture (with area of a few μm^2) was a homogeneous volume of an anticlinic ferroelectric structure, and appeared as a nearly perfect birefringent medium with clear extinction directions. The racemic configuration was obtained whenever the sample was cooled from the isotropic phase and could not be turned into a homochiral one by means of square or triangular-wave electric fields or temperature variations.

A different situation occurred when the B_2 phase was entered from the low temperature B_4 one. Then the system stabilized predominantly in a homochiral structure characterized by a grainy fan-shaped texture that switched to different macroscopic states for positive and negative electric field polarities [2]. Each of the field-induced domains was a synclinic ferroelectric structure. This state however could not be maintained indefinitely and the structure transformed into the racemic configuration after a few switching cycles. In contrast to other studies [9], the original homochiral structure could not be re-obtained within the B_2 phase by means of electric fields, irrespective of the shape (triangular, sinusoidal, or rectangular) and frequency of the applied wave.

SHG IN THE B_2 PHASE

As was mentioned in the Introduction, SHG in the B_2 phase has been observed in recent experiments [3,6]. However, with the exception of Ref. [10], only qualitative estimates for the nonlinear coefficients have been given. Quantitative measurements are difficult to carry out given the small size of the domains in the currently available samples. In Ref. [10], this problem was solved in part by strongly focusing the laser beam on a small sample area. Nevertheless, this procedure usually implies very high values of the incident light intensity (between 30 and 80 MW/cm^2 in Ref. [10]) which are, according to our experience in these materials, near or above the optical damage threshold.

In our studies of SHG we have followed a different approach to the problem based on a model for the molecular hyperpolarizability β recently published [5]. Given the peculiar shape of the molecules there are only 2 dominant components for the β tensor, $\beta_{\zeta\zeta\zeta}$ and $\beta_{\xi\xi\zeta}$ (see Fig. 1). Under the assumption of a high degree of molecular order in the B_2 phase, these components give rise to the appearance of 2 independent non-null coefficients for the second order susceptibility tensor referred to the (ξ,η,ζ) frame

$$D=Nf^3\beta_{\xi\xi\zeta}, \quad d=Nf^3\beta_{\zeta\zeta\zeta}, \tag{1}$$

where N is the density of molecules in the bulk state and f a local field factor. Consequently, depending on the 4 possible monodomain configurations for the B_2 phase, we obtain the following tensors for the nonlinear susceptibility:
Homochiral with applied electric field (2 symmetry):

$$\mathbf{d}=\begin{bmatrix} 0 & 0 & 0 & D\sin\theta\cos\theta & D\cos^2\theta & 0 \\ 0 & 0 & 0 & D\sin^2\theta & D\sin\theta\cos\theta & 0 \\ D\cos^2\theta & D\sin^2\theta & d & 0 & 0 & D\sin\theta\cos\theta \end{bmatrix}. \tag{2}$$

Racemic with applied electric field ($mm2$ symmetry):

$$\mathbf{d}=\begin{bmatrix} 0 & 0 & 0 & 0 & D\cos^2\theta & 0 \\ 0 & 0 & 0 & D\sin^2\theta & 0 & 0 \\ D\cos^2\theta & D\sin^2\theta & d & 0 & 0 & 0 \end{bmatrix}. \tag{3}$$

Homochiral without field (222 symmetry):

$$\mathbf{d}=\begin{bmatrix} 0 & 0 & 0 & D\sin\theta\cos\theta & 0 & 0 \\ 0 & 0 & 0 & 0 & D\sin\theta\cos\theta & 0 \\ 0 & 0 & 0 & 0 & 0 & D\sin\theta\cos\theta \end{bmatrix}. \tag{4}$$

Racemic without field ($\bar{1}$ symmetry):

$$\mathbf{d}=\mathbf{0}. \tag{5}$$

The **d** tensors are expressed in a reference frame where x is perpendicular to the smectic layers and z is parallel to the polar axis, and θ is the tilt angle.

The whole set of randomly oriented domains is to be considered now. A few points are to be taken into account in this respect: The polar axis (z axis) and the tilt angle are the same for every domain, which differ only in their x direction. On the other hand, the domains are small enough to be the laser spot size sufficient to illuminate a representative randomly oriented set. However, they are macroscopic units and, therefore, the total second harmonic intensity must be calculated incoherently, i.e., adding up the intensities generated by the different domains. The calculation was performed numerically as a function of the incidence angle for different polarizers configurations: p-input—p-output, p-input—s-output, and s-input—p-output, being the sample rotated about the vertical direction. Finally, D and d were calculated from the fits of the numerical predictions to the experimental results.

The measured SHG intensity as a function of the angle of incidence for p-input—p-output configuration is represented in Fig. 2 together with the corresponding theoretical curve. The sample was in the racemic state with an applied electric field of 12.5 V/μm. The **d** tensor corresponding to each domain is therefore given by expression (3). As can be seen the SHG intensity is zero at normal incidence as expected from the planar cell geometry and the molecular symmetry. A tilt angle $\theta=35°$ taken from the literature [4] as well as other optical data typical of liquid crystals were considered here. A value of $D=9$ pm/V was obtained from the fit. Unfortunately, the quantity d was found to have a very weak influence on the theoretical prediction and, therefore, it could not be determined with a reasonable degree of reliability. It is to be pointed out however that d should result lower than D as expected from the fact that $\beta_{\zeta\zeta\zeta}(=15.3\times10^{-30}$ esu in this material [5]) is smaller than $\beta_{\xi\xi\zeta}(=61.5\times10^{-30}$ esu). The SHG signals obtained for the p-input—s-output and s-input—p-output configurations were smaller, but the shape and size of the curves were consistent with Eq. (3) and the same numerical value for D. (See Fig. 2.)

We also intended to obtain D and d by performing a simi-

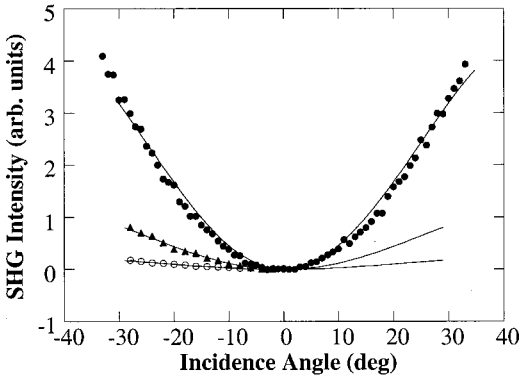

FIG. 2. SHG in the B_2 phase as a function of the angle of incidence for different input–output polarization combinations: p-p (closed circles), p-s (triangles) and s-p (open circles). The data were taken at a temperature of 155 °C. The sample was in the racemic configuration under an electric field of 12.5 V/μm. The continuous lines are theoretical curves for a parameter $D=9$ pm/V. The error margin corresponds in each case to the scattering of the experimental points.

lar study in the homochiral configuration [**d** is given by expressions (2) and (4)]. These measurements however were not possible because of the following reasons: A high light scattering was always observed in the homochiral state when the electric field was applied to the sample (a simple qualitative explanation for this effect will be proposed later). On the other hand, the SHG signal was very weak when the field was removed. Finally, it is worth to be commented that, in agreement with Eq. (5), absolutely no SHG signal could be detected for the racemic structure without applied electric field.

In summary, the **d** tensors, which characterize the SHG efficiency for the different structures of the B_2 phase, are given by expressions (2)–(5), with $D=9$ pm/V and a nondetermined (but lower) value for d. In agreement with Macdonald *et al.*, the SHG efficiencies for these banana-shaped mesogens are one order of magnitude higher than the largest ones ever reported for calamitic ferroelectric liquid crystals. However, we have obtained $d_{31}=7.4$ pm/V in Eq. (2) instead of $d_{31}=16.3$ pm/V determined by Macdonald *et al.* for the same symmetry. This discrepancy is not too surprising in view of the different assumptions considered in each work. Here we have made an average of SHG intensities assuming that the sample is composed of small domains with a definite form for the **d** tensor, and random x directions in the illuminated area (our spot diameter was 1.6 mm). On the other hand, in Ref. [10] the most general **d** tensor was considered, but it was supposed that the laser spot (of 50–100 μm of diameter) covered just a single domain during the whole measurement.

A comment is now in order with respect to the strong light scattering observed for the homochiral structure under an applied electric field. First, it is to be pointed out that a similar effect occurs for the racemic configuration without field. Light scattering seems therefore to be characteristic of a synclinic ordering in the structure. An explanation for this fact can be given in terms of the different thickness of the sample regions where the macroscopic optic tensor is homogeneous. It can be shown that for anticlinic ordering these regions are larger than for synclinic structures. For anticlinic states, the orientation of the principal optic axes is exclusively defined by the orientation of the smectic layers normal. In the studied samples these domains occupied the complete thickness of the specimen. For synclinic states, however, regions with opposite tilts appear along the sample thickness. This gives rise to a different optical indicatrix in each of these regions even if the smectic layers normal is maintained. Therefore a stronger light scattering is to be expected in synclinic structures, which is experimentally observed.

B_4 PHASE

In accordance to previous investigations [7], our microscopy studies revealed that the B_4 phase presents a dark-blue color, and two types of domains can be observed between crossed polarizers. None of these domains shows birefringence in any direction according to the measurements we carried out at different incidence angles. However these two kinds of domains exhibit a large optical activity ($\rho \approx 500°\ \mathrm{mm}^{-1}$) and opposite chirality, being the probability of appearing each of them the same. On the other hand, the sample shows a small proportion of birefringent inclusions with a completely different texture.

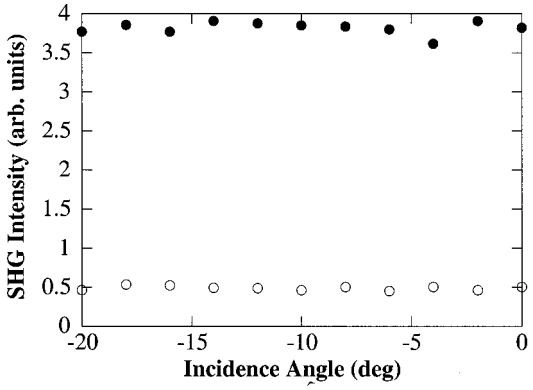

FIG. 3. SHG in the B_4 phase as a function of the angle of incidence for parallel (closed symbols) and perpendicular (open symbols) polarizers. The data were taken at room temperature without any applied field. The error margin corresponds in each case to the scattering of the experimental points.

All the optical properties described above remained unchanged when applying electric fields. Indeed, no response to electric fields was observed in this phase. Therefore SHG measurements were performed without any electric field applied to the sample. The SHG signal did not depend on the polarization direction of the incident fundamental beam, but only on the relative angle between polarizer and analyzer. The largest SHG intensity was achieved when the polarizer and analyzer were parallel to each other, and the smallest one was attained in a perpendicular disposition. The ratio between both signals had a value about 7.5. This result was confirmed in different areas of the sample and also in several specimens. On the other hand, an almost undetectable change in the SHG intensity was observed when changing the incidence angle (see Fig. 3).

The structure of the B_4 phase is still object of debate. In this respect, Sekine *et al.*, on the basis of some similarities between this phase and the TGB ones, suggested the existence of helical arrangements with the helix axis parallel to the smectic layers. Under this assumption they explained the blue color of this phase in terms of a Bragg selective reflection. In fact, these authors explored the spectrum of the scattered light in a similar compound (P-8-O-PIMB) in the B_4 phase, illuminating with circularly polarized light. In this measurement, a sharp reflection band around 430 nm was found and they concluded that the origin of this band is a helical structure perpendicular to the sample surface that gives rise to selective reflection at that wavelength.

On the other hand, Colling *et al.* [11] disagreed with the previous work and explained the blue color exhibited by this phase in terms of Rayleigh-like scattering superimposed by self absorption of the compound in the near UV region. In this work it is reported that surface imaging with atomic force microscopy reveals smectic layers in ''worm-like''

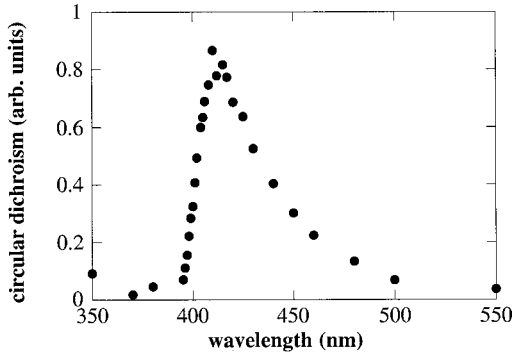

FIG. 4. Circular dichroism as a function of wavelength in the B_4 phase. The data were taken at normal incidence, but measurements at oblique incidences revealed no shift of the wavelength corresponding to the maximum (410 nm). The error margin was estimated to be about 10%.

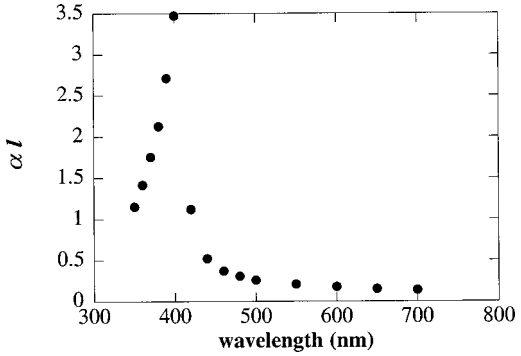

FIG. 5. Absorption coefficient α of the B_4 phase as a function of wavelength. The incident light was linearly polarized. The thickness of the sample was $l=4.9\ \mu$m. The error margin was estimated to be less than 10%.

structures that tend to form a superimposed periodical orientation order.

In a third work carried out by Kentischer *et al.* [3] the authors proposed a noncentrosymmetric glassy state for this phase. They observed SHG in this phase and estimated a d_{eff} value as high as 1 pmV^{-1}. To explain this result, a structure made up of randomly oriented domains, with spontaneous polar order, was suggested.

In order to evidence the existence of a helical arrangement in the B_4 phase we carried out measurements of circular dichroism as a function of wavelength, using the experimental setup described above. The existence of a selective reflection band due to a helical structure should be detected as a circular dichroism band centered at a given wavelength. Furthermore, according to Bragg's law, this wavelength should depend strongly on the incidence angle. Figure 4 shows the ratio V_f/V_0 versus wavelength at normal incidence. This quantity is proportional to the circular dichroism exhibited by the illuminated area of the sample. It is to be pointed out that the circular dichroism in each domain was very high, as was checked out by direct observation illuminating the sample with circularly polarized light. However, even using a high-power microscope objective it was not possible to isolate a unique domain and, therefore, a small signal corresponding to a slightly unbalanced proportion of each type of domain was detected. As can be seen in Fig. 4, a sharp peak appears at 410 nm which resembles that obtained by Sekine *et al.* for the spectrum of scattered light. Measurements at various incidence angles were performed in order to check a shift of the peak wavelength, in agreement to Bragg's law. The results of Fig. 4 were always reproduced, indicating unambiguously that Bragg's law does not hold in this material.

Absorption measurements were also carried out in this sample at different wavelengths under linearly polarized incident light. Figure 5 shows the absorption coefficient α versus wavelength. A sharp peak can also be observed in this figure around 400 nm. It is interesting to notice that the maximal absorption is much larger than should be expected if a pure selective reflection had taken place. In fact, at the maximum, only 1/33 of the incident intensity is transmitted by the sample (the sample thickness was 4.9 μm). However, if selective reflection had occurred, the transmission should have been close to 1/2 when illuminating with linearly polarized light. This result reinforces the previous one and, therefore, the possibility of helical arrangements responsible for a selective Bragg reflection must be ruled out.

Regarding now the NLO properties, and in accordance with previous observations, the material presents SHG even in the absence of any electric field. However, some characteristics of the NLO behavior of the B_4 phase are rather unusual. First, there is no point group for this phase compatible with the absence of birefringence and with the polarization characteristics of the SHG light. More specifically, an isotropic phase does not allow SHG and, although several cubic point groups permit the existence of this property, it can be shown that in no case the theoretical ratio of SHG intensities for parallel and perpendicular polarizers can attain a value as high as the experimentally observed 7.5. A second unusual feature is the fact that the SHG intensity depends on the time the material has remained in the B_4 phase, i.e., it shows a relaxational behavior. In fact, if measurements are carried out after maintaining the sample 24 h in this phase, the SHG signal decreases in approximately one order of magnitude. These results are shown in Fig. 6 in which the SHG signal versus temperature is depicted in a sample that had remained more than 24 h at room temperature. The measurements were carried out setting the polarizer and analyzer in parallel configuration. Open circles represent the SHG intensity on heating the sample form room temperature up to the B_2 phase, and solid circles shows the signal when cooling down again to room temperature. As can be observed, at the beginning the SHG signal is very weak and slightly decreases when entering the B_2 phase. This is an expected behavior if an homochiral configuration is achieved in the B_2 phase. However, on cooling down again to the B_4 phase a large enhancement of the SHG is observed after undergoing the phase transition. Finally, the signal slightly decreases as the temperature diminishes.

Remarkably, we have observed that the SHG behavior is correlated to the amount of birefringent inclusions in the B_4 phase. At the beginning of the above experiment, the sample showed a typical texture of the B_4 phase with a very small

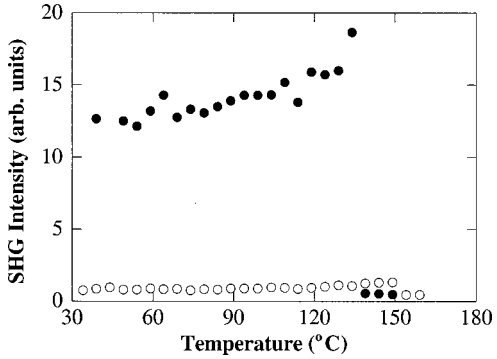

FIG. 6. SHG in the B_4 phase as a function of temperature. The data correspond to normal incidence with parallel polarizers. Open symbols were taken on heating from room temperature up to the B_2 phase, after having maintained the sample at room temperature during more than 24 h. Closed symbols were obtained on a subsequent cooling run. Heating and cooling rates were about 1 °C/min. The error margin corresponds in each case to the scattering of the experimental points.

amount of inclusions, but after entering the B_2 phase and cooling down again into the B_4 one, the proportion of such inclusions clearly increased. This is connected to the enhancement of the SHG shown in Fig. 6. This fact has been confirmed in several samples. It was also checked that the birefringent domains are metastable since they disappear as the sample remains in the B_4 phase for several hours. The above experimental results indicate unambiguously that these inclusions are responsible for the SHG, being the stable B_4 phase inactive. Furthermore, no matter the SHG intensity, the ratio between the signals when polarizer and analyzer were set parallel and perpendicular remained constant and took the value of 7.5.

With the aim of explaining the SHG features described above, a model for the inclusions that are responsible for this effect will be now proposed. Since the SHG intensity is rather strong and the proportion of inclusions in a typical sample is relatively small, this suggests that such inclusions should present a strong polar order. On the other hand, an electric field is not required to produce SHG. Therefore a glassy or crystalline polar structure can be proposed for these domains. In this respect, we will consider two possible configurations for the molecules in the inclusions: polar synclinic (like the homochiral domains under field in the B_2 phase) and polar anticlinic (like the racemic ones in the same situation). The whole SHG signal in the sample must be obtained by incoherently summing the SHG intensities produced by all the randomly oriented inclusions.

Assuming a perfect thermodynamic order and considering the SHG coherence length much larger than the size of the inclusions, the SHG intensity can be easily computed. After performing the orientational average the result for polar anticlinic domains is

$$I_{2\omega}^{\parallel} \propto \langle (d_{\mathrm{eff}}^{\parallel})^2 \rangle = \frac{27}{128} D^2 (\cos^4\theta + \sin^4\theta) + \frac{9}{64} D^2 \sin^2\theta \cos^2\theta + \frac{3}{16} Dd + \frac{5}{16} d^2 \tag{6}$$

if the polarizers are parallel. For perpendicular polarizers the intensity is

$$I_{2\omega}^{\perp} \propto \langle (d_{\mathrm{eff}}^{\perp})^2 \rangle = \frac{23}{256} D^2 (\cos^4\theta + \sin^4\theta) - \frac{3}{128} D^2 \sin^2\theta \cos^2\theta - \frac{1}{32} Dd - \frac{1}{32} d^2 \tag{7}$$

If synclinic polar inclusions are considered, Eqs. (6) and (7) are valid with $\theta = 0$.

The model predicts SHG signals almost independent of the angle of incidence, since the interaction length is practically constant for low incidences. In addition, if we take for the tilt angle θ a value in the range 35°–40° (which are typical in the B_2 phase) and use the relative size of both intensities in our SHG measurements

$$I_{2\omega}^{\parallel} / I_{2\omega}^{\perp} \approx 7.5, \tag{8}$$

a ratio $D/d = 2.4-2.8$ is obtained depending on the selected tilt angle (35°–40°). Taking into account the rough approximations used in this model, these results reasonably agree with those previously reported by Arauoka *et al.*, who predicted a ratio $D/d \approx 4$ on the basis of the geometry of the molecule. On the other hand if a synclinic polar structure were assumed for the inclusions, this ratio would be $D/d = 1.0$ independent of the tilt angle. Therefore, although both types of structure give the same order of magnitude, the anticlinic polar structure fits the results better. Comparing the SHG signal in the racemic phase B_2 under an electric field, with the largest signal detected in our measurements in the B_4 phase, an estimation of the proportion of the inclusions in this phase can be made. This value turned out to be around 1%.

Summing up, the B_4 phase exhibited by this material is an optically isotropic phase that present two types of domains with opposite chirality and a very high optical activity. This phase is strongly absorbent in the blue region but no selective reflection occurs. Moreover the phase does not present SHG intrinsically, being the detected signal produced by some birefringent inclusions that could be metastable glassy states of a polar structure.

CONCLUSIONS

SHG studies performed on the B_2 phase have confirmed previous investigations, in the sense that banana-shaped liquid crystals exhibit NLO efficiencies in the range of 10 pm/V. The quantitative results are consistent with a simplified model for the mesophase, where the molecules contribute to the NLO response with 2 dominant components of the β tensor.

Regarding the B_4 phase, strong absorption and circular dichroism have been found in the blue region of the spectrum. The large optical activity and light scattering displayed by the material in this region cannot be explained on terms of helical arrangements satisfying Braggs's law. Finally, it has

been found that this phase has not inherent NLO activity. The SHG signal is generated by metastable birefringent inclusions which are originated at the B_2 to B_4 transition and slowly disappear after several hours. These inclusions are probably glassy states with strong polar order.

ACKNOWLEDGMENTS

One of us (N.P.) is grateful to the Ministry of Education of Spain for a grant. This work was supported by the CICYT of Spain (Project No. MAT97-0986-02).

[1] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, and H. Takezoe, J. Mater. Chem. **6**, 1231 (1996).
[2] D. R. Link, G. Natale, R. Shao, J. E. Maclennan, N. A. Clark, E. Körblova, and D. M. Walba, Science **278**, 1924 (1997).
[3] F. Kentischer, R. Macdonald, P. Warnick, and G. Heppke, Liq. Cryst. **25**, 341 (1998).
[4] G. Pelzl, S. Diele, and W. Weissflog, Adv. Mater. **11**, 707 (1999).
[5] F. Araoka, B. Park, Y. Kinoshita, K. Ishikawa, H. Takezoe, J. Thisayukta, and J. Watanabe, Jpn. J. Appl. Phys., Part 1 **38**, 3526 (1999).
[6] S. W. Choi, Y. Kinoshita, B. Park, H. Takezoe, T. Niori, and J. Watanabe, Jpn. J. Appl. Phys., Part 1 **37**, 3408 (1998).
[7] T. Sekine, T. Niori, J. Watanabe, T. Furukawa, S. W. Choi, and H. Takezoe, J. Mater. Chem. **7**, 1307 (1997).
[8] N. Pereda, C. L. Folcia, J. Etxebarria, J. Ortega, and M. B. Ros, Liq. Cryst. **24**, 451 (1998).
[9] G. Heppke, A. Jákli, S. Rauch, and H. Sawade, Phys. Rev. E **60**, 5575 (1999).
[10] R. Macdonald, F. Kentischer, P. Warnick, and G. Heppke, Phys. Rev. Lett. **81**, 4408 (1998).
[11] P. Collings, G. Heppke, D. Krüerke, C. Löhning, J. Rabe, and W. Stocker (unpublished) .