

# Coexistence of polar and nonpolar domains and their photocontrol in the $B_7$ phase of a bent-core liquid crystal containing azo dyes

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(Received 27 September 2003; revised manuscript received 20 January 2004; published 1 June 2004)

Coexisting polar and nonpolar domains have been studied by means of texture observation, x-ray analysis, optical second-harmonic generation (SHG), and SHG microscopy in the  $B_7$  phase of a bent-core mesogen doped with azo dyes. The bent-core molecules take a planar orientation and show high birefringence in the polar domain, while they take a homeotropic orientation and show low birefringence in the nonpolar domain. Good correspondence between real and SHG images was observed under a SHG microscope; the bright (high-birefringent) domain is SHG active and the dark (low-birefringent) domain is not SHG active. Photoisomerization of the azo dyes causes layer reorientation from the layer perpendicular to the substrate to that parallel to it.

DOI: 10.1103/PhysRevE.69.061701

PACS number(s): 61.30.-v

## I. INTRODUCTION

Recently, there has been strong interest in achiral bent-shaped liquid crystals (LCs), sometimes called banana mesogens, due to their unique properties of polarity and chirality. Since the discovery of ferroelectricity in one of the banana mesogens [1], extensive investigations have been done mainly on the  $B_2$  phase of these materials [2,3]. In contrast, the  $B_7$  phase has been less studied partly because of its complicated textures. The  $B_7$  phase is characterized by the appearance of helical filaments when cooled from the isotropic phase [3–5]. The structure of the  $B_7$  phase in several materials was attributed to a modulated layer structure [6], although some other models have been proposed [5]. In this sense, it is important to add further experimental information about the  $B_7$  phase.

It has long been known that the illumination of polarized light on rodlike liquid crystals doped with azo dye molecules, such as methyl orange shown in Fig. 1(a), orients the LC molecules in a specific direction due to the reorientation of the dye through a photoisomerization process [7–10]. In addition to such photoinduced LC molecular reorientation, other types of effect can be realized by photoirradiation. In fact, Nair *et al.* studied the photoinduced change of the spontaneous polarization in the  $B_2$  phase of an azo-dye-doped bent-core LC and found that the spontaneous polarization decreases when the LC is illuminated by polarized UV light. They inferred that the isomerization of the dye into the bent-shaped *cis* state expands the intermolecular spacing within each layer of LC molecules [11].

The present compound PBCOB (1,3-phenylene bis[4-(3-chloro-4-*n*-octyloxy-phenyliminomethyl) benzoate]) shown in Fig. 1(b) was synthesized by Lee and Chien [12]. Subsequent work has shown the existence of the  $B_7$  phase in this

compound [12,13] and ferroelectric switching in a mixture of this compound and xylene [13,14]. The existence of additional periodicity in the layer structure suggests the modulated layer structure proposed by Coleman *et al.* [6], although Lee *et al.* [13] interpreted it differently. Experimental evidence was not enough to identify the macroscopic polar order (ferroelectric phase). Thus further experiments on this material to examine the layer structure and the polar order are necessary. In the present study we discovered that there are two different domains coexisting in the  $B_7$  phase of PBCOB, one with low birefringence and no second-harmonic generation (SHG) activity and the other with high birefringence and SHG activity. We also found that the illumination of the azo-dye-doped LC with light can furthermore cause a domain change from the former to the latter through the photoisomerization process of the dye.

## II. EXPERIMENTAL PROCEDURES

PBCOB has the  $B_7$  phase below the isotropic phase (about 160°C) [12] with some thermal hysteresis. The material was filled in cells with a gap of 1.5  $\mu\text{m}$  and the cell surfaces were coated with a polyimide alignment layer. We also made cells containing PBCOB doped with 5 wt% azo dye, methyl orange shown in Fig. 1(a).

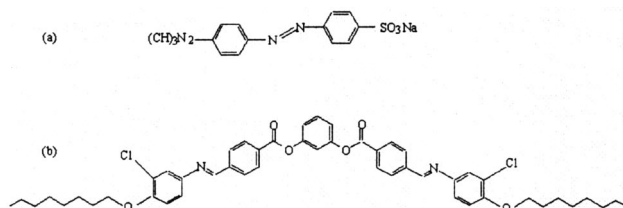


FIG. 1. The molecular structure of (a) methyl orange and (b) PBCOB.

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The optical textures and electro-optic (EO) switching behaviors were observed under a crossed polarizing microscope, and the birefringence was measured using a compensator under the polarizing microscope. The optical transmission of a He-Ne laser light through the cell was measured under a crossed polarizer combination at incidence angles of  $0^\circ$  (normal incidence) and  $\pm 26^\circ$ . Polarized Raman spectra were measured using a confocal microscope (Nanofinder, Tokyo Instruments Co.), which makes it possible to select a uniform domain. The polarized Raman scattering intensities corresponding to the phenylene group supply the dichroic ratio. Second-harmonic generation was also measured, which can provide definitive evidence for the polar order in each domain. The fundamental beam incident on the sample was from a  $Q$ -switched neodymium-doped yttrium aluminum garnet (Nd-YAG) laser (GCR 150-10, Spectra-Physics Co.) with the intensity of 80 MW per pulse and 10 Hz repetition rate. In order to examine the correlation between the microscope texture and polar order, we constructed a SHG microscope using a charge-coupled device to detect 532 nm SH light. This system enables us to observe two-dimensional (2D) SHG images (resolution about  $1 \mu\text{m}$ ) as well as real images (texture). X-ray diffraction measurements were conducted using a Rigaku RU-200 instrument in the  $B_7$  phase. Two-dimensional patterns were observed using an imaging plate at normal incidence of the x-ray beam on a cell fabricated using a pair of thin ( $80 \mu\text{m}$  thick) glass substrates.

The azo-dye-doped PBCOB was found to have similar textures and EO properties to those of pure PBCOB. We illuminated this cell with a linearly or circularly polarized Ar laser beam (Innova 305, Coherent Co., 890 mW), while observing the variation under a polarizing microscope. Simultaneously, the switching current was measured using the conventional triangular electric field application method and determined the spontaneous polarization ( $P_s$ ) values before, during, and after the irradiation of light.

### III. EXPERIMENTAL RESULTS

When the cell was slowly cooled down from the isotropic phase into the  $B_7$  phase, helical filaments characteristic of the  $B_7$  phase appeared. In the  $B_7$  phase, two domains with distinctively different brightness and textures were observed. By controlling the cooling rate carefully we could select either the bright or the dark domain to be dominant in the whole LC cell; slower and faster cooling processes, respectively, nucleate the dark and bright domains. The typical bright and dark textures are shown in Fig. 2. The birefringence measured with the polarizing microscope was 0.057 for the bright domains and 0.0085 for the dark domains. The bright domains showed distinctive EO switching behaviors such as change of brightness and rotation of the extinction brush (about  $\pm 10^\circ$ ); by applying a triangular wave voltage to the bright circular domains, the brushes continuously rotated without any threshold. Analogous switching in the  $B_7$  (or  $B_7$ -like) phase has been reported by Mieczkowski *et al.* [14]. The difference, however, is the absence [14] and presence (PBCOB) of a switching current peak under a triangular

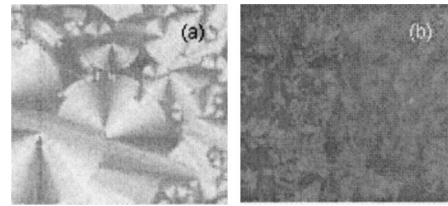


FIG. 2. Two types of domains spontaneously formed in the  $B_7$  phase of PBCOB: (a) bright domain and (b) dark domain.

field, i.e., the PBCOB bright domains show a broad single peak, the area of which (spontaneous polarization) changes with the field amplitude. In contrast, the dark domains did not show any EO response, at least to a field applied along the cell surface normal. The optical transmission was higher by a factor of 5 for the bright domains than for the dark domains for all incidence angles, which is consistent with the birefringence measurement results.

Polarized Raman spectra for each domain are shown in Figs. 3(a) and 3(b), where parallel polarizers were set parallel ( $0^\circ$ ) or perpendicular ( $90^\circ$ ) to the director. We can summarize the results as follows. (1) The dichroic ratio is much larger for the bright domain than for the dark domain, which essentially shows no dichroism. (2) The scattered intensity at  $90^\circ$  in the bright domain is almost the same as that in the dark domain. (3) We performed the measurements at  $45^\circ$  and  $135^\circ$ , although the polarization condition was not good because of the optical geometry, and found no essential change in the Raman intensities for the dark domain at any angle of polarizer.

The SHG measurements were conducted in the condition which both the input and output beam polarization planes are along with the incidence plane. The incident beam size is a few millimeters, so that the average SHG activity over many

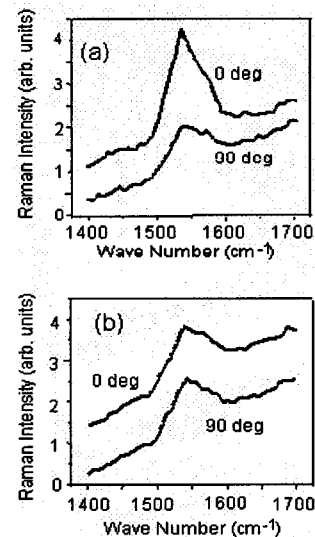


FIG. 3. Polarized Raman spectra of (a) bright and (b) dark domains. Polarizer and analyzer are parallel to each other and they are set parallel or perpendicular to the director. The peak assigned to the phenyl group shows dichroism in the bright domains but not in the dark domains.

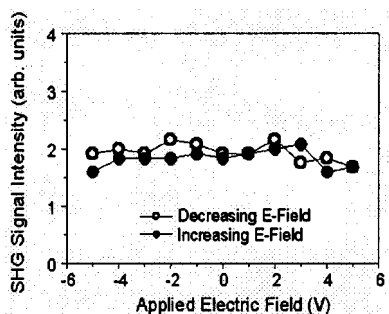
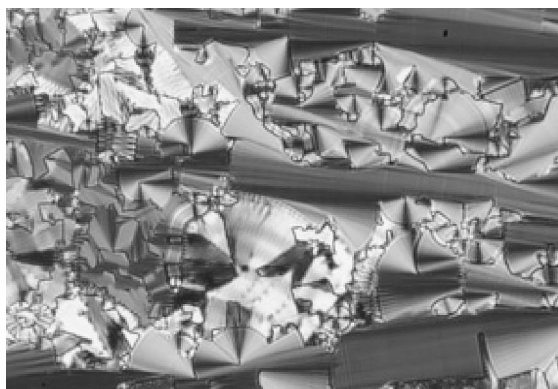
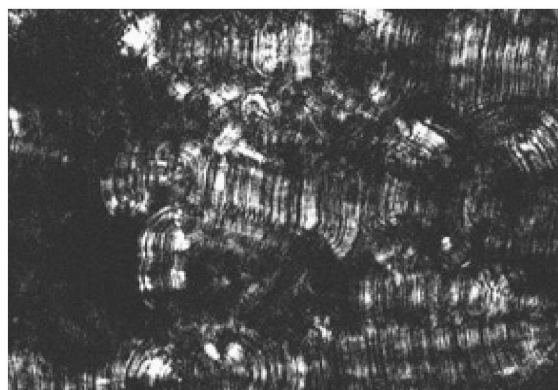


FIG. 4. SHG intensity vs the applied electric field in the bright domains using parallel input and output polarizers.

domains was examined. It was found that the bright domain shows SHG activity even without a biasing electric field at normal incidence, while the dark domain does not generate any SHG signals even under moderate electric fields for any possible combinations of light polarization. Change in the incidence angle does not cause any essential change. As shown in Fig. 4, the SH intensity for the bright domain does not depend on the applied electric field, although EO switching occurs in this field range. To further confirm the corre-



(a) Real image



(b) SHG image

FIG. 5. (a) Polarizing microscope image of the  $B_7$  phase of bent-shaped LCs and (b) the microscope SHG image measured at  $116.9^\circ\text{C}$ . Good correspondence can be seen, i.e., only the bright domains are SHG active.

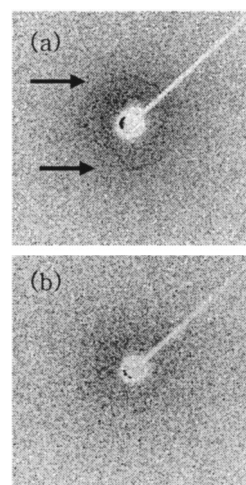


FIG. 6. X-ray diffraction patterns for bright domains (a) and for dark domains (b). In the bright domains, layer diffractions can be observed as shown by arrows.

spondence between the domains (bright and dark) and the SHG activity, SHG microscopy was conducted. The SHG microscope image together with a real image (microphotograph) are shown in Figs. 5(a) and 5(b). It is clear from the comparison between the two images that only the bright domains exhibit distinctive SHG while the dark domains do not.

For the x-ray measurements, we prepared bright and dark domains, respectively, by fast and slow cooling processes. The 2D patterns shown in Fig. 6 clearly show a layer reflection (arrows) for a bright domain (a) and no layer reflection for a dark domain (b). In this way, we found that the smectic layer is perpendicular to the substrate surface for the bright domain, while it is more or less parallel for the dark one.

Let us turn to observation of the photoinduced texture change in the cell containing PBCOB doped with azo dyes. Before the exposure of the cell to the Ar laser beam, it contains both bright and dark domains, as shown in Figs. 7(a) and 7(d). Figures 7(b) and 7(c) are the domains after the cell shown in Fig. 7(a) was irradiated with linearly polarized light for 20 and 30 min, respectively. A gradual transformation of the dark domains to the bright domains was observed. On the other hand, the bright domains initially formed by cooling show no change on irradiation with light. The same behavior was observed by the irradiation of the cell shown in Fig. 7(d) with circularly polarized light, as shown in Figs. 7(e) and 7(f). Thus the texture change from dark to bright domain is independent of the polarization state of the incident light.

## IV. DISCUSSION

### A. Model structures of bright and dark domains

On the basis of the experimental observations mentioned in the previous section, we want to discuss the molecular orientation structures of the bright and dark domains and photoinduced structural change. It is quite evident that the bright domains are in a ferroelectric state. Because of the

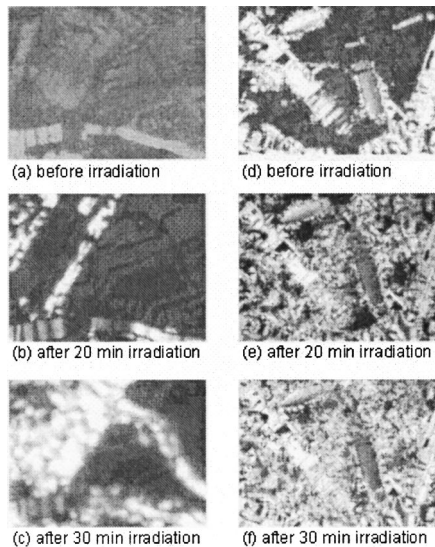


FIG. 7. Textural change by irradiation with linearly (a), (b), and (c), and circularly (d), (e), and (f) polarized light.

clear electric-field-induced rotation of the extinction brush by about  $\pm 10^\circ$ , this domain can be assigned to a synclinc ferroelectric state, i.e.,  $\text{Sm}C_S P_F$  (smectic phases with synclinc molecular tilt and ferroelectric polarization). If the bright domains had the anticlinic layer structure, i.e.,  $\text{Sm}C_A P_F$  (smectic phases with anticlinic molecular tilt and ferroelectric polarization), there should be no change of the optical axis under the application of ac electric fields.

For the dark domains, one can first postulate that they are in antiferroelectric states because of the absence of a SHG signal under zero electric field. The  $\text{Sm}C_A P_A$  (smectic phases with anticlinic molecular tilt and antiferroelectric polarization) state could give a small optical anisotropy, if the molecular tilt and the dihedral angle are appropriate. The situation is essentially the same for  $\text{Sm}C_S P_A$  (smectic phases with synclinc molecular tilt and antiferroelectric polarization), if the size of two homochiral domains along the layer normal direction is small compared with the optical wavelength. However, the present molecular tilt angle of about  $10^\circ$  cannot give small optical anisotropy, irrespective of the molecular orientation with respect to the surface, i.e., whether the bent plane is perpendicular or parallel to the surface. Moreover, the dark domain does not show an EO response, unlike the  $\text{Sm}C_A P_A$  and  $\text{Sm}C_S P_A$  states in the  $B_2$  phase. Hence, a simple antiferroelectric molecular orientation is ruled out.

Then what about a homeotropic molecular orientation, namely, the smectic layer is parallel to the substrate surface? Actually, this configuration was proposed by Jakli *et al.* [15]. They used PBCOB with 3–10 wt % of xylene and observed the texture when cooled from the isotropic phase. The low-birefringent texture formed after wide smooth and weakly birefringent stripes grew was assigned as homeotropic and was transformed into highly birefringent domains as the temperature was lowered. However, these authors showed no experimental evidence for the homeotropic alignment. In the present experiment, we confirmed that the dark domain shows no layer diffraction at normal incidence of the x-ray beam, indicating that the layer is more or less parallel to the

substrate surface and the molecules are homeotropically oriented. Let us continue to consider the model structure of the dark domain under the condition of a homeotropic orientation.

To have a low birefringence in homeotropic cells of bent-core mesogens, where the polarization is parallel to the surface, a random orientation or helical arrangement of polarization is required. Otherwise, relatively high birefringence results, as actually observed by Lee *et al.* [13] using a shear-induced homeotropic cell. The random or helical arrangement of polarization is also an attractive idea to explain the lack of SHG activity. It is also consistent with the lack of EO response, because all the polarizations are perpendicular to the field applied along the surface normal. One of the experimental observations inconsistent with this homeotropic model with random or helical polarization orientation is the texture. We can clearly see domains even in the dark regions, as shown in Figs. 2 and 5, although they are not very distinct because of the darkness. However, the homeotropic model is still a possible candidate to account for the visibility of domains, if the layer normal of each domain is slightly tilted randomly with respect to the surface normal. Then this model is also valid to account for low birefringence, no EO switching, no SH activity, and even the existence of domains of optically observable size.

Another molecular orientation model by which the present experimental observations can be explained is the modulated structure proposed recently [6]. This structure is realized by spontaneous splay of the polarization in the  $\text{Sm}C_S P_F$  structure. The polarization is locally canceled along the modulated direction, so that no SHG should appear. Low birefringence is not always the case, but is still possible under certain molecular geometries. However, to confirm this model, further experiments including detailed x-ray analyses are necessary. For the time being, the discussion will be made using the homeotropic model.

## B. Photoinduced domain change

Let us consider the mechanism of the photoinduced domain change from dark to bright on the basis of the homeotropic orientation model for the dark domain. One may consider that merely the molecular decomposition of the Schiff base compound PBCOB causes the structural change. However, this is not the case as shown by the following observations. (1) Light irradiation of pure PBCOB under the same conditions does not cause any structural change. (2) The structural change occurs only in the dark domains. Instead we propose the structural model of Fig. 8 to explain the above phenomena. Before the irradiation with light, molecules in the  $B_7$  phase have two coexisting configurations shown in Fig. 8(a), planar oriented (bright domains), and Fig. 8(c) homeotropically oriented (dark domains), where the doped azo dye molecules are intercalated parallel to the LC molecules. When the cell is exposed to light, the dye molecules change their form from *trans* to *cis*. Since azo molecules in the *cis* state have a larger effective volume than *trans* state azo molecules, they will expand the intermolecular distance of bent-core LC, as previously concluded by

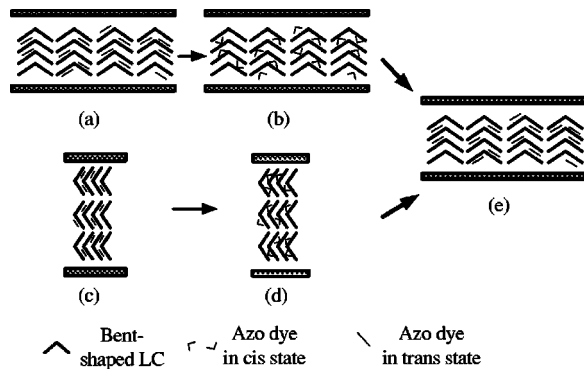


FIG. 8. Structural modeling of the transformation of LC alignment in the  $B_7$  phase of PBCOB doped with azo dyes by Ar laser light irradiation. Planar arrangement of LC molecules with azo dyes (a) in *trans* state and (b) in *cis* state homeotropic LC alignment with azo dyes (c) in *trans* state and (d) in excited *cis* state; (b) remains planar but (d) transforms to (e).

Nair *et al.* [11] through Ps and x-ray measurements. The expansion shown in Figs. 8(b) and 8(d) may cause the LC molecules to move more freely, and thereby permit the structural change. Experimentally, we found that a structural change from the homeotropic to the planar structures occurs, while the planar structure remains the same state, as shown in Fig. 8.

As mentioned above, slow cooling from the isotropic phase predominantly nucleates the dark domains, suggesting that the dark state is more stable. Therefore, the photoinduced structural change is a process from a stable state to an unstable one. However, not only the bent-core molecules but also rodlike molecules preferably take a planar alignment, unless the substrate surfaces are homeotropically treated. In this sense, the present homeotropic arrangement appearing when the cell is slowly cooled from the isotropic phase may not be a stable orientation but may be followed by helical filament formation. Instead, the bright domain could be the more stable orientation. If this is the case, the observed

photoinduced change is a process toward a stable orientation. The isomerization near surfaces may also help make structural change possible by modifying the interaction between the bent-core molecules and the surfaces.

Polarization reversal current measurements were also carried out simultaneously with the irradiation of light using the triangular field method. In contrast to the experimental results of Nair *et al.* [11], however, the Ps values show no meaningful change upon light irradiation, although slightly different switching current profiles were observed before and during the light irradiation. Nair *et al.* observed a remarkable Ps decrease during light irradiation, and ascribed it to the expansion of intermolecular spacing. In the present case, however, the light irradiation can cause not only an increase in intermolecular spacing but also a structural change from nonswitchable dark domains to switchable planar bright domains. The two effects, the former decreasing the Ps values and the latter increasing the Ps values, may be compensated, resulting in no Ps change.

## V. CONCLUSIONS

In conclusion, we discovered the coexistence of high-birefringent bright and low-birefringent dark domains. The bright domain is SHG active, while the dark one is not. We assign the bright and dark domains, respectively, to planar and homeotropic molecular orientations, based on various experimental results including x-ray diffraction. We also found that the dark domains are transformed to the bright domains by irradiation of the  $B_7$  phase doped with azo dye with Ar laser light. A possible mechanism for this transformation was discussed.

## ACKNOWLEDGMENTS

This work was partly supported by Korea Research Foundation (Grant No. KRF-2000-D2008-DP01691) and a Grant-in-Aid for Scientific Research on Priority Area (B) (Grant No. 12129202) by the Ministry of Education, Science, Sports and Culture of Japan. The authors express thanks to Chiwoong Jang for help in experiments.

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