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Polar structure in a ferroelectric bent-core mesogen as studied by second-harmonic generation

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Second-harmonic generation (SHG) measurements have been conducted in the ferroelectric liquid crystalline phase of a chiral bent-core molecule, *P*-8-OPIMB6*. Well-aligned cells were obtained by applying an electric field parallel to the substrate surfaces. In-plane anisotropy of the SHG signal observed at normal incidence of light shows two- or four-leaf patterns depending on polarization conditions, indicating a ferroelectric uniform structure. The detailed analysis of the data by taking account of optical anisotropy in the SHG active bulk leads to the determination of nonlinear susceptibility tensor components, $d_{333}=14.4$ pm/V and $d_{311}=49.2$ pm/V. Using the *d* coefficients thus determined, the hyperpolarizability tensor components of the molecule are also determined as $\beta_{zzz}=14.5\times 10^{-30}$ esu and $\beta_{zxx}=67.6\times 10^{-30}$ esu. These values well agree with those of the achiral homolog *P*-12-OPIMB previously determined by hyper-Rayleigh scattering.

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Bent-core molecular systems have evoked considerable interest in the field of liquid crystals (LCs) due to the emergence of polarity and chirality in achiral systems since the discovery by Niori *et al.* [1]. The bent-core molecules produce in-layer polar order because of their close packing [1] and result in a ferroelectric/antiferroelectric LC that shows ferroelectric/antiferroelectric (bistable/tristable) switching in achiral LCs [1–7]. The introduction of chirality due to the tilt of bent-core molecules from the smectic layer normal [8], spontaneous formation of chiral domains [9,10], and enhanced twisting power by doping conventional chiral phases with achiral bent-core molecules [11] are topical features from the viewpoint of chirality.

In the present paper we confine ourselves to presenting the polar nature. Although numerous kinds of bent-core LC compounds have been synthesized, only a very few ferroelectric phases have been confirmed [6,7,12–14]. However, the unambiguous identification of the ferroelectric ground state is not easy, since the electric-field-induced ferroelectric state is sometimes quasistable [15]. In fact, the bistable electro-optic switching misled us into identifying the ferroelectric phase. In this sense, the recently synthesized chiral bent-core molecule [*P*-8-OPIMB6*, Fig. 1(a)], which is a chiral analog of the standard achiral bent-core molecule *P*-8-OPIMB, is an unambiguously confirmed ferroeletric LC [6]. In the ferroelectric phase of this material, it is suggested that the molecules form a tilted smectic phase with an anticlinic ferroelectric order (Sm-C_AP_F), so that the chirality of each layer alternates from layer to layer to form a racemic layer structure in spite of chiral mesogens [7]. In sandwich cells, twisted molecular orientation is suggested with a uniform dipole orientation parallel to the cell surfaces in the middle of the cell, as shown in Fig. 1(b) [7]. In the present experiment, an electric field was applied parallel to the surface to produce a uniform alignment [Fig. 1(c)].

Since the polar order is equivalent to a noncentrosymmetric molecular arrangement, the ferroelectric system can be highly active for second-order nonlinear optics. Hence the second-order nonlinear phenomenon becomes a powerful tool to investigate these polar properties. So far, the second-harmonic generation (SHG) technique has been widely used for confirming the existence of a polar order in rod-shaped molecular systems [16–20]. Recently, the application of this technique was also made to bent-core molecular systems [21–23]. In fact, it was found that the bent-core molecules allow remarkably high values of molecular hyperpolarizability due to their characteristic molecular geometry [24] and that they show remarkably high macroscopic hyperpolarizability (nonlinear suscesptibility). However, the detailed comparison between molecular and macroscopic hyperpolarizabilities has never been made, partly because of the lack of well-aligned sample cells. Second-order nonlinear optic phenomena are characterized by certain components of the third-rank nonlinear susceptibility tensor, so that the tensor analysis gives us direct information of the symmetries and polar

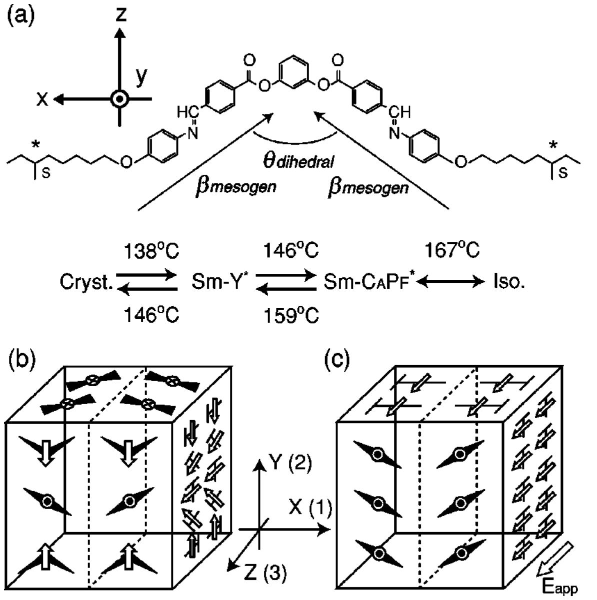

FIG. 1. (a) Chemical structure and phase transition sequence of *P*-8-OPIMB6*. The present experiments were made in the anticlinic ferroelectric Sm-C_AP_F phase. (b) Molecular orientation in the unperturbed state, where a twisted molecular orientation is suggested. (c) Molecular orientation under an electric field parallel to substrate surfaces.

properties. In this study, we report transmitted SHG from well-aligned domains in the ferroelectric phase of *P*-8-OPIMB6* to investigate the symmetry and packing of bent-core molecules into a layer structure, and demonstrate that the SHG method is very useful for structure investigation on the bent-core molecular system.

In this study, a modified three-layer model was used for analyzing the SHG results. In the conventional three-layer model [25], linear and nonlinear wave equations are solved under two boundary conditions at two bounding interfaces between an SHG active layer and two SHG inactive isotropic media. Here, in-plane optical isotropy of the active layer is assumed. This assumption does not bring about serious problems, when in-plane analyses are carried out for very thin media. However, since most of the liquid crystalline systems have optical anisotropy and are treated in a bulk form, the contribution of this anisotropy becomes serious when the bulk thickness becomes comparable with the coherent length. To overcome this problem, we modified the model (modified three-layer model) to be able to calculate the wave propagation of ordinary and extraordinary light separately, by taking account of the optical anisotropy in the SHG active layer at fundamental and SH wavelengths. The usefulness of using the modified three-layer model will be mentioned when presenting the data and simulation.

Let us consider the wave propagation at normal incidence. For isotropic media, the dielectric tensor is expressed by a diagonal matrix form with an identical component ϵ. For the isotropy, the tensor form is always the same, being independent of the media rotation angle, and hence wave propagation is also independent of the media rotation. Moreover, the wave behavior is dominated only by one tensor component ϵ, independently of its polarization direction. In contrast, we have to use a diagonal matrix of the dielectric tensor for an anisotropic medium as follows:

$$\begin{pmatrix} \epsilon_1 & 0 & 0 \\ 0 & \epsilon_2 & 0 \\ 0 & 0 & \epsilon_3 \end{pmatrix}. \tag{1}$$

When the beam propagates parallel to the Y axis, the electric field of the wave exists in the Z-X plane. Then the fundamental light E_0 is separated into $E_X = E_0 \sin\phi$ and $E_Z = E_0 \cos\phi$, where ϕ is the media rotation angle. By solving a linear wave equation using the modified three-layer model, we got four wave solutions in the SH active medium $E_X^{mf}, E_X^{mb}, E_Z^{mf}$, and E_Z^{mb}. Here the superscripts mf and mb denote forward and backward waves of the fundamental light, respectively. Then the nonlinear polarization is given by

$$P_i^{(2)} = \sum_{i,j} N_p \chi_{ijk} (E_j^{mf} E_k^{mf} + E_j^{mb} E_k^{mf} + E_j^{mf} E_k^{mb} + E_j^{mb} E_k^{mb}),$$

$$\text{where } N_p = \begin{cases} 1 & (j=k) \\ 2 & (j \neq k). \end{cases} \tag{2}$$

The SH wave generated from the nonlinear polarization is also calculated separately for two polarization directions by solving the nonlinear wave equation using the modified three-layer model and gives four wave solutions, $E_X^{MF}, E_X^{MB}, E_Z^{MF}$, and E_Z^{MB}, where MF and MB stand for the forward and backward waves of the SH light, respectively. Then the SH signal outputted from the sample is obtained as the summation of these two directional contributions.

As a fundamental beam for SHG measurements, we used an Nd: YAG laser system (HOYA continuum SL-II) of $\lambda = 1064$ nm with a repetition frequency of 10 Hz and a pulse duration of 8 ns. The pulse energy was about 0.4 mJ/cm^2. A reference beam was separated from the fundamental beam by a beam splitter and led onto a powder cell of methylnitroaniline to generate a reference signal. The polarization of the fundamental beam was controlled with an input polarizer and a half-wave plate. Visible light was cut by a color filter in front of the sample cell. The diameter of the incident beam was precisely controlled to be 200 μm by using a pinhole. The sample cell was settled in a heater block and illuminated from the cell normal. Transmitted SH light generated from the sample was led into an output polarizer and finally detected by a photomultiplier tube (Hamamatsu model-R955) after passing through IR-cut and interference filters. The electronic-converted signals were accumulated with a BOXCAR integrator (Stanford Research Systems) and outputted to a personal computer system. For the quantitative determination of the d components, the SH intensity from a Y-cut quartz ($d_{111} = 0.4$ pm/V) was also measured under the same condition.

The sample compound *P*-8-OPIMB6* was introduced into the sandwich-shaped glass cell of a thickness of 13 μm at a temperature of 190 °C (isotropic phase) with capillary action. The cell has in-plane electrodes with a gap of 1 mm on one side of its inner surfaces. Molecular alignment was achieved by an application of a triangular field to avoid electrolytic decompression. The triangular field was applied synchronously with the laser pulses through a delay circuit.

Figure 2 shows the temporal variation of the SH signal intensity during the application of a triangular field for two fixed combinations of the input (in) and output (out) polarizations. The SHG signal was detected at a certain delay time after $t = 0$ ms of the triangular field and was accumulated to give each data point. The input and output polarizations are (a) 0°(in)-0°(out) and (b) 90°(in)-0°(out) with respect to the electric field. The SH intensities in Figs. 2(a) and 2(b) can be compared to each other. Two facts are readily seen in Fig. 2. (1) The off-diagonal nonlinear susceptibility component gives major contribution, since the signal for 90°(in)-0°(out) geometry is much larger than that for 0°(in)-0°(out). (2) A polar structure changes just after changing the polarity of the field, showing narrow peaks (dips) at about delays of 8 ms and 58 ms, and remains after these changes. Thus, ferroelectric bistable switching occurs.

To analyze the polar structure of the ferroelectric uniform state, a polarizer rotation method (PRM) was adopted. The input and output polarizers were set to be parallel or crossed to each other, and were rotated in the same direction at the same time. The anisotropic SHG response with respect to the

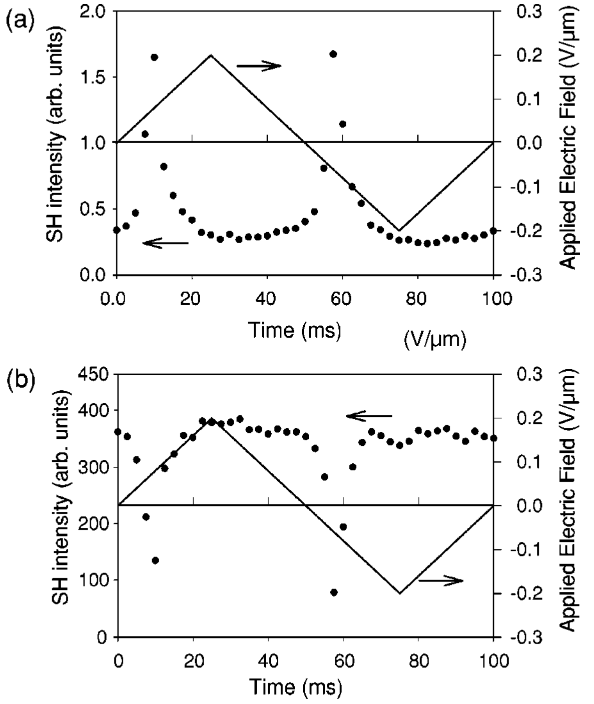

FIG. 2. Temporal change of the SH signal intensity for two fixed combinations of the input (in) and output (out) polarization; (a) 0°(in)-0°(out) and (b) 90°(in)-0°(out). The latter shows stronger SHG than the former. SHG peaks are attributed to ferroelectric switching motion of the molecules.

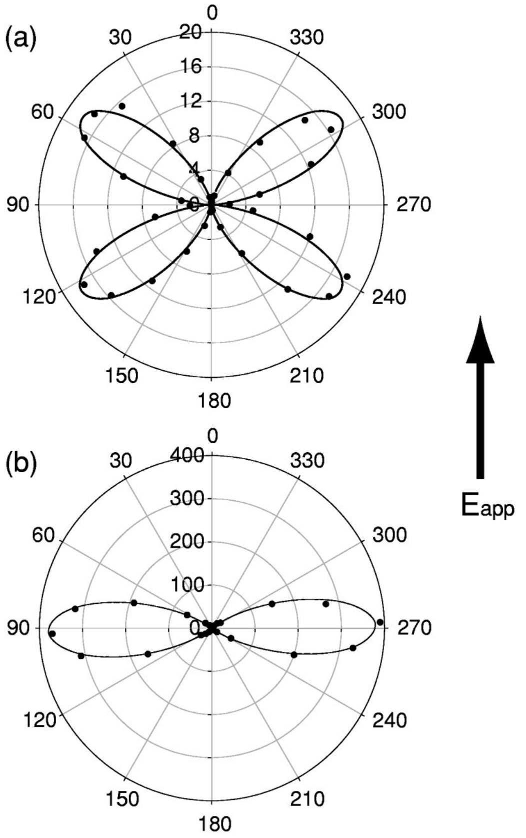

FIG. 3. Polar plots of the SHG intensity obtained by the polarizer rotation method for (a) paranicol and (b) crossnicol polarization geometries. The angles denote input polarization angles with respect to an applied electric field. Closed circles and solid curves represent experimental points and theoretical best fit, respectively.

polarizer rotation directly reflects the in-plane polar structure. The PRM results are shown in Fig. 3. The angles represent those between the directions of the input polarizer and the electric field. The delay time was fixed at 40 ms where the ferroelectric uniform state was maintained (see Fig. 2). The experimental plots exhibit (a) four- and (b) two-leaf patterns, suggesting the existence of a uniform anisotropic structure, the symmetry of which is C_{2v}, C_2, or higher. The previous texture observation suggested the structure shown in Fig. 1(c). This structure has C_{2v} symmetry, being consistent with Fig. 3, although the active components of the nonlinear coefficient tensors of C_{2v} and C_2 are common in the present optical geometry and these symmetries are undistinguishable. There are only three nonvanishing components, d_{333}, d_{311}, and d_{131}, and, moreover, the active components are reduced to only two, d_{333} and $d_{311}=d_{131}$, under Kleinnmann's symmetry and intrinsic permutation.

Introducing these two independent components to the modified three-layer model, we can simulate the best-fitted patterns, as shown by solid curves in Fig. 3. The theoretical curves are well fitted to the experimental results for both optical geometries. It is worth noting that such good agreement cannot be obtained on the basis of the conventional three-layer model. Hence the introduction of optical anisotropy to the theory is essential to analyze relatively thick polar films with in-plane anisotropy such as liquid crystal cells. From the fit, we deduced the quartz-normalized values of d_{333} and d_{311} as 14.4 pm/V and 49.2 pm/V, respectively. These values are much larger than those of usual ferroelectric liquid crystalline materials [26,27]. SHG measurements have also been carried out in the field-induced synclinic ferroelectric Sm-C_SP_F phase of an achiral bent-core mesogen *P*-12-OPIMB by Macdonald *et al.* [21]. The symmetry of their system is C_2, being different from that of the present system. They obtained d_{333} and d_{311} as 10.1 pm/V and 16.5 pm/V, respectively, using a multidomain cell. The relatively good agreement in d_{333} values is due to the application of an electric field, which aligns the *z* axis to the field, and the disagreement in d_{311} values is due to the random in-plane anisotropy in their cell.

To discuss the microscopic structure, let us assume the oriented gas model that describes a relation between nonlinear susceptibility *d* and hyperpolarizability β as

$$d^{(2)}_{IJK}=Nf_I^{2\omega}f_J^{\omega}f_K^{\omega}\frac{1}{N_g}\sum_{ijk}\sum_{n}^{N_g}(\cos\theta_{Ii}\cos\theta_{Jj}\cos\theta_{Kk})\beta_{ijk}, \tag{3}$$

where *N*, *f*, and N_g are the number densities of the LC molecules, Lorentz factor, and coordination number, respectively. If the molecules are packed with a perfect alignment into the C_{2v} (Sm-C_AP_F) space group, as illustrated in Fig. 1(c), Eq. (3) is written as

$$d_{333}^{(2)}=Nf_3^{2\omega}f_3^{\omega}f_3^{\omega}\frac{1}{N_g}(\beta_{zzz}\cos^3\theta_{3z}+\beta_{zxx}\cos\theta_{3z}\cos^2\theta_{3x}), \tag{4}$$

$$d_{311}^{(2)}=Nf_3^{2\omega}f_1^{\omega}f_1^{\omega}\frac{1}{N_g}(\beta_{zzz}\cos\theta_{3z}\cos^2\theta_{1z}+\beta_{zxx}\cos\theta_{3z}\cos^2\theta_{1x}). \tag{5}$$

For the bent shape, we consider a bis-dipolar model that is based on the realistic assumption that the molecule consists of two rodlike mesogens linked with a certain dihedral angle $\theta_{dihedral}$. We also consider that each mesogen unit has only one dominant hyperpolarizability component $\beta_{mesogen}$ along its long axis [28,29]. Then β's are described as

$$\beta_{zzz}=2\left(\cos\frac{\theta_{dihedral}}{2}\right)^3\beta_{mesogen}, \tag{6}$$

$$\beta_{zxx}=2\left(\cos\frac{\theta_{dihedral}}{2}\right)\left(\sin\frac{\theta_{dihedral}}{2}\right)^2\beta_{mesogen}. \tag{7}$$

From these four equations [(4)–(7)] and the molecular tilt of 34° determined by texture observation [7], the molecular hyperpolarizability tensor components were also estimated as $\beta_{zzz}=14.5\times10^{-30}$ esu and $\beta_{zxx}=67.6\times10^{-30}$ esu. These well agree with the values of $\beta_{zzz}=15.3\times10^{-30}$ esu and $\beta_{zxx}=61.5\times10^{-30}$ esu previously reported by the hyper-Rayleigh scattering method for the achiral homolog *P*-12-OPIMB [24]. This comparison leads us to conclude that the ferroelectric phase of the chiral bent-core molecules has a highly ordered molecular arrangement. The dihedral angle $\theta_{dihedral}$ was determined as 127.6° at the same time and is also consistent with the values reported by surface SHG for the Langmuir-Blodgett (LB) monolayer of *P*-12-OPIMB (127°) [28] and x-ray diffraction (XRD) measurement for *P*-8-OPIMB (122°) [30]. This is an additional distinct evidence of the high-ordered ferroelectric packing of the chiral bent-core molecules.

Finally a comment should be made on the SHG signal in the absence of an electric field. As we have already shown [6,7], the unperturbed states after terminating a field are also SHG active and are bistable. We suggested the twisted structure shown in Fig. 1(b) by the texture observation without distinct evidence [7]. The SHG in-plane anisotropy was also observed in these states. However, the pattern is very complicated, i.e., six peaks for a full polarizer rotation of 2π, and cannot be simulated using any uniform molecular orientations. The simulation by assuming the twisted structure is now going on and will be reported in the near future.

To summarize, the polar structure of the ferroelectric phase of a chiral bent-core molecule *P*-8-OPIMB6* was investigated by means of the SHG method. The result was well explained by the modified three-layer model, which includes in-plane optical anisotropy in SHG active media. The good agreement between experimental and simulated results demonstrates that the modified three-layer model is useful to investigate high birefringent bulk media such as LC cells. Their nonlinear coefficients $d_{333}=14.4$ pm/V and $d_{311}=49.2$ pm/V are much larger than those of usual ferroelectric materials. From this result and the bis-dipolar model, hyperpolarizability components of the molecules were estimated as $\beta_{zzz}=14.5\times10^{-30}$ esu and $\beta_{zxx}=67.6\times10^{-30}$ esu, and the molecular dihedral angle was also determined as 127.6°. These values are consistent with previous reports by hyper-Rayleigh scattering, XRD, and surface SHG for the LB monolayer. Hence we proved that the chiral bent-core molecules are highly ordered in their ferroelectric phase.

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[1] T. Niori, T. Sekine, J. Watanabe, and H. Takazoe, J. Mater. Chem. **6**, 1231 (1996).
[2] S. Diele, S. Grande, H. Kruth, Ch. Lischka, G. Pelzl, W. Weissflog, and I. Wirth, Ferroelectrics **212**, 169 (1998).
[3] G. Pelzl, S. Diele, S. Grande, A. Jakli, Ch. Lischka, H. Kresse, H. Schmalfuss, I. Wirth, and W. Weissflog, Liq. Cryst. **26**, 401 (1999).
[4] M. Zennyoji, Y. Takanishi, K. Ishikawa, J. Thisayukta, J. Watanabe, and H. Takezoe, J. Mater. Chem. **9**, 2775 (1999).
[5] M. Zennyoji, Y. Takanishi, K. Ishikawa, J. Thisayukta, J. Watanabe, and H. Takezoe, Jpn. J. Appl. Phys., Part 1 **39**, 3536 (1999).
[6] E. Gorecka, D. Pociecha, F. Araoka, D.R. Link, M. Nakata, J. Thisayukta, Y. Takanishi, K. Ishikawa, J. Watanabe, and H. Takezoe, Phys. Rev. E **62**, R4524 (2000).
[7] M. Nakata, D.R. Link, F. Araoka, J. Thisayukta, Y. Takanishi, K. Ishikawa, J. Watanabe, and H. Takezoe, Liq. Cryst. **28**, 1301 (2001).
[8] D.R. Link, G. Natale, R. Shao, J.E. Maclennan, N.A. Clark, E. Körblova, and D.M. Walba, Science **278**, 1924 (1997).
[9] J. Thisayukta, Y. Nakayama, S. Kawauchi, H. Takezoe, and J. Watanabe, J. Am. Chem. Soc. **122**, 7441 (2000).
[10] J. Thisayukta, H. Takezoe, and J. Watanabe, Jpn. J. Appl. Phys., Part 1 **40**, 3277 (2001).
[11] J. Thisayukta, H. Niwano, H. Takezoe, and J. Watanabe, J. Am. Chem. Soc. **124**, 3354 (2002).
[12] D.M. Walba, E. Korblova, R. Shao, J.E. Maclennan, D.R. Link, M.A. Glaser, and N.A. Clark, Science **288**, 2181 (2000).
[13] J.P. Bedal, H.T. Nguyen, J.C. Rouillon, J.P. Marcerou, G. Sigaud, and P. Barois, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **332**, 163 (1999).
[14] H. Nadasi, W. Wiessflog, A. Eremin, G. Pelzl, S. Diele, B. Das, and S. Grande, J. Mater. Chem. **12**, 1316 (2002).
[15] D. R. Link, M. Nakata, J. Thisayukta, Y. Takanishi, K. Ishikawa, J. Watanabe, and H. Takezoe, in Abstracts of the 8th

International Conference on Ferroelectric Liquid Crystals, Washington, D.C., 2001, p. 9.

[16] I. Drevensek Olenik, R. Torre, and M. Copic, Phys. Rev. E **50**, 3766 (1994).

[17] M.I. Barnik, L.M. Blinov, A.M. Dorzhkin, and N.M. Shtykov, Mol. Cryst. Liq. Cryst. **98**, 1 (1983).

[18] D.M. Walba, M.B. Ros, T. Sierra, J.A. Rego, N.A. Clark, R. Shao, M.D. Wand, R.T. Vohra, K. Arnett, and S. Velsko, Ferroelectrics **121**, 247 (1991).

[19] T. Furukawa, K. Ishikawa, H. Takezoe, A. Fukuda, T. Watanabe, S. Miyata, T. Nishi, M. Sone, and J. Watanabe, Mol. Cryst. Liq. Cryst. **15**, 167 (1996).

[20] B. Park, Y. Kinoshita, H. Takezoe, and J. Watanabe, Jpn. J. Appl. Phys., Part 2 **37**, L136 (1998).

[21] R. Macdonald, F. Kentischer, P. Warnick, and G. Heppke, Phys. Rev. Lett. **81**, 4408 (1998).

[22] F. Kentischer, R. Macdonald, P. Warnick, and G. Heppke, Liq. Cryst. **25**, 341 (1998).

[23] S.-W. Choi, Y. Kinoshita, B. Park, H. Takezoe, T. Niori, and J. Watanabe, Jpn. J. Appl. Phys., Part 1 **37**, 3408 (1998).

[24] F. Araoka, B. Park, Y. Kinoshita, K. Ishikawa, H. Takezoe, J. Thisayukta, and J. Watanabe, Jpn. J. Appl. Phys., Part 1 **38**, 3526 (1999).

[25] H. Hoshi, T. Yamada, K. Ishikawa, H. Takezoe, and A. Fukuda, Phys. Rev. B **52**, 12 355 (1995).

[26] D.M. Walba, M. Blanca Ros, T. Sierra, J.A. Rego, N.A. Clark, R. Shao, M.D. Wand, R.T. Vohra, K.E. Arnett, and S.P. Velsco, Ferroelectrics **121**, 247 (1991).

[27] K. Schmitt, R.-P. Herr, M. Schadt, J. Funfshilling, R. Buchecker, X.H. Chen, and C. Benecke, Liq. Cryst. **14**, 1735 (1993).

[28] Y. Kinoshita, B. Park, H. Takezoe, T. Niori, and J. Watanabe, Langmuir **14**, 6256 (1998).

[29] H.J. Deussen, E. Hendrickx, C. Boutton, D. Krog, K. Clays, K. Bechgaard, A. Persoons, and T. Bjϕrnholm, J. Am. Chem. Soc. **118**, 6841 (1996).

[30] G. Pelzl, S. Diele, and W. Weissflog, Adv. Mater. **11**, 707 (1999).