Splayed polarization in the ferroelectric phase of a bent-core liquid crystal as studied by optical second-harmonic generation

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Splayed polarization orientation has been confirmed in the anticlinic ferroelectric phase of a bent-core liquid crystal containing chiral end chains, P-8-OPIMB6*, by optical second-harmonic generation (SHG). The in-plane anisotropy of the SHG signal exhibits an unusual six-peak pattern under the rotation of parallel polarizers in the absence of an electric field, while a usual four-peak pattern simulatable using a uniform molecular orientation model is observed under a field. The unusual pattern was explained by considering a splayed polarization orientation including the effect of polarization charges.

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Macroscopic polar order is not stable in soft condensed matters such as liquid crystals (LCs) and Langumuir films. Actually many types of structures to escape from the polar structures have been suggested and observed. The structures with a splayed polarization have been observed in many soft materials [1–5]. It was reported quite recently that the splayed polarization in ferroelectric bent-core molecules induces modulated layer structures with boundaries separating domains with opposite polarizations and opposite layer chirality [6], resulting macroscopically in an antiferroelectric structure. Here we report another type of splayed polarization bounded by substrate surfaces without the layer modulation, so that finite macroscopic inlayer polarization is preserved parallel to the substrate surfaces in a bent-core LC shown in Fig. 1(a).

Bent-core LCs opened a new era of LC science particularly in the viewpoint of polarity and chirality. Closed packing of bent-core molecules results in polar order in each smectic layer [7]. Both ferroelectric and antiferroelectric phases are possible depending on polar correlation between adjacent layers. Since molecules are nonchiral, molecular tilt with respect to the smectic layer and the inlayer polarization direction has no correlation unlike the conventional ferroelectric chiral smectic $C(\mathrm{Sm}C^*)$ and antiferroelectric chiral smectic $C_\mathrm{A}(\mathrm{Sm}C^*_\mathrm{A})$ phases. Moreover, the molecules tilting right and left with the same polarization direction comprise the opposite chiral layers [8]. This layer chirality brings about a variety of interesting phenomena. In this paper, we focus on polarity in the B2 phase of bent-core LCs.

The most widely studied B2 phase has four different structures that are characterized by interlayer correlations of clinicity and polarity. We specify these structures as $\mathrm{Sm}C_{\mathrm{S,A}}P_{\mathrm{A,F}}$, where the tilt to the same and opposite directions is specified by S (synclinic) and A (anticlinic) and the polar order is specified by A (antiferroelectric) and F (ferroelectric). Among bent-core LCs ever synthesized, only a few materials unambiguously show the ferroelectric phase. Some of them were assigned to the $\mathrm{Sm}C_\mathrm{S}P_\mathrm{F}$ state. This state relaxes to a modulated layer structure because of polarization modulation consisting of splayed polarization [6], as already mentioned above. However, the situation is different in $\mathrm{Sm}C_\mathrm{A}P_\mathrm{F}$. Because of the alternate tilt in adjacent layers, the modulated layer structure would bring about large elastic deformation in alternate layers, suppressing the modulation [6]. Therefore, $\mathrm{Sm}C_\mathrm{A}P_\mathrm{F}$ could be the only ferroelectric structure retaining macroscopic polar order. Then, is there any splayed polarization structure in $\mathrm{Sm}C_\mathrm{A}P_\mathrm{F}$? The answer is yes. We will show in the following that polarization splay occurs between two substrate surfaces without introducing layer deformation.

Such a splayed polarization structure has already been proposed, as shown in Fig. 1(c) based on polarizing microscope observation [9]; the extinction direction under crossed polarizers is always along the layer normal, the birefringence is small and gives only a slight change in the absence and presence of a field across the cell. No optical rotation occurs for normal incidence of light, since the projection of molecules onto the plane parallel to the substrate rotates clockwise and counterclockwise in adjacent layers from the top to the bottom of the cell. In this sense it is quite difficult to confirm the splayed polarization structure in $\mathrm{Sm}C_\mathrm{A}P_\mathrm{F}$. In this paper, we use the second-harmonic generation (SHG) in-plane anisotropy and its simulation to convince the splayed polarization structure.

A ferroelectric bent-core LC molecule P-8-OPIMB6* [Fig. 1(a)] [9,10] was introduced into a sandwich cell which had a pair of in-plane electrodes on one side of the inner surfaces of the glass substrates [Fig. 1(b)]. By applying an in-plane field of 0.1 V_{pp}/μm in the tilted smectic (ferroelectric) LC phase, we obtained a well-aligned layer structure perpendicular to the substrates [Figs. 1(c) and 1(d)] without using rubbing treatment [9]. Polarizer rotation measurements (RPM) have been carried out to obtain in-plane anisotropy of the SHG signal [11]. Polarized SHG signals parallel to the input polarization of light were detected along the transmis-

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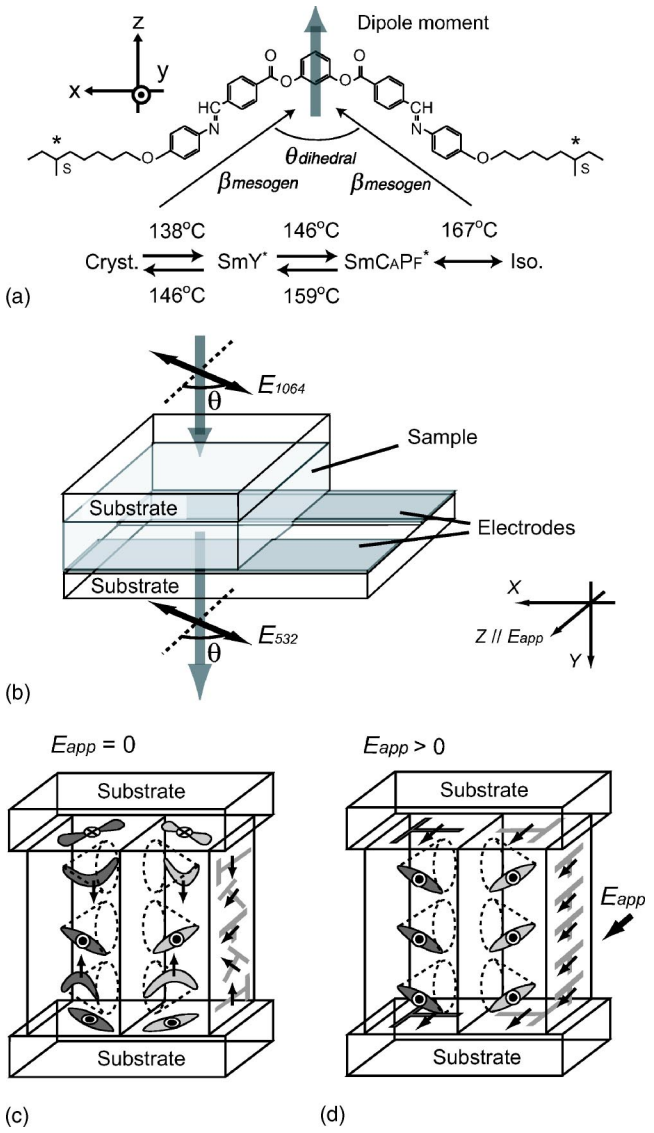

FIG. 1. (a) Chemical structure and phase sequence of P-8 -OPIMB6*. (b) Cell and optical geometries for SHG measurements. The input and SHG beams propagate perpendicular to the cell surface and parallel to the smectic layer. (c) Molecular orientation in the unperturbed state. A twisted structure of molecular director or splayed orientation of polarization has been suggested by texture observation. (d) Uniformly aligned state under an in-plane electric field. This structure was used to determine the nonlinear susceptibility elements.

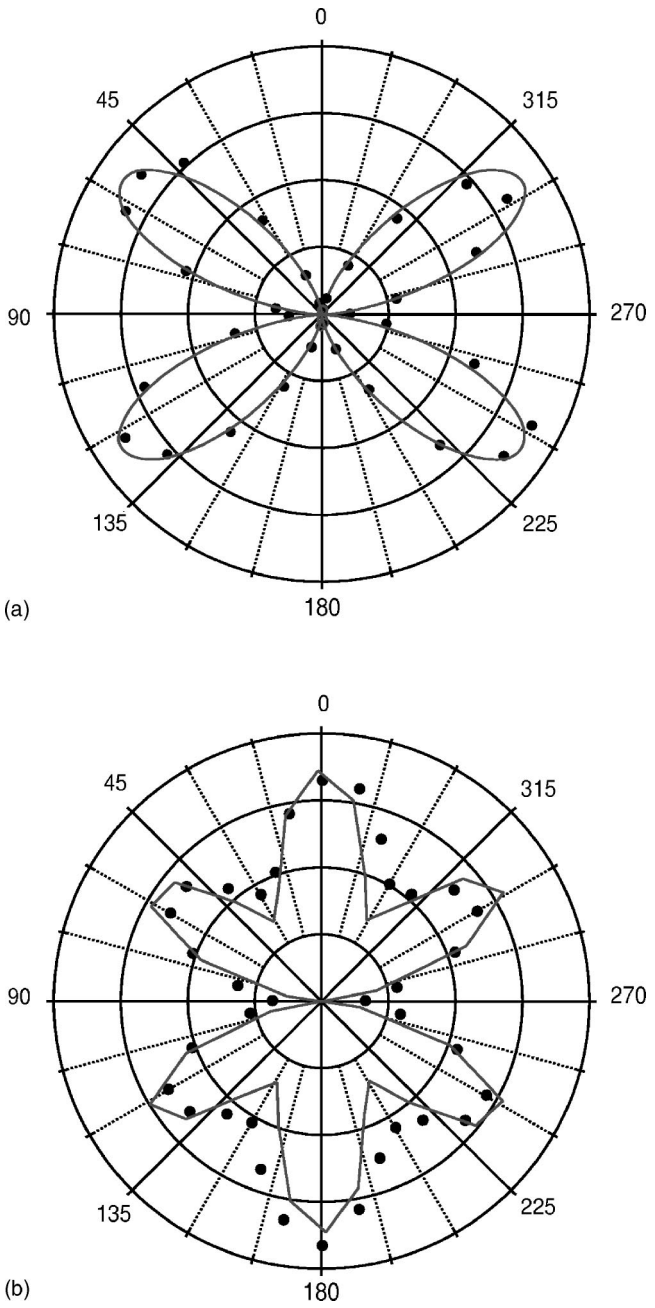

FIG. 2. Polar plots of the experimental results of SHG in-plane anisotropy as a function of rotation angle of parallel polarizers: (a) perturbed (under an in-plane electric field, from Ref. [11]) and (b) unperturbed (in the absence of a field) conditions. The solid lines are the simulated results under the condition given in the text. Good agreement is obtained.

sion direction with rotating parallel polarizers [Fig. 1(b)].

We have already shown that RPM signal from a cell under an in-plane field has four peaks, as shown in Fig. 2(a). In our previous work, we succeeded in simulating the data using the structure shown in Fig. 1(d) having point group C_{2V} and determining nonlinear susceptibility elements [11]. In the unperturbed state after field termination, on the other hand, RPM signal under the same optical condition shows six peaks, as shown by dots in Fig. 2(b). Although the polar plot pattern looks like symmetric, this six-peak result cannot be simulated using any uniform structure.

To simulate the unusual six-peak pattern, we examined the molecular orientation model shown in Fig. 1(c). This structure could be realized by surface polar interaction and/or splayed polarization. The energy to be taken into account is an elastic energy, the surface polar interaction, and the intermolecular polarization interaction including the effect of polarization charge. If the surface polar interaction is very strong, the molecular dipoles in the vicinity of substrate surfaces stick perpendicular to the substrate, being considered

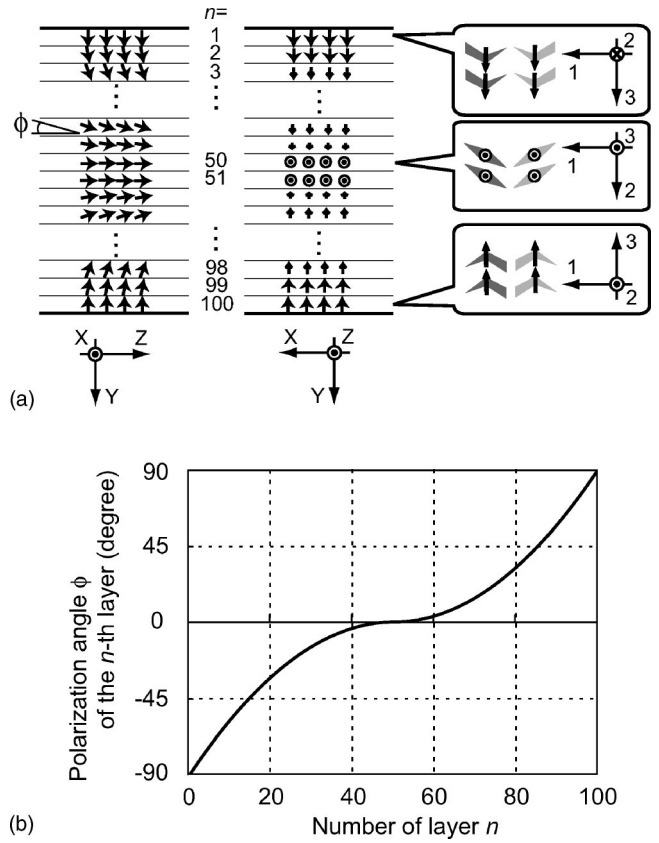

FIG. 3. The model structure used in the present simulation: (a) polarization (coordinate axes fixed to a molecule) variation in a cell and (b) the depth profile of the polarization angle with respect to the surface.

as a boundary condition. Then the structure results in uniform splayed polarization orientation. However, the splayed polarization produces polarization charges, which cost higher energy. To avoid this, splay rate in the middle of the cell becomes less, pushing the polarization charges toward surfaces, as also shown in chiral SmC^* ferroelectric liquid crystals [12,13].

Based on such qualitative consideration, we assumed the model structure as a quadratic function for upper and lower halves of a cell, as shown in Fig. 3. The thickness of a LC cell is 13 μm. SHG signals for the present model were calculated by a stacked multilayer method in Ref. [14]. In this method, LC cell was sliced into 100 anisotropic layers parallel to the substrate and perpendicular to the smectic layer. Each layer was assumed to obey the biaxial crystal optics. Under the assumption that the power depletion of the fundamental wave is negligible, we consider the solutions for

$$\nabla \times \nabla \times \boldsymbol{E}(\omega) + \frac{\epsilon(\omega)}{c^2}\frac{\partial^2 \mathbf{E}(\omega)}{\partial t^2} = 0,$$

$$P_i(2\omega) = \sum \chi_{ijk} E_j(\omega) E_k(\omega),$$

$$\nabla \times \nabla \times \mathbf{E}(2\omega) + \frac{\epsilon(2\omega)}{c^2}\frac{\partial^2 \mathbf{E}(2\omega)}{\partial t^2} = -\frac{4\pi}{c^2}\frac{\partial^2 \mathbf{P}(2\omega)}{\partial t^2},$$

where $\mathbf{E}(\omega)$ and $\epsilon(\omega)$ are the electric field and the dielectric tensor for the fundamental wave, $\mathbf{P}(2\omega)$ is the nonlinear polarization, $\mathbf{E}(2\omega)$ and $\epsilon(2\omega)$ are the electric field and dielectric tensors for the SH wave. All the boundary conditions are considered in this method. Therefore, it enables us to simulate the SH signal from the media even having variation of optical properties along light propagation axis. Each sliced layer has the point group C_{2V}. But the polarization directions, i.e., twofold axis (z axis) of the layers, is continuously twisted by 180° from the top layer to the bottom layer. Figure 3(b) shows a functional image representing such a continuous change of the angle ϕ between the z axis of each layer and the cell plane (Z-X plane). The parameters for each layer are the values determined for the uniform Sm$C_A P_F$ structure in Ref. [11]. Actually, Ref. [11] gave merely the partial elements of the nonlinear coefficient tensor $d^{(2)}_{IJK}$ because of normal incident geometry. Nevertheless, we can estimate the entire elements required for the calculation by using the bis-dipolar model [15]. Then the generalized formula,

$$d^{(2)}_{IJK} = 2N f_I^{2\omega} f_J^{\omega} f_K^{\omega} \frac{1}{N_g} \left\{ \beta_{mesogen} \cos\frac{\theta_{dihedral}}{2} \times \left[\cos^2\frac{\theta_{dihedral}}{2} \cos\theta_{Iz}\cos\theta_{Jx}\cos\theta_{Kz} + \sin^2\frac{\theta_{dihedral}}{2} (\cos\theta_{Iz}\cos\theta_{Jz}\cos\theta_{Kx} + \cos\theta_{Ix}\cos\theta_{Jz}\cos\theta_{Kx} + \cos\theta_{Ix}\cos\theta_{Jz}\cos\theta_{Kz}) \right] \right\},$$

is available for the tilted smectic phase of the bent-core molecular system [16]. Here, $\beta_{mesogen}$ is a second-order molecular hyperpolarizability component along the mesogenic axis and $\theta_{dihedral}$ is a dihedral angle of two linked mesogens, as shown in Fig. 1(a). N and N_g represent density and number of molecules in a unit cell, respectively. And f_I^{ω} is Lorentz factor along I axis at frequency ω. The estimated nonzero elements were $d^{(2)}_{333}=14.4$ pm/V, $d^{(2)}_{311}=d^{(2)}_{131}=d^{(2)}_{113}=49.2$ pm/V, $d^{(2)}_{322}=d^{(2)}_{232}=d^{(2)}_{223}=18.1$ pm/V.

The solid line in Fig. 2(b) is the theoretical result, also showing a six-peak pattern and well tracing the experimental result shown by dots. We also confirmed that the uniformly splayed orientation does give six-peak pattern but with a largely different shape. Thus we can conclude that a very characteristic six-peak SHG in-plane anisotropic pattern can be simulated by the splayed polarization model including the effect of polarization charge. In other words, the splayed polarization orientation shown in Fig. 1(c) is confirmed and the six-peak pattern provides a distinct evidence of the existence of the splayed polarization structure.

In conclusion, we succeeded in simulating a distinctive six-peak SHG in-plane anisotropic pattern by the model based on splayed polarization including the effect of polarization charge. Although we could not clarify the cause of the splayed polarization, two possible ideas, i.e., polar surface interaction and escape from macroscopic polarization, were proposed. In the former case, the splayed structures must exist even in other structures such as Sm$C_A P_A$ and Sm$C_S P_A$ The splayed structures in these phases have never

been discussed in bent-core mesogens, because it is difficult to prove the structure by simple optical methods. The splayed structure may be related to the experimental observation of large CD(circular dichroism) and rotatory power, so that the problem is of prime importance for the future works on bent-core mesogens. If the escape from the polar structure plays a dominant role for the splayed structure, the contrast to the splayed polarization structure in SmC^* is also quite interesting. The effect of polarization charge was also evidently obtained by the comparison between the experiments and simulation, i.e., uniform splayed structure cannot provide the in-plane anisotropic SHG pattern experimentally obtained. The effect of polarization charge was also discussed to study the mechanism of *V* shaped switching [12,13]. The present work is important in the sense that in-plane SHG technique could be a powerful tool to identify the nonuniform splayed polarization structure.

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