

Time-resolved infrared spectroscopic study of the switching dynamics of a surface-stabilized ferroelectric liquid crystal

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本研究では時間分解赤外分光法により、印加電場極性反転に伴う Sm-C*相強誘電性液晶分子再配向過程の、各遅延時間における赤外バンド吸光度偏光角依存性について調べた。遷移双極子モーメントの分布状態とその平均の方向（配向角）との関係を明確にし、また、配向角時間変化プロファイルから分子官能基レベルでの再配向動的挙動を検討し、そのスイッチングメカニズムを明らかにした。

1 Introduction

The surface-stabilized ferroelectric liquid crystals (SSFLC) in the smectic-C* (Sm-C*) phase are some of the most interesting liquid crystals because of their potential applications in high resolution flat panel displays and fast electro-optic devices [1]. Ferroelectric liquid crystal molecules have a permanent electric dipole moments perpendicular to their molecular long axis, so that by changing the polarity of the external applied electric field, the permanent electric dipole will rotate by 180° to point in the opposite direction; the molecular can switch between the two surface-stabilized states.

Fourier transformed infrared (FTIR) spectroscopy has proven itself to be one of the most useful techniques for investigating liquid crystal. This method is commonly used for obtaining information about the order parameter, for studying the conformational changes that may occur, the dynamics of molecules, and of the molecular segments.

The purpose of the present study is to explore the molecular dynamical orientation of the FLC with a naphthalene ring [FLC-3; Fig. 1] during the electric-field-induced dynamical switching by measuring temporal absorption responses of selected infrared bands over a continuous range of polarizer orientation.

2 Experiments

The sample was synthesized and characterized according to the reported procedure [3]. The structure and phase transition sequence of the liquid crystal molecule are shown in Figure 1. The sample cell consisted of two BaF₂ plates was filled with the molten sample by capillary action, heated to the isotropic phase, and then slowly cooled down to a temperature in the Sm-C* phase.

To investigate the segmental dynamics of the FLC, the time-resolved infrared measurements were made by use of a multichannel asynchronous time-resolving FT-IR system [2,4]. The measurement geometry is illustrated in Fig. 2. These spectra were measured in the 1800~1000 cm⁻¹ region over a delay time range from 0.5 to 30.5 μs at an interval of 2 μs and for the polarization angles ω from 0° to 180° at an interval of 5°. From these spectra one can get the polarization angle dependence of absorbance A(ω) at each delay time, and from the absorption maximum A_{max} = A(ω=β), the information about the molecular orientation angle β(φ,χ) in the spatial dimension can be obtain (φ is the azimuth angle of the director around layer normal, χ is the molecular rotation azimuth angle around the director). Furthermore, by analyzing the time dependence of the absorption maximum A(ω=β(t)), one can reach the information concerning the molecular reorientation angle β(φ(t),χ(t)) in time dimension. The absorbance versus the time and polarization angle can be described as follows:

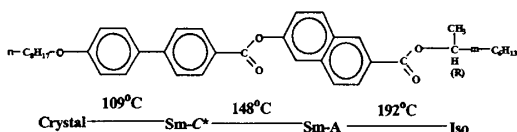


FIG. 1. Structure and the phase transition temperature of FLC-3.

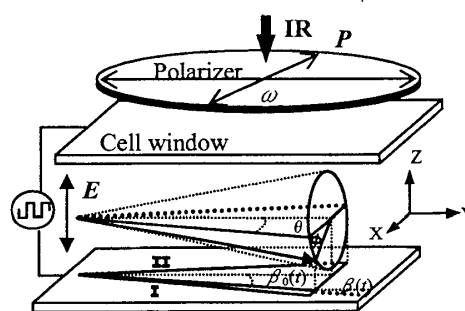


FIG. 2. Schematic arrangement for the time-resolved infrared measurements. I and II are the projections of the directions of the molecular long axis in the plane of the cell window for surface-stabilized states of the ferroelectric liquid crystal, φ=φ(t), φ(t) is the azimuth angle of the director around the cone at a delay time, θ is the cone angle, β₀(t) is the angle between the projection of the molecular long axis and the projection of layer normal in the plane of the cell window, β(t) is the angle between the projection of the molecular long axis and the projection of the horizontal polarization of the incidence infrared light in the plane of the cell window.

$$A(\omega) = -S \ln(e^{-2A_{\text{min}} \cos^2 \alpha(\varphi(t), \chi(t))} \cos^2(\omega - \beta(\varphi(t), \chi(t))) + e^{-A_{\text{min}}} \sin^2(\omega - \beta(\varphi(t), \chi(t)))) + (1 - S)A_{\text{iso}} \quad (1)$$

where A_{iso} is the absorbance of an absorption band for a perfectly isotropic phase, $S > 0$ is a constant that represents the contribution of a perfectly uniaxial phase to $A(\omega)$. In this model the transition dipole moment of the absorption band investigated lies on a cone with semiangle α around the molecular long axis of the ferroelectric liquid crystal. For perfect uniaxial orientation, the dichroic ratio R is found from the following equation;

$$R = \frac{A_{max}}{A_{min}} = 2 \cot^2 \alpha \quad (2)$$

where A_{max} and A_{min} are the absorbances measured with polarized radiation parallel and perpendicular to the direction of the molecular long axis, respectively. Hence, we can apply curve fitting using Eq. (1) by a least squares method to obtain the polarization direction of the maximum absorbance [3].

Here we describe the switching dynamics of the ferroelectric liquid crystal molecule. During the electric-field induced switching, the electric torque $\Gamma = \mathbf{P} \times \mathbf{E}$ (\mathbf{P} is the total polarization of the FLC) plays two roles: (i) to make the molecule revolve around its own axis and (ii) to make the molecule rotate around the tilt cone [1,4]. Therefore, the equation for the molecular motion in the ferroelectric phase can be written as follows:

$$\eta_\varphi \frac{d\varphi(t)}{dt} = P_{s\varphi}(S) E_\varphi \sin \varphi(t) \quad (3)$$

$$\eta_\chi \frac{d\chi(t)}{dt} = P_{s\chi}(S) E_\chi(\varphi) \sin \varphi(t) + C(S)(\varphi(t) - \chi(t)) \quad (4)$$

where η_φ , η_χ is the rotational viscosity with respect to φ , χ , $P_{s\varphi}(S)$, $P_{s\chi}(S)$ is the spontaneous polarization depending on S , E_φ , $E_\chi(\varphi)$ is the applied electric field, and $C(S)$ is the constraint constant, respectively.

3 Results and discussion

The plot of the absorbance for the band at 1602 cm^{-1} versus the polarization angle ω at all the delay times is presented Fig. 3. Each symbol represents the measurement data, and the lines represent the results of the curve-fitting [3]. The angle $\omega = \beta(t)$, which corresponds to the absorption maximum in the polarization angles, means the orientation projection direction of the molecular long axis in the cell window. Figure 3 reveals that the maximum and minimum absorbance changes for the delay times at $12.5 \mu\text{s}$ and $14.5 \mu\text{s}$ are different from those for other delay times. In this case, it can be seen from Fig. 2 that the orientation of the FLC molecules at the delay times of $12.5 \mu\text{s}$ and $14.5 \mu\text{s}$ makes a larger inclination than that at other delay times with respect to the plane of the cell window. These experimental results suggest that the molecules of the FLC rotate on the orbit of the cone.

To analyze the changes in the direction of the molecular long axis with the delay time, $\beta_0(t)$ for the representative bands was calculated and shown in Fig. 4. One can observe that $\beta_0(t)$ is very similar for the bands at 1602 , 1524 , 1496 , 1274 , 1262 , 1188 , 1146 , and 1066 cm^{-1} at different delay times. This reveals that the core moiety of the FLC molecule retains a rod-shape conformation during the electric-field-induced switching. $\beta_0(t)$ of the bands at 1736 and 1715 cm^{-1} exhibits a large deviation from those of other bands e.g. the bands at 1602 and 1188 cm^{-1} . This is due to the hindered rotation of the C=O groups. Moreover, it can be seen from Fig.4 that $\beta_0(t)$ for all selected bands switches symmetrically from a positive angle to a negative angle. These results reveal that the FLC molecule not only rotates around the layer normal but also revolves around its own long axis.

References

- [1] S. T. Lagerwall, *Ferroelectric and Antiferroelectric Liquid Crystals* (Wiley-VCH, Weinheim, 1999), p.169.
- [2] K. Masutani, K. Numahata, K. Nishimura, S. Ochiai, Y. Nagasaki, N. Katayama, and Y. Ozaki, *Appl. Spectrosc.* 53, 588 (1999).
- [3] Zhao, J. G.; Yoshihara, T.; Siesler, H. W.; Ozaki, Y. *Phys. Rev. E* 64, 031704-1 (2001).
- [4] Zhao, J. G.; Yoshihara, T.; Siesler, H. W.; Ozaki, Y. *Phys. Rev. E* 65, 021710-1 (2002).

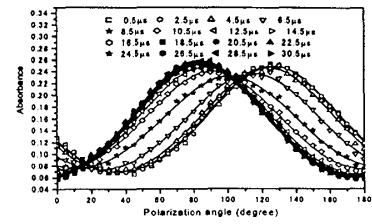


FIG. 3. Peak absorbance versus the polarization angle for the band at 1602 cm^{-1} due to the ring stretching mode of the benzene and naphthalene rings during the electric-field-induced switching of FLC-3 in the Sm-C* phase at $117 \text{ }^\circ\text{C}$ at a rectangular electric field of $\pm 20\text{V}$ with 5kHz repetition rate for the delay times from 0.5 to $30.5 \mu\text{s}$ with an interval of $2 \mu\text{s}$.

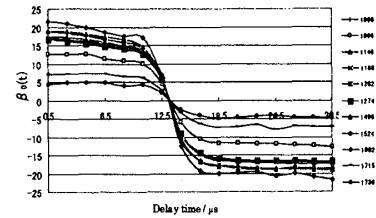


FIG. 4. $\beta_0(t)$ vs delay time for representative infrared bands of FLC-3 in the Sm-C* phase