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Collective fluctuation in chiral smectic phases of main-chain liquid crystalline polymers

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We have investigated the collective fluctuation in the chiral smectic phases of main-chain polyesters having a mesogenic *p,p'*-dibenzoate unit via dielectric and dynamic electrooptical measurements. A relaxation due to the Goldstone mode was observed at several tens of Hz in the chiral smectic C (SmC*) phase in both measurements, where another relaxation associated with the soft mode was also confirmed around the SmA–SmC* phase transition temperature. Although the mesogens are linked together in a main-chain liquid crystalline polymer, the observed soft mode is associated with the tilt fluctuation of the average direction of the mesogens.

1. Introduction

Since the discovery of fast electrooptical switching in surface-stabilized ferroelectric liquid crystal cells [1], a variety of ferroelectric liquid crystalline materials have been synthesized in order to improve the material properties for device applications. Recently, the search for new materials has expanded to the field of liquid crystalline polymers (LCPs). Using chiral mesogenic groups already used in low-molar-mass ferroelectric liquid crystals (FLCs), numerous ferroelectric liquid crystalline polymers (FLCPs) have been synthesized [2–8]. While mesogenic groups can be incorporated into a polymer not only as side chains but also as part of the main chain, most of the FLCPs described thus far belong to the former category, which gives rise to the so-called side-chain FLCPs, the physical properties of which are usually predictable from those of the low-molar-mass FLCs.

Since a novel and/or high-performance physical property is acquired in a main-chain liquid crystalline polymer (main-chain LCP) because of its close coupling between polymeric and mesogenic effects, several kinds of main-chain LCPs have been developed and have played an important role in different industrial applications [9–12]. As for ferroelectric properties and electrooptical applications of main-chain LCPs, however, the

details are still controversial, even though several studies have been carried out to date [13–19]. About a decade ago, Watanabe *et al.* [16] confirmed ferroelectricity in the chiral smectic C* (SmC*) phase of a main-chain liquid crystalline polyester designated BB-4*(2Me)/6, which was constructed from *p,p'*-dibenzoate and mixtures of (*S*)-2-methylbutanediol and hexanediol. Moreover, Furukawa *et al.* [19] have investigated the collective and molecular fluctuations of the main-chain LC polyester by broadband dielectric spectroscopy. They observed two kinds of molecular fluctuations: ‘local mode’ fitted to the Arrhenius type and ‘segment mode’ analyzed by the Vogel–Fulcher law.

In this paper, we report the details of the collective fluctuation of the main-chain ferroelectric LC polyester by dielectric measurement and dynamic electrooptical analysis. A relaxation due to the Goldstone mode is observed at several tens of Hz in the SmC* phase in both experiments. In addition, another relaxation associated with the soft mode is also confirmed around the SmA–SmC* phase transition temperature. Although the mesogens are linked together in a main-chain LC polymer, a soft mode associated with the electric-field-induced tilt fluctuation of the average direction of the mesogens is observed. We discuss the change in molecular orientation during the SmA–SmC* phase transformation in the main-chain LCPs on the basis of an analysis of the collective fluctuations.

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2. Experimental

2.1. Materials

The sample used was designated BB-4*(2Me)/6, which has the chemical structure shown in figure 1 [14, 16]. The polymer was synthesized by a melt transesterification of dimethyl *p,p'*-dibenzoate and a 50/50 w/w mixture of (*S*)-methylbutanediol and hexanediol. Here, the dimethyl *p,p'*-dibenzoate and hexanediol were used as received from Ihara Chemical Co, Ltd, and Tokyo Kasei Kogyou Co, Ltd, respectively. Chiral (*S*)-methylbutanediol was also used as received from Nippon Oil Co, Ltd, and Azmax Co, Ltd. The inherent viscosity of the prepared polymer, as determined at 25°C using 0.5 g dl⁻¹ solutions in a 60/40 w/w mixture of phenol and tetrachloroethane, was approximately 0.18 dl g⁻¹. The polymer showed the following phase sequence:

solid – (114°C) – SmC* – (134°C) – SmA – (221°C) – Iso.

The transition temperatures listed above were determined by differential scanning calorimetry (Seiko, SSC-500) at a heating rate of 10°C min⁻¹. Because the heat of the transition between the SmC* phase and the solid phase has been recognized in the DSC curve, the solid phase seems to be one of the higher-ordered phases. However, the details of the structure have not been disclosed. In addition, the transition from the solid phase to another phase was not observed in the temperature range measured in our experiments (50–250°C).

2.2. Measurements

Details of the techniques used can be found elsewhere [20, 21]. In order to measure both dielectric constant and electrooptical response, homogeneously aligned cells were prepared. The material was sandwiched between glass plates with ITO separated by 12 μm thick spacers. For the homogeneous alignments, the glass plates were coated with polyimide (Toray Industry, SP510), and one of them was rubbed unidirectionally. Because we observed selective reflection phenomena during the sample preparation procedure, a helical pitch caused by chirality is thought to occur at visible

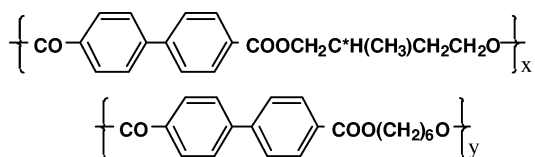


Figure 1. Structure of the main-chain ferroelectric LC polyester BB-4*(2Me)/6.

wavelengths. In addition, we have not observed the broken lines due to a helix in the 12 μm cell. This implies that the helical pitch may be too short to be observed in our microscope observation. In addition, an induced CD peak, which was not observed in SmA, appeared around 240 nm in the SmC* phase in our preliminary CD experiments.

The dielectric constant was measured using an impedance analyser (Solartron, 1260). The measuring ac voltage was 1.0 V_{rms}, and no biased dc field was applied. The sample was mounted in a microfurnace (Mettler FP82) for temperature regulation. The impedance analyser and temperature regulator were controlled by a microcomputer, so that the dielectric constant in the frequency range between 1 Hz and about 10 MHz were automatically measured.

We measured the angle between the layer normal and the optical axis of the sample under an electrostatic field to investigate the electrooptical response of the main-chain FLCs. In addition, the dynamic electrooptical measurement was also carried out for analysis of the relaxation behaviour of the electrooptical response. Here, the optical response under a sinusoidal electric wave of 5 V_{rms} was measured using a photomultiplier (Hamamatsu, R955) attached to a polarizing optical microscope. The signal was detected by a lock-in amplifier (NF, 5610B). The transmitted light intensity, *I*, through a sample cell of thickness *d* placed between crossed polarizers is described as

$$I = I_0 \sin^2(2\Theta) \sin^2(\pi d \Delta n / \lambda), \quad (1)$$

where Θ is the angle of the optical axis with respect to one of the polarizer directions, Δn is the difference between the long and short axes of the projection of the index ellipsoid on the glass surface and λ is the wavelength of the incident light. We measured the light intensity at $\Theta = 22.5^\circ$, where a linear response between *I* and Θ is expected. The incident light wavelength λ of 546 nm was selected using an interference filter. The sample was also mounted in the microfurnace (Mettler FP82) for temperature regulation.

3. Results and discussion

Figure 2 shows the temperature dependence of the dielectric constants (ϵ') measured in the heating process. Three temperature regions corresponding to the phase sequence confirmed by DSC are recognized. Here, two vertical dotted lines indicate the solid–SmC* and SmC*–SmA phase transition temperatures. In the temperature dispersion measured at 10 Hz, the dielectric constants in the SmC* phase are larger than those in the other phases because of the contribution of spontaneous polarization. Since the relaxation of the corresponding

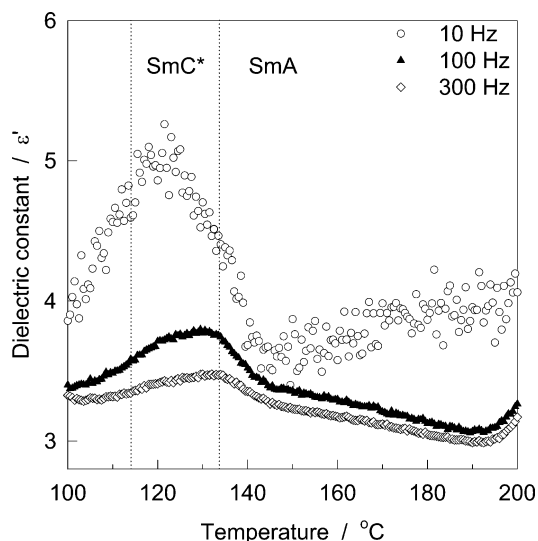


Figure 2. Temperature dependence of dielectric constant of main-chain ferroelectric liquid crystalline polyester BB-4*(2Me)/6.

fluctuation probably occurs at several tens of Hz, the contribution of the polarization in SmC* is barely recognized in the dispersion curve measured at 100 Hz. Since the helical structure of BB-4*(2Me)/6 has already been recognized as having selective reflection phenomena in our sample preparation and has also been confirmed in previous papers [14, 16], the relaxation of the polymeric SmC* phase seems to be due to the Goldstone mode associated with the helical fluctuation. In addition, one may notice that the relaxation frequency is about the same as that of the Goldstone mode of low-molar-mass FLCs [22].

In addition, another dielectric contribution exhibiting softening behaviour seems to be observed in the dispersion curves measured at both 100 and 300 Hz; the dielectric constant increases in the SmC* phase with increasing temperature until it attains a maximum at the SmC*–SmA phase transition point, after which it decreases in the SmA phase. Although the frequency dispersion of the dielectric constant in the SmA and SmC* phases was measured in a previous study, the conductive contribution seriously disturbed a detailed analysis of these dielectric relaxation processes [18]. Therefore, the further investigation is a future problem.

We subsequently attempted to carry out electrooptical measurements free from the disturbance of the conductivity. Figure 3 shows the electrostatic field (E) dependence of the apparent tilt angle θ between the optical axis and the layer normal in the SmA phase. It is reasonable to suppose that the optical axis corresponds to an average direction of the mesogens despite the existence of spacers in the LC polymer. Here, the

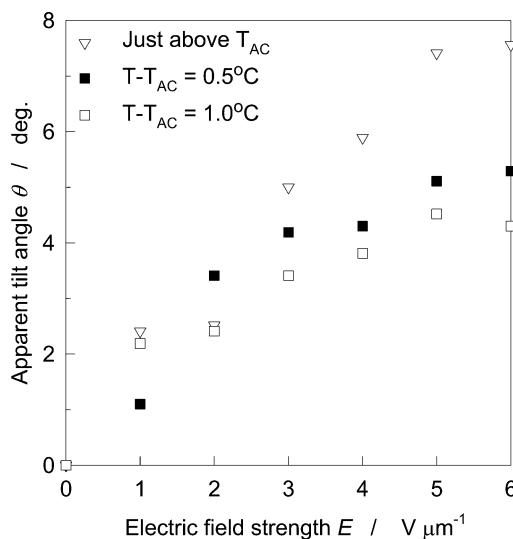


Figure 3. Electric field dependence of apparent tilt angle in SmA of BB-4*(2Me)/6. An electrostatic field was applied.

‘electroclinic effect’, namely an electric field-induced tilt in the average direction of the mesogens is recognized in a similar way to that in low-molar-mass FLCs [23]. The field-induced apparent tilt angle θ increases with increasing field, and it reaches 7.8° under $6.0 \text{ V } \mu\text{m}^{-1}$ in the measurement just above the SmA–SmC* phase transition temperature. Whereas θ also increases with the field at different temperatures, the value of θ at the same electric field decreases with increasing temperature in SmA because of softening behaviour.

To analyse the details of the electroclinic effect, we plotted the apparent tilt angle θ under electrostatic field strengths of $4 \text{ V } \mu\text{m}^{-1}$, $5 \text{ V } \mu\text{m}^{-1}$ and $6 \text{ V } \mu\text{m}^{-1}$ as a function of temperature in figure 4. Typical softening behaviour is observed in these temperature dispersions; θ increases in the SmA phase with decreasing temperature until it attains a maximum at the SmA–SmC* phase transition point (T_{AC}), after which it decreases in the SmC* phase.

Let us consider the molecular dynamics under an electric field in the main-chain FLCP, illustrated by schematic models suggested for the Goldstone and soft modes in figure 5. For the sake of simplicity, we assume that the length of the spacer does not change during the fluctuation. The polymeric effect due to the linkage between mesogens might not suppress the Goldstone mode, described as the fluctuation of the azimuthal angle ϕ around the helical axis, because no conformational change in the polymer is caused by the azimuthal fluctuation, as shown in figure 5 a. We expect, therefore, that the Goldstone mode of the main-chain FLCP behaves in a similar way to that of low-molar-mass FLCs. On the other hand, we notice that the tilt

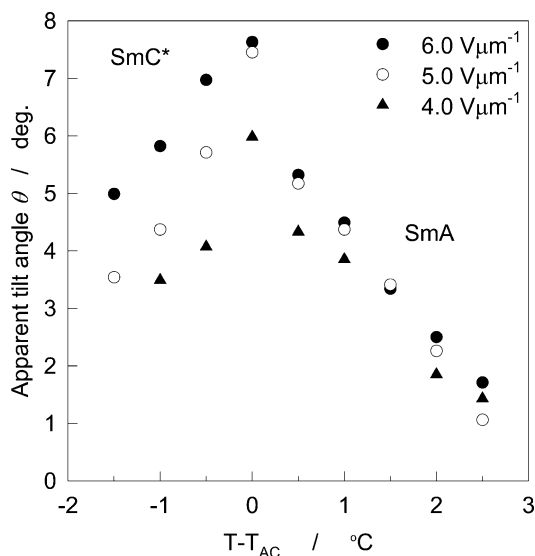


Figure 4. Temperature dependence of electric field-induced apparent tilt angle of BB-4*(2Me)/6.

fluctuation due to the soft mode brings about the deformation of the polymeric chain in figure 5 b, which shows that the polymer bends at a joint between the mesogenic core and the spacer during the fluctuation of the tilt angle θ . In the case of the material used, i.e. BB-4*(2Me)/6, we can easily imagine that the deformation is due to the conformational change of the alkylene spacer. Hence, the emergence of the electroclinic effect means that the spacer is flexible enough to allow mesogens to tilt in low electric fields. However, the induced tilt angle θ deviates significantly from the value

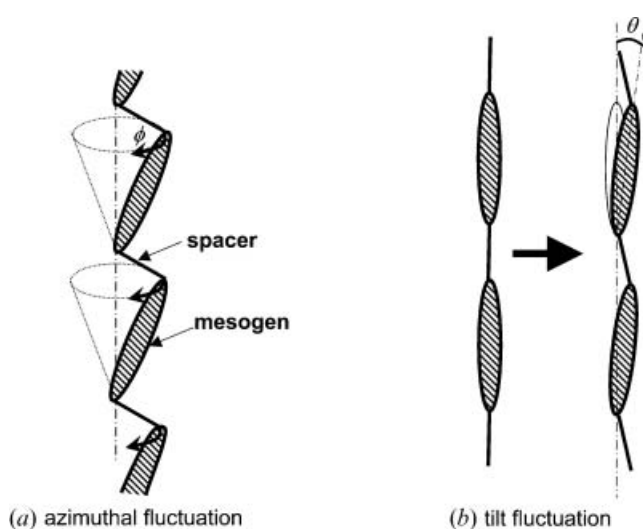


Figure 5. Schematic models for (a) Goldstone mode associated with azimuthal fluctuation and (b) soft mode corresponding to tilt fluctuation of main-chain liquid crystalline polymer. The helical axis corresponds to the dash-dotted line in (a).

predicted from the linear dependence on E at high fields in figure 3. Because the mesogens are linked together in a main-chain LCP, the linkage may hinder mesogens from further tilting.

Dynamic electrooptical measurements have been carried out to investigate the relaxation behaviour of the collective tilt fluctuation appearing as the electroclinic effect. Because the measuring ac field ($0.42 \text{ V}_{\text{rms}} \mu\text{m}^{-1}$) is low enough, a linear relationship between the induced tilt angle and the signal strength of the optical response is expected from equation (1). The intensity of the electrooptical response, I^* , can be described in the following Cole–Cole type equation:

$$I^* = (\Delta I) / (1 + i\omega\tau)^\alpha + I_b, \quad (2)$$

where ΔI is the relaxation strength of the electrooptical response, ω is the angular frequency of the applied sinusoidal electric wave, τ is the relaxation time and α is the distribution factor of the relaxation time. Figure 6 shows the frequency dispersion curves of the signal strength $|I^*|$ measured at several temperatures in the SmA phase. Here, relaxation is recognized at several tens of Hz in the dispersion curve measured just above the SmA–SmC* phase transition temperature ($T - T_{\text{AC}} = 0.4^\circ\text{C}$), and it exhibits behaviour typical of the soft mode. Namely, the relaxation strength becomes smaller with increasing temperature, and the relaxation frequency simultaneously increases with increasing temperature.

To analyse quantitatively the relaxation behaviour of the soft mode as well as of the Goldstone mode, the relaxation strength ΔI and the relaxation frequency f_r obtained from equation (2) are plotted as functions of

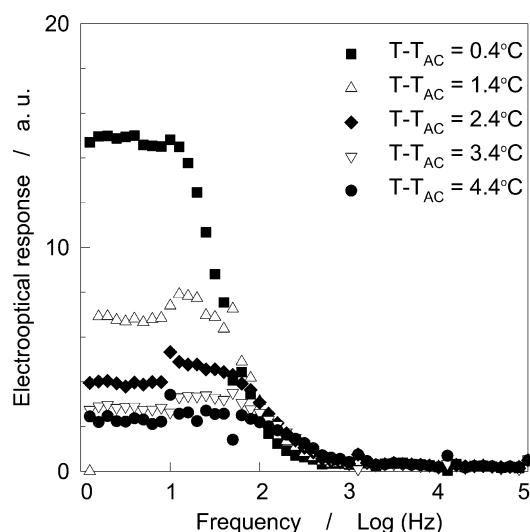


Figure 6. Frequency dispersion curves of dynamic electrooptical response in SmA of BB-4*(2Me)/6.

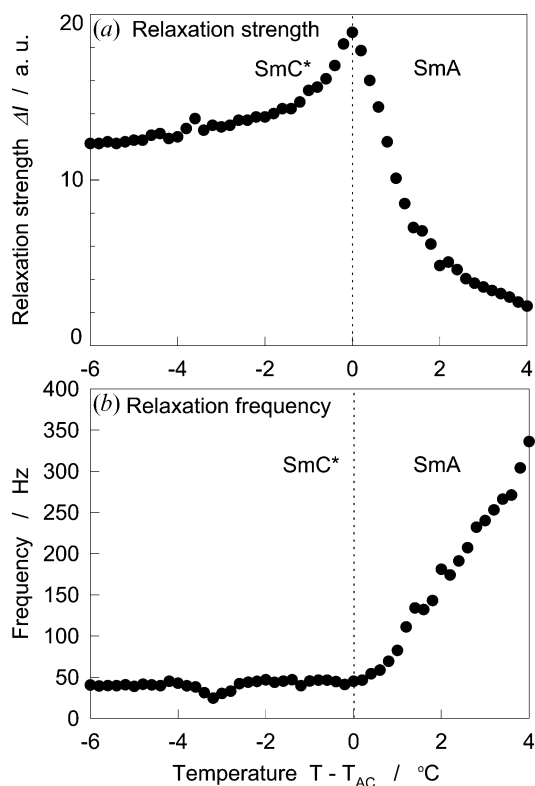


Figure 7. Temperature dependences of (a) relaxation strength and (b) relaxation frequency in dynamic electrooptical measurements.

temperature in figure 7. Here, the softening behaviour is clearly seen around the SmA–SmC* phase transition temperature. ΔI increases with decreasing temperature in SmA until it attains a maximum at the SmA–SmC* phase transition point, and then it decreases in the SmC* phase (see figure 7a). On the basis of the observed softening behaviour, we can easily determine the SmA–SmC* phase transition temperature, which is indicated by a vertical dotted line in figure 7. In addition, the value of ΔI remains large in the SmC* phase because of the contribution of the Goldstone mode. Typical softening behaviour is also confirmed in the temperature dependence of the relaxation frequency f_r shown in figure 7b. f_r , which is plotted at approximately 300 Hz on the right ordinate axis, decreases with decreasing temperature in SmA until the SmA–SmC* phase transition temperature is reached. Since the optical response is mainly dominated not by the soft mode but by the Goldstone mode in the SmC* phase, f_r is almost independent of temperature and is constant at approximately 30 Hz. The contribution of the Goldstone mode is too big to distinguish the soft mode in the frequency dispersion curve of the electrooptical response measured in SmC*. Because dielectric and electrooptical measurements under a dc field are

useful for observing the softening behaviour in the SmC* phase, they form the subject of further experiments. Experimental results measured under a dc field will be presented in a forthcoming publication.

Because the softening of the tilt angle θ has been confirmed in the electrooptical measurements of the main-chain FLCP, the mesogens must incline with respect to the layer normal during the SmA–SmC* phase transformation, as depicted in figure 8a [24]. However, Watanabe *et al.* [25, 26] previously reported that not mesogens but layers were tilted in the X-ray patterns for the same type of main-chain LC polyesters. In their X-ray studies, the average direction of mesogens (*the director*) remained unchanged through the phase transformation, whereas the layer normal tilted [27] with respect to *the director*, as illustrated in figure 8b.

Focusing on the boundary condition of the samples used in both the electrooptical measurements and the X-ray observations, we discuss the discrepancy between two SmA–SmC* transformational models in figure 8 on the basis of these experiments. It is noteworthy that the sample polymer is sandwiched between glass plates in the electrooptical measurements, whereas it is simply suspended in the X-ray observations. Because the X-ray observations are performed with the free-surface condition of the sample polymer, the mesogens are allowed to slide against each other along *the director* during the SmA–SmC phase transformation. The layer normal ultimately tilts with respect to *the director* under the temperature-dependent X-ray observations; this behaviour is illustrated as the ‘layer-tilting model’ in figure 8b. As for the electrooptical measurements,

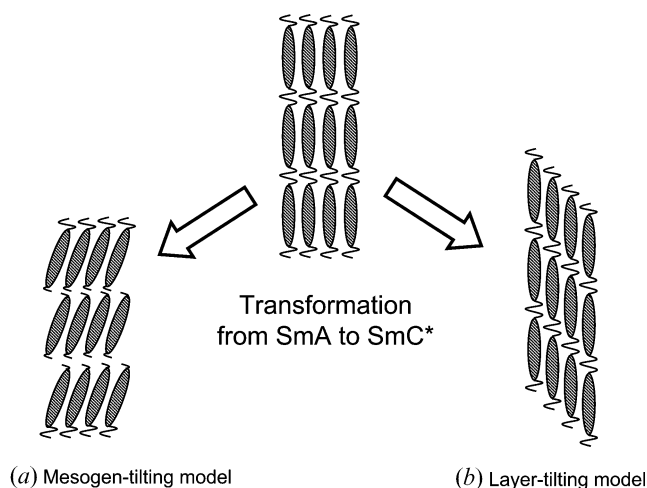


Figure 8. Two schematic models of molecular reorientation during SmA–SmC* phase transformation in main-chain liquid crystalline polymer. (a) Mesogen-tilting model based on electrooptical measurements and (b) layer-tilting model confirmed by X-ray observations.

however, the sample polymer is confined to the cell composed of glass. The sliding of mesogens, i.e. 'layer tilting', is suppressed by the boundary condition at the interface between the glass and the sample polymer. Therefore, the applied electric field induces 'mesogen tilting' instead of 'layer tilting', as depicted in figure 8 a. Consequently, we can explain the inconsistent results between the electrooptical measurements and the X-ray observations, by considering the difference in the boundary conditions of the sample polymers used in these experiments. Because the boundary conditions seem to be delicate, both 'mesogen tilting' and 'layer tilting' may simultaneously and partially occur in these measurements. In addition, we should examine the possibility of 'polymer tilting without conformational change' which may bring sample-shape change during the SmA–SmC* transformation [28]. In the meantime, we continue further electrooptical experiments and X-ray observations to elucidate these questions about the transformation behaviour from SmA to SmC* in main-chain liquid crystalline polymers. We will show experimental details to confirm our hypothesis in a forthcoming publication.

4. Conclusions

We investigated the collective fluctuations in the smectic A (SmA) and chiral smectic C (SmC*) phases of main-chain polyesters having a mesogenic *p,p'*-dibenzoate unit by both dielectric and dynamic electrooptical measurements. In the SmC* phase, a relaxation due to the Goldstone mode was observed at several tens of Hz in both measurements. In addition, another relaxation associated with the soft mode was also observed around the SmA–SmC* phase transition temperature. The softening of the tilt fluctuation, which was estimated as an electric-field-induced tilting of the average direction of mesogens, took place around the SmA–SmC* phase transition point, even though the mesogens were linked together in a main-chain liquid crystalline polymer. Although 'mesogen tilting' was confirmed by the electrooptical measurements around the SmA–SmC* transition temperature, 'layer tilting' was previously observed in X-ray studies. We explained the discrepancy between the electrooptical measurements and the X-ray observations, considering the difference in boundary conditions between the samples used in these experiments.

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