

## Appearance of Ferrielectric Phases in a Confined Liquid Crystal Investigated by Photon Correlation Spectroscopy

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Dynamic light scattering was used to examine ferrielectric liquid-crystalline phases in porous media. Whereas in larger pores (2000 Å) ferrielectric phases were observed, they were not found in the smallest pores (200 Å). Additionally, the temperatures of several phase transitions were found to be suppressed in the pores relative to bulk. These observations have been explained by the structural aspects of antiferroelectric liquid-crystalline materials in a confined geometry. [S0031-9007(98)07214-7]

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During the 1980s a new type of chiral smectic liquid crystal—the antiferroelectric liquid crystals (AFLC)—was discovered [1,2]. Since that discovery a variety of ferrielectric phases have been found [3,4] in the temperature range between antiferroelectric ( $\text{SmC}_A$ ) and ferroelectric ( $\text{SmC}^*$ ) phases. The appearance of these phases is due to competition between the antiferro- and ferroelectric interactions in adjacent smectic layers that stabilize the  $\text{SmC}_A$  and the  $\text{SmC}^*$  phases. In ferrielectric liquid crystals the directions of the local spontaneous polarizations in any two neighboring smectic layers can be ferroelectriclike or antiferroelectriclike. The antiferroelectric order is believed to exist due to steric factors since it appears in racemic chiral liquid crystals [3] as well as in nonchiral tilted smectics [5]. The molecular dipole moment is also considered to be important for the existence of the  $\text{SmC}_A$  phase [6–10]. On the other hand, we are unaware of any report of ferrielectricity in nonchiral and/or racemic liquid crystals. It seems, therefore, that the existence of local spontaneous polarization is a determining factor for ferrielectricity.

Two main theoretical approaches have been advanced for explaining the variety of phases. One is based on an expanded Landau model [7] (Orihara-Ishibashi [11,12]) and the other on the Ising model [13] adapted to liquid crystals [4]. The Ising model, which takes into account the interaction between all smectic layers, predicts the existence of an infinite number of ferrielectric phases [4], while only a limited number of ferrielectric phases seems to exist. According to the Ising model, these phases can be characterized by the parameter  $q_T = F/(A + F)$ , which denotes the fraction of ferroelectric ordering ( $F$ ) which appears together with antiferroelectric ordering ( $A$ ) in the periodic structure. Following this definition, the  $\text{SmC}_A$  is the antiferroelectric phase with  $q_T = 0$ , the  $\text{SmC}_\gamma$  is ferrielectric phase with  $q_T = 1/3$ , the AF is antiferroelectric phase with  $q_T = 1/2$  and the  $\text{SmC}^*$  is ferroelectric with  $q_T = 1$ . Additionally other ferrielectric subphases (FiLC,  $\text{SmC}_\alpha$ ) have been found which cannot be described by the  $q_T$  parameter. The Orihara-Ishibashi model has failed to explain the existence of some experimentally observed ferrielectric phases, although it predicts

the possibility of some incommensurate phases, which can be treated as ferrielectric. On the other hand, the Orihara-Ishibashi approach [7,11] provides information about relaxation processes due to the fluctuations of both ferroelectric and antiferroelectric order parameters. These models were developed for bulk liquid crystals, and the effect of the surface has not been taken into account.

The effect of the surface on the appearance of ferrielectric phases has been reported in several publications [14,15]. Substrates may cause a preferable orientation of molecular tilt, and also affect the delicate energy balance among ferrielectric phases. Therefore in a sufficiently thin cell the ferrielectric phases can be suppressed or induced by the surface [14,15]. A different situation may be expected in parallel cylindrical pores because of their symmetry. In such pores the molecular tilt directions are equivalent with respect to azimuthal angle if planar boundary conditions are assumed. Therefore the question “What happens to ferrielectric phases in liquid crystals confined in cylindrical pores?” is of great interest and importance.

The dynamic light scattering provides information about relaxation processes in the sample, which are different in different ferrielectric/antiferroelectric phases. The relaxation processes in bulk ferrielectric/antiferroelectric phases have been studied theoretically [16–18] and experimentally by dielectric [14,19–21] and electro-optic [17,19] spectroscopy and dynamic light scattering [18,22,23]. A total of four relaxation processes have been observed: Two molecular processes due to the reorientation around the short and long axes, and two collective processes, viz., an opticlike phason [18] (or antiphase mode [20]) and acousticlike phason [18] (or in-phase mode [20]). In this paper we report on the influence of confinement on the appearance of antiferroelectric/ferrielectric phases in AFLCs.

We have performed investigations in both bulk and AFLC confined in cylindrical pores (anopore membranes) of two different diameters: 200 and 2000 Å. The AFLC used in the experiments was (*R*)-1-methylheptyl-4-(4''-*n*-dodecyloxybiphenyl-4'-carbonoyloxy)-3-fluorobenzoate (AS-573, Hull, U.K.). The phase transitions sequence

of the bulk sample ( $\pm 0.5^\circ\text{C}$ ) has been determined by the macroscopic polarization measurements and dielectric spectroscopy [14]: SmC<sub>A</sub> 78 SmC<sub>γ</sub> 83 AF 85 FiLC 91 SmC\* 93 SmA 106 Iso.

In our experiments the bulk liquid crystal was placed between two untreated glass plates having a 100 μm gap. The liquid crystal was observed to be planar disordered with a helix. The helical pitch was about 0.2–0.3 μm. The liquid crystal structure within the pores is believed to be helical, with helical axes along the pores, because a selective reflection in the blue region was observed. A few comments are in order: (i) The existence of a helix in such small pores may be surprising at first, but if one takes into account cylindrical symmetry it becomes reasonable. (ii) The suggested structure of the liquid crystal in pores, where the smectic layers are perpendicular to the pore's wall (similar to the set of coins in the tube), is consistent with our results below. (iii) We were unable to achieve homeotropic alignment in an ordinary planar cell using several different surface treatments. This again would tend to argue for—although not prove—planar alignment in the pores.

We performed photon correlation measurements using a He-Ne laser and an ALV-5000/fast correlator. The depolarized component of scattered light was investigated. In a dynamic light scattering experiment, one measures the intensity-intensity autocorrelation function  $g_2(t) = \langle I(t)I(0) \rangle / \langle I(0) \rangle^2$  related to the dynamic structure factor  $f(q, t)$  of the sample by  $g_2(t) = 1 + kf(q, t)^2$ , where  $k$  is a contrast factor that determines the signal-to-noise ratio,  $q = 4\pi n \sin(\Theta/2)/\lambda$ ,  $n$  is the refractive index,  $\Theta$  is the scattering angle, and  $\lambda$  is the light wavelength. All the dynamic light scattering data discussed below were obtained at  $\Theta = 30^\circ$ . The temperature-dependent measurements were carried out in the temperature range  $72 < T < 94^\circ\text{C}$  on cooling the sample from the isotropic phase. The data were taken after stabilizing the temperature for 1 h at each value of  $T$ , sufficiently long to guarantee thermal equilibrium.

Figures 1a–1c present the intensity/intensity autocorrelation functions of AS573 in the 100 μm cell (bulk) and in pores for three different temperatures corresponding to different phases over the time range  $10^{-2} < t < 10^4$  ms. Faster processes were not investigated. The autocorrelation function of bulk AFLC (Fig. 1b, curve 1) consists of three decays corresponding to three relaxation processes: (i) The “fast” process ( $\tau_1 = 27 \mu\text{s}$ ), (ii) “middle frequency” process ( $\tau_2 = 50$  ms), and (iii) “low frequency” process ( $\tau_3 = 850$  ms). The amplitude of the fast relaxation process strongly depends on the temperature. In the bulk sample this process is very prominent in the temperature range below  $88^\circ\text{C}$ , which corresponds to antiferroelectric/ferrielectric phases (Figs. 1a and 1b, curve 1). In the temperature region above  $88^\circ\text{C}$  the contribution of the fast relaxation process decreases with increasing temperature, and it vanishes in SmC\* phase (Fig. 1c, curve 1). This fact allows us to assign the fast

relaxation process to fluctuations of the antiferroelectric order parameter (or opticlike phason [18]). The fast relaxation process is strongly affected by confinement, and is pore size dependent. In the bulk sample this process is described by a single exponential decay, while in pores it is a stretched exponential. The fast relaxation process exists in the temperature range corresponding to antiferroelectric/ferrielectric phases in bulk as well as in 2000 Å pores. Therefore one can conclude that the antiferroelectric/ferrielectric phases appear in 2000 Å pores as well as in bulk. In 200 Å pores the fast relaxation process appears only in the SmC<sub>A</sub> phase. This means that the ferrielectric phases do not appear in 200 Å pores. Combining these facts we can conclude that antiferroelectric order in 200 Å pores does not appear in the temperature range corresponding to the bulk ferrielectric phases. The reasons for this will be discussed below.

Two low frequency relaxation processes appear in all smectic phases, including the SmA. Recently, Tang and Sprunt [24] have observed two slow relaxation processes in chiral SmA phase. These are assigned to new hydrodynamic modes due to the existence of one-dimensional modulation of smectic layers (stripe domains). Such domains exist also in tilted smectic phases. Therefore in our case we assign these two slow relaxation processes to stripe domain hydrodynamic modes.

The dynamic structure factor  $f(q, t)$  of the autocorrelation functions has been fitted by the superposition of three decays:

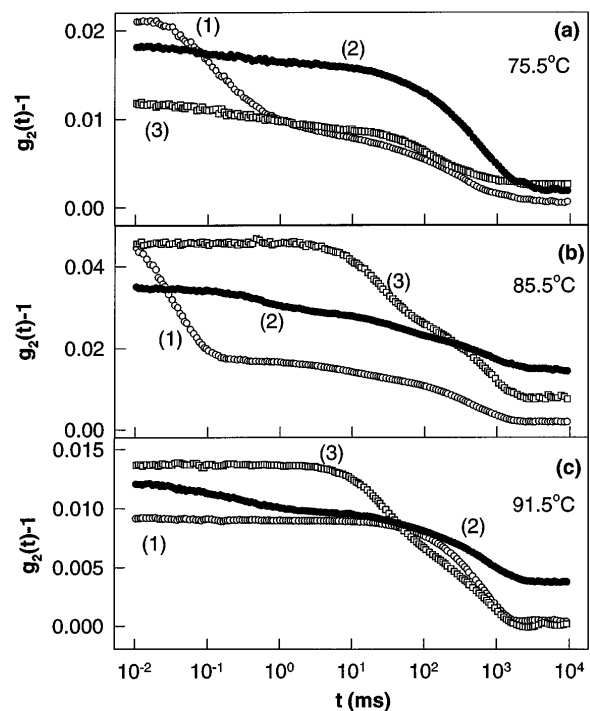


FIG. 1. Intensity/intensity autocorrelation functions of AS573 in bulk (1), in 2000 Å pores (2), and in 200 Å pores (3) measured at (a) 75.5 °C, (b) 85.5 °C, and (c) 91.5 °C.

$$f(q, t) = b + \sum_{i=1}^3 a_i \cdot \exp[-(t/\tau_i)^{\beta_i}],$$

where  $b$  is the baseline and  $a_i$ ,  $\tau_i$ , and  $\beta_i$  are the amplitude, relaxation time, and stretch coefficient of the  $i$ th relaxation process. The fast relaxation process in bulk is almost a single exponential, while in pores it was found to be stretched. The middle and low frequency relaxation processes are exponential in all samples.

The relaxation times of all three processes are found to be dependent on the temperature. Figures 2 and 3 present the temperature dependencies of the relaxation times for middle frequency and low frequency processes. These plots are rather noisy because the autocorrelation functions are complicated in shape and the relaxation processes are not well separated. Nevertheless, the temperature dependencies of the relaxation times of all three processes together reveal some interesting features.

Figure 2 shows the temperature dependence of the relaxation time of the middle frequency process, which has been satisfactorily separated from the low frequency process over the entire temperature range for 200 Å pores and over a limited temperature range for 2000 Å pores and the bulk sample. The temperature dependencies of the relaxation times of all samples reveal a peak at the same temperature 77.5 °C, indicating the  $\text{SmC}_A$ - $\text{SmC}_\gamma$  phase transition. The temperature dependence of the relaxation time of the bulk sample shows two more small peaks (cusps) at 80.5 and 83 °C, corresponding to phase transitions between three ferroelectric phases  $\text{SmC}_\gamma$ -AF-FiLC. In contrast, the temperature dependence of the middle relaxation time in the 200 Å pores reveals no extra peaks in this temperature range. This is in agreement with the above conclusions that in the 200 Å pores those ferroelectric phases are not formed. On the other hand, the temperature dependence of the relaxation time in the 200 Å pores shows a peak at 88 °C, whereas a similar

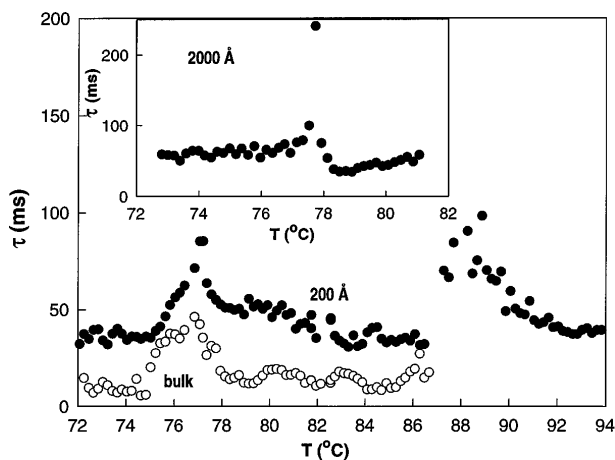


FIG. 2. Temperature dependence of the relaxation time of the middle frequency relaxation process in the bulk AS573 (open circles) and in 200 Å pores (filled circles). Inset: In 2000 Å pores.

peak does not exist in the bulk sample. This peak is the highest temperature peak, and therefore it can be assigned to the  $\text{SmC}^*$ - $\text{SmA}$  phase transition.

Figure 3 shows the temperature dependence of the relaxation time of the low frequency process. In the low temperature region there is a sharp peak at the temperature 78 °C, which corresponds to  $\text{SmC}_A$ - $\text{SmC}_\gamma$  phase transition. Such a phase transition apparently occurs in bulk and in pores at almost the same temperature. In the high temperature region there is only one peak in all three dependencies, which can be separated from noise. This peak is the highest temperature peak, which corresponds to the  $\text{SmC}^*$ - $\text{SmA}$  phase transition. In the bulk sample it is centered at about 92 °C, whereas in 200 Å porous sample it is at 88 °C, and in 2000 Å pores it is centered at 89 °C. The temperature dependence of the relaxation time of the fast relaxation process supports the conclusions about the appearance of the ferroelectric phase in pores.

The analysis of the temperature dependencies of the relaxation times shows that the temperature of the  $\text{SmC}^*$ - $\text{SmA}$  phase transition is strongly affected by confinement as well as pore size, whereas the temperature of  $\text{SmC}_A$ - $\text{SmC}_\gamma$  phase transition is not. These facts can be understood from the following considerations. At the  $\text{SmC}_A$ - $\text{SmC}_\gamma$  phase transition a molecular reorientation by the azimuthal angle  $\phi$  occurs. This phase transition is not significantly affected by confinement because of the cylindrical symmetry of the pores. A different situation holds for the  $\text{SmC}$ - $\text{SmA}$  phase transition. At this transition (on cooling) the smectic layers shrink due to the molecular tilt. This changes the number of smectic layers in the pores and costs much more energy than the reorientation of molecules. The phase transition therefore moves down in temperature by 3 °C in 2000 Å pores and by 4 °C in 200 Å pores.

The ferroelectric phases exist in 2000 Å pores and do not exist in 200 Å pores. According to the Ising model

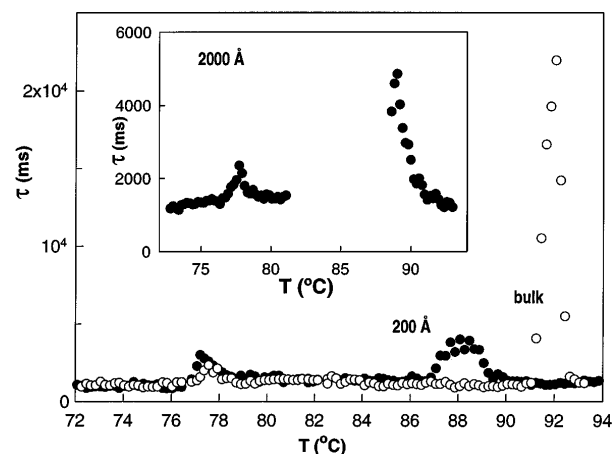


FIG. 3. Temperature dependence of the relaxation time of the low frequency relaxation process in the bulk AS573 (open circles) and in 200 Å pores (filled circles). Inset: In the 2000 Å pores.

the existence of ferroelectric phases is explained by long range electrostatic interactions between local spontaneous polarizations (spins) of smectic layers. The importance of this interaction is supported by the results of several investigations on freestanding films [25–27]. The stability of the ferroelectric phases depends on strength of this electrostatic interaction, i.e., how rapidly it varies with the distance between smectic layers. In general, the electric field of the limited electrically charged surface is almost independent of distance ( $x$ ) from the surface when the distance is much smaller than the linear size ( $D$ ) of the surface:  $x \ll D$ . At longer distance the electric field begins to decrease faster with distance. In other words, the confinement in the direction perpendicular to the layer normal should limit the interaction in the direction along the layer normal. In the bulk liquid crystal the smectic layer thickness ( $L \approx 30 \text{ \AA}$ ) is much smaller than the dimensions of the area of smectic layers, giving an interaction along an infinite number of infinite (in extent) smectic layers. In sufficiently small cylindrical pores ( $\sim 200 \text{ \AA}$ ), the area of the smectic layer becomes commensurate with the smectic layer thickness, limiting the number of interacting smectic layers. For this case the electric field of the spontaneous polarization of smectic layers is due to fewer molecules, and it decays more rapidly (as a function of distance) than in bulk and in  $2000 \text{ \AA}$  pores.

In conclusion, we stress that cylindrical confinement exerts a strong influence on the appearance and dynamic properties of the ferroelectric phases. The results obtained can be summarized as follows: (i) The fast relaxation process is very prominent in the bulk sample, but is partly suppressed in  $2000 \text{ \AA}$  pores and does not exist in  $200 \text{ \AA}$  pores. (ii) The temperature of the phase transitions  $\text{SmC}_A\text{-SmC}^*$  in  $200 \text{ \AA}$  pores and  $\text{SmC}_A\text{-SmC}_\gamma$  in bulk and in  $2000 \text{ \AA}$  pores are of similar value, whereas (iii) the temperature of the  $\text{SmC}^*\text{-SmA}$  phase transition in  $2000 \text{ \AA}$  pores is about  $3^\circ\text{C}$  lower and in  $200 \text{ \AA}$  porous sample is about  $4^\circ\text{C}$  lower than in the bulk sample, and (iv) the ferroelectric phases in AS573 exist in  $2000 \text{ \AA}$  pores as well in bulk, but they are not formed in  $200 \text{ \AA}$  pores on cooling from the isotropic phase.

The observed behavior in cylindrical pores is extremely rich, and provides an important platform for better understanding the phase behavior of antiferroelectric liquid crystalline materials.

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