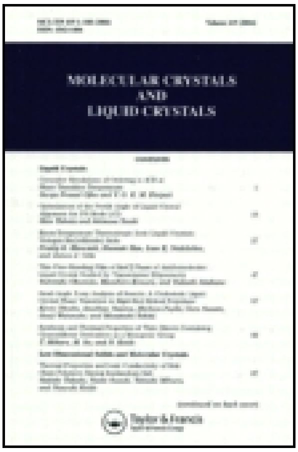

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Evidence for Different Liquid Crystal Mesophases in Confinement by Dielectric Spectroscopy

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Dielectric measurements confirm existence of the characteristic feature of the nematic phase under examined geometrical restrictions. The dynamics of the relaxation processes present in the bulk antiferroelectric liquid crystal changes noticeably under Anopore confinement. Analysis of the non-linear variation of the temperature dependence of the dielectric strength at the SmA-SmC phase transition prove the existence of the tilted smectic phase in Anopore's cylindrical channels.*

Keywords Antiferroelectric phase; confinement; dielectric relaxation; ferroelectric phase; molecular and collective relaxation processes; nematic phase; porous membranes

1. Introduction

The variety of new attractive phenomena observed in liquid crystals (LCs) under confinement has resulted in growing attention in recent investigations [1–4]. Selecting a porous material with a specific structure of the pores provides good chance to study the influence of the surface ordering or quenched random disorder effects on the ordering of the LC phases. Dielectric spectroscopy (DS) measurements bring information about molecular and collective dynamics of the relaxation processes and permit conclusions about molecular or smectic layers orientation in confinement. The changes in the relaxation rate, dielectric strength, and the broadening and/or asymmetry of the relaxation processes, provide important information about variation of molecular and collective dynamics in confinement. However, DS is less sensitive to the different possible orientations of the LC director field in pores, and more accurate results can be obtained with nuclear magnetic resonance (NMR) method.

In this study, experimental evidence is given for the existence of particular LC phases in different confinements. In more detail the relation between changes of the dielectric parameters and orientation and order of liquid crystal in confinement is discussed.

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2. Experimental

Dielectric measurements were performed using Novocontrol broadband dielectric spectrometer with high resolution impedance analyzer Alpha working in the frequency range 10^{-2} Hz–10^{7} Hz. In the high frequency range 10^{6} Hz–10^{9} Hz the HP 4291B RF and HP 4191A impedance analyzers with home-made sample holder were applied. The complex dielectric function $\varepsilon^*(\omega,\ T)$ in bulk liquid crystal and in composite samples was measured in well known nematic liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl (5CB), ferroelectric liquid crystal S-(-)-2-methylbutyl 4-*n*-nonanoyloxybiphenyl-4′-carboxylate (FLC) and antiferroelectric liquid crystal (S)-(+)-4′-(1-methylheptyloxycarbonyl)biphenyl-4-yl 4-(6-heptanoyloxyhex-1-oxy)-benzoate (AFLC). The porous Anopore membranes with well defined cylindrical pores of diameter 200 nm and thickness about 60 μm were used. For instance, the size of a 5CB molecule (0.7 nm diameter and 1.9 nm length) [5] is much smaller than the diameter of the Anopore pores. Preparation of the composite samples was described elsewhere [1–4].

The dielectric spectra were evaluated using superposition of empirical formula given by Havriliak and Negami [6] and a conductivity contribution:

$$\varepsilon^*(\omega,\ T) = \varepsilon_\infty + \sum_{j=1}^{k} \frac{\Delta\varepsilon_j}{\left[1 + (i\omega\tau_j)^{1-\alpha_j}\right]^{\beta_j}} - \frac{i\sigma}{\varepsilon_0\omega^n}, \tag{1}$$

where τ_j is the relaxation time of the *j*-th relaxation process and $\Delta\varepsilon_j$ its relaxation strength, while α_j and β_j describe broadening and asymmetry of the relaxation time distribution, respectively. ε_∞ and ε_0 are the high frequency limit of the permittivity and the permittivity of the free space, respectively. The conductivity part is expressed by the term $i\sigma/\varepsilon_0\omega^n$, where σ is the Ohmic conductivity and n a fitting parameter.

3. Results and Discussion

The evidence procedure of the liquid crystal phases in confinement should consist of the following steps:

- determination of the structure of porous matrix or dispersed system. For Anopore membranes the analysis of scanning electron microscopy (SEM) photographs at different magnifications permits the determination of pore size, porosity and surface area. The nature of cavity wall and surface area can be determined from nitrogen adsorption isotherms and NMR [7]. The particle fineness and structure of aerosil fumed silica can be obtained from infrared spectroscopy, X-ray diffraction, SEM and transmission electron microscopy (TEM) [8].
- recognition of molecular and collective relaxation processes in the bulk LC under investigation. Dielectric measurements can be performed in LC aligned homogeneously or homeotropically in the measuring capacitor with gold-plated electrodes. For better orientation of the bulk LC the sample can be slowly cooled near the specific phase transition or measuring electrodes can be coated by proper surfactant.
- determination the dielectric relaxation processes in confinement and comparison with the bulk processes. In this step the porous material is embedded with the

LC in the isotropic phase [1–4]. Composite samples prepared by the described method are mounted between the gold-plated electrodes of the measuring capacitor and DS measurements are performed.

It is well recognized and confirmed, that molecules in the nematic phase of 5CB orient parallel to the axis of untreated cylindrical channels of Anopore membranes, while in treated membranes the molecules orient homeotropically to the walls of the pores [2]. The observed changes in the relaxation rate of the molecular processes in different confinement (Synpor membranes, hydrophilic and hydrophobic aerosil dispersions) exhibit the same tendency compare to the bulk 5CB [4]. The observed differences arises mainly from surface interactions and disorder introduced in the LC.

The dielectric measurements of the antiferroelectric liquid crystal (S)-(+)-4′-(1-methylheptyloxycarbonyl)biphenyl-4-yl 4-(6-heptanoyloxyhex-1-oxy)-benzoate filed in cylindrical pores of Anopore membrane exhibit considerable differences with the dynamics of the relaxation processes present in the bulk AFLC [1]. As a result of the confinement a substantially modified soft mode (SM) and Goldstone-like mode (GM) are observed, with the first one superimposed on the molecular process. The competition between the molecular process and the soft mode in the confinement results from the distribution in orientation of the smectic layers in the cylindrical pores. The relatively weak P_H and P_L modes present in the bulk AFLC are missing in confinement due to the geometry of the experiment but also the role of the strong deformation of the SmC_a^* phase can not be ignored. The presence in the dielectric spectrum the soft mode and Goldstone-like mode although the geometry of the experiment (in this geometry these modes should be dielectrically inactive [2]) reveals that the smectic layers orientation is not perfect and the structure of the smectic phases in cylindrical geometry is strongly deformed. As a result of deformation and compression of the smectic layers the frequency degeneration of the SM and GM modes is removed and relaxation rate of the soft mode increases at the SmA-SmC* phase transition.

Figure 1 shows temperature dependence of the dielectric strength $\Delta\varepsilon$ and relaxation frequency f_{max} in the SmA and SmC* phases of the ferroelectric liquid crystal S-(-)-2-methylbutyl 4-*n*-nonanoyloxybiphenyl-4′-carboxylate confined in Anopore membrane. For this FLC-Anopore composite the collective relaxation processes are completely undetectable as a result of perfect orientation of the smectic layers perpendicular to the long axis of the pores and the direction of the measuring electric field. Only one relaxation process assigned to the rotation of the molecule around the molecular short axis appears throughout all smectic phases. The temperature dependence of the relaxation frequency follows the Arrhenius law with the activation energy in the SmA phase of about $105\,\mathrm{kJ \cdot mol^{-1}}$ and in the SmC* phase of about $115\,\mathrm{kJ \cdot mol^{-1}}$.

In the SmA phase dielectric strength $\Delta\varepsilon_A$ changes linearly with decreasing temperature as a result of antiparallel correlations of the parallel component of the dipole moments. The dielectric strength in the SmC* phase should be a simple extrapolation of dielectric strength from the SmA phase, $\Delta\varepsilon_{ext}$. However, the temperature dependence of the dielectric strength $\Delta\varepsilon_{C^*}$ in the SmC* phase changes non-linearly as a consequence of the temperature dependence of the tilt angle of the molecules in this phase. This result indicates undoubtedly the existence of a tilted smectic phase in the cylindrical channels of Anopore membrane. A convenient method to determine the temperature dependence of the tilt angle from analysis of the dielectric strength

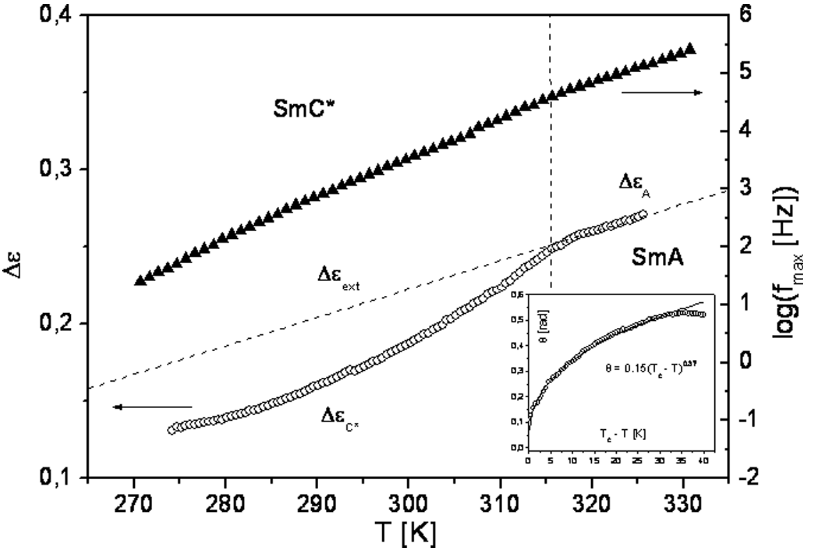

Figure 1. Temperature dependence of $\Delta\varepsilon$ and relaxation frequency $f_{\max}$ for ferroelectric liquid crystal confined in Anopore membrane. The inset shows temperature dependence of the dielectric tilt angle calculated from the formula: $\cos\theta = (\Delta\varepsilon_{C^*}/\Delta\varepsilon_{ext})^{1/2}$.

changes at the phase transition was proposed in [9]. Knowing $\Delta\varepsilon_{\mathrm{A}}$, $\Delta\varepsilon_{\mathrm{ext}}$ and $\Delta\varepsilon_{\mathrm{C}^*}$ the dielectric tilt angle can be calculated from the equation: $\cos\theta = (\Delta\varepsilon_{C^*}/\Delta\varepsilon_{ext})^{1/2}$. The inset in the Figure 1 shows temperature dependence of the dielectric tilt angle calculated from the above formula.

4. Conclusions

The temperature dependence of the relaxation rate of the molecular relaxation processes observed in the nematic liquid crystal 5CB embedded in macroporous membranes and in 5CB-aerosil dispersions is qualitatively quite similar to these in the bulk 5CB. The observed change in the dynamics of the molecular processes arises from the competition between ordering and quenched random disorder effects in confinement. Dielectric measurements confirm that the main feature of the nematic phase under geometrical restrictions is preserved.

In the AFLC-Anopore system the relatively weak $\mathrm{P_H}$ and $\mathrm{P_L}$ relaxation processes present in the bulk AFLC are missing in confinement due to the geometry of the experiment and significant deformation of the smectic layers in the $\mathrm{SmC}_{\mathrm{a}}^*$ phase. Moreover, the dynamics of the other relaxation processes present in the bulk AFLC changes noticeably under Anopore confinement.

The dielectric measurements certainly confirm existence of the tilted smectic phase in the FLC confined in Anopore cylindrical pores. In some cases of composite systems the dielectric measurements can give useful information about origin of the LC phase in confinement.

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