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Dielectric spectroscopy of aerosil-dispersed liquid crystal embedded in Anopore membranes

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The complex dielectric permittivity ϵ^* values are presented for aerosil-dispersed 4-pentyl-4′-cyanobiphenyl (5CB) confined in Anopore membranes. The dielectric permittivities are measured in the frequency range from 10^{-2} Hz to 1 GHz at temperatures ranging from 50 °C down to −20 °C. In bulk 5CB, which has only a nematic phase, there exist two main relaxation processes: one due to the rotation of molecules around their short axes for parallel orientation of the director to the probing field and another fast relaxation process due to the librational motion of molecules for perpendicular orientation. Inside Anopore membranes both these main relaxation processes can be observed, but with subtle differences. The relaxation process due to the rotation of molecules around the short axis is faster in Anopores at all temperatures in comparison with the bulk process. Hydrophilic aerosil particles, when dispersed in the liquid-crystal (LC) phase, attach to each other via hydrogen bonds and form a three-dimensional interconnecting aerosil network, thus dividing the LC phase into small domains. Dispersing 5CB with different concentrations of hydrophilic aerosils leads to a decrease in relaxation time with aerosil concentration. In these dispersed systems a slow additional relaxation process emerges. This slow process becomes stronger with higher concentrations of aerosil. From our experiments we conclude that this process is the relaxation of 5CB molecules homeotropically aligned to the surface of the aerosil particles. In the case of 5CB-aerosil dispersions enclosed in Anopore membranes this slow process still exists and increases also with aerosil concentration. The relaxation time of the rotation of the 5CB molecules around their short axis systematically increases in these 5CB-aerosil samples in Anopore membranes with aerosil concentration from the 5CB-Anopore behavior towards the behavior observed for 5CB-aerosil dispersions. We explain the evolution as resulting from opposing tendencies from size effects (in the Anopore membranes) and disorder effects (in the aerosil dispersions).

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I. INTRODUCTION

Confining and dispersing liquid crystals (LCs) has been a field of active research recently [1–4]. Confinement of liquid crystals in diminutive pores, which have an inherent large interfacial area, has yielded several interesting results [5–8]. Some of the issues that have been addressed in these studies are the influence of confinement on the structure and phase and glass transitions, as well as on the molecular motion [9–15]. In most of the published work in this area modifications of the phase transitions, orientational order, and elastic properties of LCs have been presented. Several theoretical and experimental review articles have also been published, exemplifying the importance of this field [16,17].

Recently, the influence of internal restrictions on liquid crystals by introducing nanosized silica particles into the phase has been investigated in great detail [8,13–15,18–20]. The particles form a gel-like network if their density exceeds the "gelation" (percolation) threshold $\rho_s \sim 0.01$ g cm^{-3}. This is the "soft" regime, where the hydrogen-bonded links between the spheres can easily break and mend with time. Yet another distinct regime comes at $\rho_s \sim 0.1$ g cm^{-3} above which it is in a "stiff" regime similar to aerogel (chemically bonded fused silica gel). In spite of all the vigorous research activity in this field, several issues still remain unresolved. An important issue that is still under discussion is whether random-field-type models are necessary to describe the new features observed in the nanoconfined systems reported in literature. In most of the explanations that involve random-field-type models the finite-size and surface effects, which are inherent characteristics of porous media, are rarely emphasized. Lately, with the use of dielectric spectroscopy, it has been shown that a slow relaxation proces exists in the confined LC systems. The slow process has universally been attributed to the relaxation of molecules adsorbed at the surface [8,13,14,21].

A simple way to avoid the random porous structure, which may be responsible for the random field, is to use cylindrical confinements that are widely available, such as those made from alumina or polycarbonate membranes. Size effects in such systems have also been reported in experiments on a positive-dielectric-anisotropy liquid crystal embedded in polycarbonate (Nucleopores) [22]. In a comprehensive study concerning anchoring, wetting, and order near the *N-I* transition of 5CB by deuterium NMR, short-range interactions have been reported, which was explained on the basis of a phenomenological Landau–de Gennes theory [23]. Studies of LCs in the cylindrical pores of Nucleopore membranes have also been performed by dynamic light scattering experiments, where surface-dominated orientational dynamics is observed [24]. In all the above-mentioned reports, there

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*Author to whom correspondence should be addressed. Present Address: NIH bldg. 50, Rm. 4151, MSC 8027, National Institutes of Health, 50 South Dr., Bethesda, MD 20892, USA. Electronic address: sinhag@nidcd.nih.gov was no need to involve considerations based on the random-field model.

Since dielectric relaxation methods are sensitive to movements of the dipoles as well as free ions, the absence of the slow process (in the frequency range around 100 kHz) in cylindrical pores [25], like that observed for LCs in random pores [21] and LC-aerosil composites [8,13,14], has raised the question as to whether such a process could be from a different origin than from surface-induced dipolar relaxation. Two specific possibilities are considered: defect dynamics and ion mobility. In the latter case one assumes that the ions can travel through the interconnected pores (in the LC-aerosil composite they can travel along the interconnected aerosil network) at a slow rate with a wide distribution of relaxation times [8,14,21] due to the many hops that they have to make through many sites (which may happen at different frequencies).

In this paper we focus on an experiment which may test these hypotheses. We fill the cylindrical channels of the Anopore membranes with LCs that have already been dispersed with nanosized aerosil particles [26]. The cylindrical Anopore channels introduce surface-induced orientational order; on the other hand, the presence of the aerosil particles in the LCs also provides a large surface area for the interaction due to the many hydroxyl groups that cover the surfaces, which can easily hydrogen-bond the nitrogen atoms at one end of the 5CB molecules [21]. The presence of aerosils increases the disorder in the system, as has been shown in several optical experiments combined with computer simulations [27–29]. The influence of disorder has also been observed on the dielectric spectra as shown in the concentration dependence of the real and imaginary parts of the dielectric permittivity [13]. An important finding of a recent study of these confined systems by dielectric spectroscopy was that only a few layers of LC molecules are affected by the aerosil surface and so its effects are lost as we move away from it [14]. Therefore, the molecular rotation around the short axis observed in the remaining bulk will constitute molecules that are weakly affected by the surface effects. Since the surface interactions are limited only to those molecules that are in the immediate vicinity [14], we additionally studied the influence of disorder and confinement on the molecular rotation of molecules around the short axis. From our results we see that disorder and confinement have opposite effects on the reorientation motion of molecules around the short axis.

II. EXPERIMENT

4-pentyl-4′-cyanobiphenyl (5CB) was obtained from MERCK and was used without further purification. We have studied aerosil-dispersed 5CB confined in untreated Whatman Anopore membranes with nominal pore sizes of 2000 Å. Hydrophilic aerosils type 300 (obtained from Degussa Corp.) with diameters around 70 Å and surface area $300 \pm 30\ \mathrm{m}^2/\mathrm{g}$ were used. On the surface of hydrophilic aerosil, there is one silanol group ($\equiv$Si—OH) per 0.28–0.33 nm^2. Hence the aerosils we used have about 9.7×10^{20} silanol groups per gram [30]. A 5CB-acetone mixture was prepared such that there was around 0.02 g of LC per cm^3 of acetone. The required amount of aerosils, dried under vacuum at 200 °C for around 15 h, was then added to the 5CB-acetone mixture. Since the LC-aerosil mixture was supposed to impregnate the Anopore membranes available in a single nominal size of 2000 Å from Whatman, we vacuum-dried the Anopore membranes beforehand at 200 °C for around 15 h. It was then added to the prepared acetone-LC-aerosil mixture. The new mixture was then sonicated for 1 h to obtain a good dispersion of the aerosils in the medium that would also enter the Anopore membranes. Acetone was then allowed to evaporate slowly while keeping the temperature of the mixture above 50 °C. The remaining sample was then kept overnight above 50 °C in vacuum, to ensure complete evaporation of acetone. The LC-aerosil that remained outside the Anopore membranes was used for the 5CB-aerosil measurements. The excess amount of LC-aerosil on top of the Anopore membranes was carefully wiped away before the final measurement. Three different concentrations of LC-aerosils in Anopore were prepared with ρ_s equal to 0.01, 0.05, and 0.15 g cm^{-3} where

$$\rho_s = \frac{m_s}{m_{LC}}\rho_{LC} \approx \frac{m_s}{m_{LC}}\ (1\ \mathrm{g\ cm}^{-3}). \qquad (1)$$

m_s and m_{LC} are the masses of the aerosils and LC's used in the mixture preparation.

Measurements of the real (ϵ') and imaginary (ϵ'') parts of the complex dielectric permittivity were done with a combination of different impedance analyzers. In the frequency range from 10^{-2} Hz to 1 MHz, the measurements were performed using a NOVOCONTROL broadband dielectric spectrometer which consists of a high-resolution dielectric/impedance analyzer ALPHA and an active sample cell. In the frequency range from 1 MHz to 1 GHz the HP4291B rf impedance analyzer was used in combination with a homemade cell [13]. For comparison bulk 5CB, 5CB in Anopores, and the LC-aerosil mixture lying outside the Anopore membranes were also measured in the same frequency range and similar temperatures. For the measurements of bulk 5CB as well as the 5CB-aerosil composites both faces of the electrodes were, beforehand, spin coated with polyimides to obtain the parallel alignment (probing electric field parallel to the director). The alignment procedure using polyimides was preferred over magnetic fields as we realized that in the case of LC-aerosil the magnetic field of 0.5 T available in our laboratory was not strong enough to orient the phase. We used polyimide SE1211 (Nissan Chemicals), which promotes homeotropic orientation of the molecules with respect to the electrode surface. For the Anopore and LC-aerosil composites embedded in Anopore membranes such surface treatment of electrodes was not required, as it is known from various experiments that the channels of the Anopores promote axial alignment of the director [31]. Thus this configuration is automatically suitable for parallel measurements of the sample. For temperature control in the low-frequency measurements the NOVOCONTROL Quatro system was used. Temperature control in the high-frequency measurements was similar to that described in Ref. [13].

The software package WINFIT provided by NOVOCON-

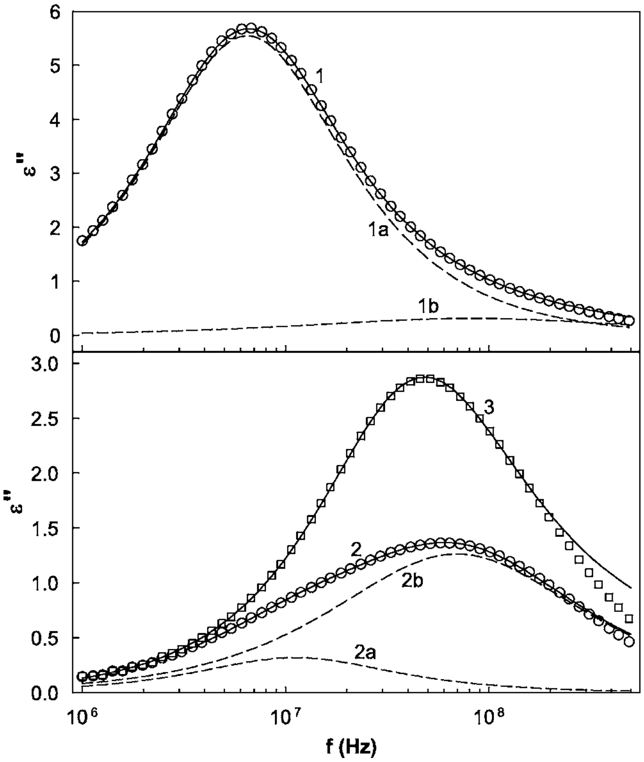

FIG. 1. ϵ'' vs frequency for bulk 5CB at $T=30.5\ ^\circ\mathrm{C}$ for $\mathbf{E}\|\mathbf{n}$ (1) and $\mathbf{E}\perp\mathbf{n}$ (2) in the nematic phase and at $T=46.0\ ^\circ\mathrm{C}$ in the isotropic phase (3). Solid lines show fitting according to Eq. (2); dashed lines represent deconvolution into elementary contributions.

TROL was used for the data analysis. For the quantitative analysis of the dielectric spectra we used the Havriliak-Negami function [32] which is incorporated in the WINFIT software. For the case of more than one relaxation process, taking into account the contribution of the dc conductivity to the imaginary part of dielectric permittivity, the Havriliak-Negami function in the frequency domain is given as

$$\epsilon^* = \epsilon_\infty + \sum_j \frac{\Delta\epsilon_j}{[1+(i2\pi f\tau_j)^{1-\alpha_j}]^{\beta_j}} - i\frac{\sigma}{2\pi\epsilon_0 f^n}, \qquad (2)$$

where ϵ_∞ is the high-frequency limit of the permittivity, $\Delta\epsilon_j$ the dielectric strength, τ_j the mean relaxation time, and j the number of the relaxation process. The exponents α_j and β_j describe the symmetric and asymmetric distributions of the relaxation times. The term $i\sigma/2\pi\epsilon_0 f^n$ accounts for the contribution of the conductivity σ, with n as fitting parameter.

III. DIELECTRIC PROPERTIES OF BULK 5CB, 5CB IN ANOPORES, AND AEROSIL-DISPERSED 5CB

A. Dielectric response of bulk 5CB

5CB is a LC that has been extensively investigated in the past. The dielectric properties of this liquid crystal with positive dielectric anisotropy are well known and hence facilitate the understanding of the complicated properties of LCs under confinement. 5CB is quite stable and has a large dipole moment of 5 D parallel to the molecular long axis. Figure 1 represents typical dielectric relaxation behavior for 5CB measured in our setup under parallel and perpendicular orientations in the nematic phase as well as in the isotropic phase.

All the data presented are taken from cooling runs.

For the probing electric field $\mathbf{E}$ parallel to the director $\mathbf{n}(\mathbf{E}\|\mathbf{n})$ of bulk 5CB, the real (ϵ') and imaginary (ϵ'') parts of the dielectric permittivity have a dispersion region with a characteristic frequency of about 5 MHz. This dispersion is due to the restricted rotation of the molecules around their short axis and is of Debye type [33–36]. This means that in Eq. (2) the fitting parameters $\alpha=0$ and $\beta=1$. In the spectra for the parallel orientation an additional contribution, although quite weak, was observed with characteristic frequencies around 80 MHz. This is most likely due to the imperfect alignment of the molecules.

In the case where the probing field is perpendicular to the director, two relaxation processes with similar relaxation times were observed, with the slow process much weaker than the fast one. The fast process, having a characteristic frequency around 70 MHz, is assigned to the librational motion of the molecules [37]. Since the 5CB molecules do not have a perpendicular component of the dipole moment, the rotation around the long axis should be inactive in the dielectric measurements. The slower process could be due to the rotation around the short axis of molecules that could not be aligned perfectly parallel to the surface of the coated electrodes.[1] The α and β parameters are around 0.15 and 1 for the main process in the nematic range.

The dielectric spectra of 5CB in the isotropic phase have characteristic relaxation frequencies around 50 MHz corresponding to the rotation of molecules around the short axis. In the isotropic phase $\alpha\sim 0.02$ and β is linearly increasing from a value of 0.7 close to T_{NI} to a value of 0.85 at $T=50\ ^\circ\mathrm{C}$.

The fitting parameters for all the curves presented in Fig. 1 are given in Table I.

The corresponding relaxation times for the main processes at different temperatures are shown in Fig. 2. The temperature dependence of the corresponding relaxation times (τ) obeys the empirical Arrhenius equation $\tau=\tau_0\exp(U/RT)$, where U is the activation energy and R is the universal gas constant. The activation energies are approximately 70.0 kJ/mol for nematic 5CB in parallel orientation and 4.4 kJ/mol for perpendicular orientation. In the isotropic phase the activation energy is around 48.1 kJ/mol. The N-I transition temperature is close to 35.7 °C.

B. Dielectric response of 5CB confined in Anopores

The dielectric behavior of 5CB embedded in Anopores has also been studied in the past [37]. Our dielectric spectra for 5CB embedded in untreated and treated Anopore mem-

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[1] In the case of the perpendicularly oriented sample a stronger homeotropically aligning force from the metal electrodes could additionally be present. This was the case in our experiment, where the slower process was slightly stronger for a sample thickness of 50 μm than for 150 μm.

TABLE I. Parameters for bulk and confined 5CB obtained from fitting by Eq. (2). *a*, *b*, *c*, and *d* represent Maxwell-Wagner type, surface relaxation, rotation around short axis, and librational motion processes, respectively. Fit parameters given in brackets are from the weak process in these spectra. When $\alpha=0$ or $\beta=1$, these parameters were fixed in the fitting process.

ρ_s [g cm^{-3}]	$\Delta\epsilon_a$	τ_a [s]	α_a	β_a	$\Delta\epsilon_b$	τ_b [s]	α_b	β_b	$\Delta\epsilon_c$	τ_c [s]	α_c	β_c	$\Delta\epsilon_d$	τ_d [s]	α_d	β_d
Nematic bulk 5CB at $T=30.5$ °C																
0 (E‖n)	—	—	—	—	—	—	—	—	11.21	2.4×10^{-8}	0	1	(0.9)	(1.8×10^{-9})	(0.26)	(1)
0 (E ⊥ n)	—	—	—	—	—	—	—	—	(0.58)	(1.5×10^{-8})	(0)	(1)	3.28	2.3×10^{-9}	0.16	1
Isotropic bulk 5CB at $T=46.0$ °C																
0	—	—	—	—	—	—	—	—	6.5	4.0×10^{-9}	0.01	0.79	—	—	—	—
5CB embedded in untreated Anopores																
0 ($T=46.0$ °C)	—	—	—	—	—	—	—	—	0.44	3.2×10^{-9}	0.02	0.7	—	—	—	—
0 ($T=30.5$ °C)	—	—	—	—	—	—	—	—	0.55	1.43×10^{-8}	0.04	1	(0.03)	(1.0×10^{-9})	(0)	(1)
0 ($T=10.6$ °C)	—	—	—	—	—	—	—	—	0.76	8.2×10^{-8}	0.04	1	(0.03)	(1.3×10^{-9})	(0)	(1)
5CB embedded in lecithin-treated Anopores																
0 ($T=46.0$ °C)	—	—	—	—	—	—	—	—	0.15	3.3×10^{-9}	0	0.5	—	—	—	—
0 ($T=30.5$ °C)	—	—	—	—	—	—	—	—	—	—	—	—	0.10	2.1×10^{-9}	0.26	1
0 ($T=10.6$ °C)	—	—	—	—	—	—	—	—	—	—	—	—	0.08	3.0×10^{-9}	0.23	1
5CB filled with hydrophilic aerosils at ($T=30.0$ °C)																
0.01	—	—	—	—	—	—	—	—	3.67	2.5×10^{-8}	0	1	1.3	5.7×10^{-9}	0.36	1
0.05	1.03	9.4×10^{-4}	0.2	1	0.11	1.7×10^{-6}	0.23	1	3.11	2.3×10^{-8}	0	1	1.6	3.4×10^{-9}	0.28	1
0.15	341	2.91	0.06	1	0.61	9.3×10^{-7}	0.5	1	3.4	2.1×10^{-8}	0.05	1	2.18	2.6×10^{-9}	0.21	1
Aerosil-dispersed 5CB embedded in Anopore at ($T=30.0$ °C)																
0.01	16.6	1.2×10^{-3}	0.1	1	—	—	—	—	0.32	1.6×10^{-8}	0.02	1	0.18	8.4×10^{-10}	0.6	1
0.05	3.6	1.3×10^{-1}	0.13	1	0.08	1.7×10^{-7}	0.2	1	0.15	1.75×10^{-8}	0	1	0.04	1.7×10^{-9}	0.21	1
0.15	0.05	2.3×10^{-3}	0.2	1	0.12	2.4×10^{-6}	0.68	1	0.57	1.8×10^{-8}	0.04	1	0.2	3.5×10^{-9}	0.39	1

branes for three different temperatures are shown in Fig. 3. The Anopore membranes have cylindrical pores in which the cylindrical axis is parallel to the probing electric field. For 5CB in untreated cylindrical pores the dielectric spectra in the nematic phase are similar to those of bulk 5CB in the case in which the director is parallel to the probing field. Thus we can conclude that in untreated cylindrical pores the molecules (at least the majority of them) are oriented along the pore axis. However, the main relaxation process is systematically faster at all temperatures in comparison to the bulk process. All other fit parameters take values comparable to the bulk ones. Supercooling by at least 20° of the nematic phase below the bulk crystallization temperature was observed. The spectra and fitting parameters in the supercooled phase are similar to those in the nematic phase. The fitting parameters corresponding to the curves in Fig. 3 are given in Table I.

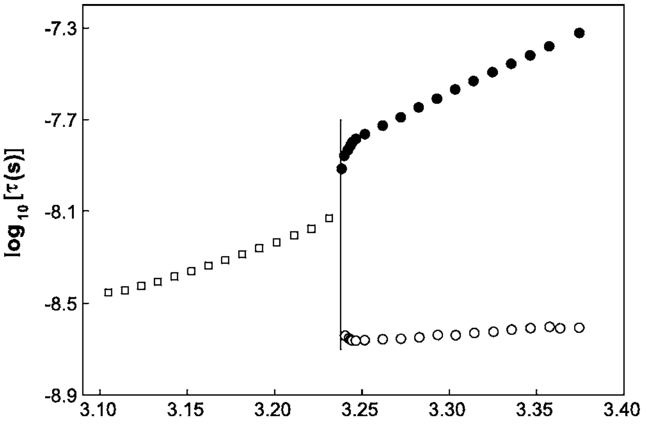

FIG. 2. Temperature dependence of the main relaxation times for the bulk processes of 5CB. Solid circles: rotation around the short axis in the nematic phase. Open circles: librational motion of molecules in the nematic phase. Open squares: rotation around the short axis in the isotropic phase.

For homeotropic boundary conditions at the pore walls, the molecules are oriented perpendicular to the probing electric field [31]. Some spectra are presented in the lower half of Fig. 3. Since molecules of 5CB do not have a component of the dipole moment perpendicular to the long axis, the only explanation for the observed high-frequency relaxation is to associate it with the librational motion. This mode also has characteristic frequencies similar to those observed in bulk 5CB for the probing electric field perpendicular to the director. The fitting parameter α was around 0.25 in the nematic and supercooled temperature ranges whereas β was always close to 1. However, in the isotropic phase α was always close to 0 whereas β ranged between 0.6 and 0.5 for the relaxation in the lecithin treated matrix. The fitting parameters corresponding to the presented curves are given in Table I.

The temperature dependence of the relaxation times for 5CB in untreated and treated Anopore membranes is pre-

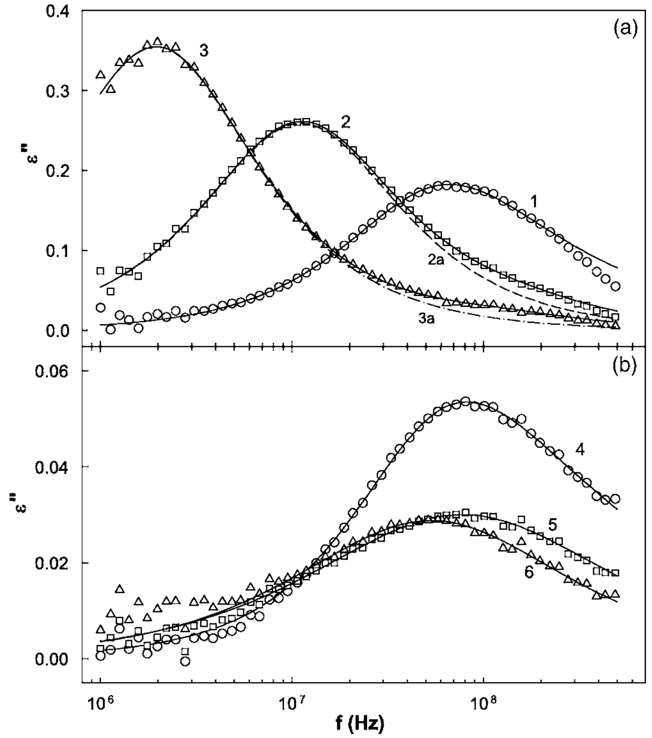

FIG. 3. (a) ϵ'' vs frequency for 5CB in untreated Anopore membranes with 2000 Å cylindrical pores at $T=46.0$ °C (isotropic, 1), 30.5 °C (nematic, 2), and 10.6 °C (supercooled, 3). (b) ϵ'' vs frequency for 5CB in lecithin treated Anopore membranes with 2000 Å cylindrical pores at $T=46.0$ °C (isotropic, 4), 30.5 °C (nematic, 5), and 10.6 °C (supercooled, 6). Solid lines show fitting according to Eq. (2); dashed (2a) and dash-dotted (3a) lines represent extracted main process due to rotation around short axis.

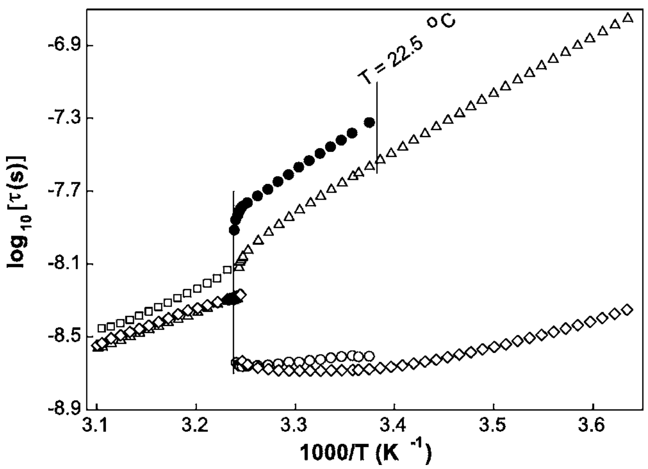

FIG. 4. Temperature dependence of relaxation times for the main processes for 5CB in Anopore membranes with 2000 Å cylindrical pores: triangles, untreated membranes; diamonds, lecithin treated membranes. For comparison corresponding bulk values are also included: solid circles, bulk 5CB ($\mathbf{E}\|\mathbf{n}$); open circles, bulk 5CB ($\mathbf{E}\perp\mathbf{n}$); open squares, bulk 5CB (isotropic).

sented in Fig. 4. For comparison the bulk values have also been included.

Some interesting differences with bulk behavior can be observed. T_{NI} is lowered in Anopore membranes by at least 0.3° in the untreated matrix and by 0.7° in the treated matrix. The main fact that is observed by comparing the $\mathbf{E}\|\mathbf{n}$ dielectric spectra of bulk and untreated Anopore-confined 5CB is the decrease in the characteristic relaxation times at corresponding temperatures. This difference is smaller in the isotropic than in the nematic phase.

The temperature dependence of the main relaxation times of the process observed for the lecithin-treated matrix is different from that observed in the untreated sample. There is a slight decrease of the relaxation times (see Fig. 4) in the temperature range (34.9–22.5 °C) of the nematic phase. However, below 22.5 °C, in the supercooled phase, the relaxation time increases continuously with decreasing temperature. This has been discussed in Ref. [31].

C. Dielectric response of aerosil-dispersed 5CB

5CB dispersed with aerosils has also been studied by dielectric spectroscopy in the past [38,39]. However, we have homeotropically oriented the nematic phase using surface treatment of the electrodes, which was not done in these earlier studies. We performed these measurements in order to compare them with our results of aerosil-dispersed 5CB embedded in Anopores. The dielectric spectra were measured at various temperatures in cooling runs for samples of 5CB filled with different concentrations of hydrophilic aerosils that were left in excess outside the Anopores during the preparation of these samples. In Fig. 5 we show typical dielectric spectra obtained for 5CB with different concentrations of aerosil. There is an increasing influence of aerosils with increasing concentration.

The bulklike relaxations for 5CB filled with 0.01 g cm^{-3} of hydrophilic aerosils are similar to those observed for bulk 5CB. The main process due to the rotation of molecules around the short axis is also observed and is of Debye type. The fast librational process is also observed in this measurement, although the measurements were done under parallel alignment. This implies that the homeotropic alignment (with $\mathbf{E}\|\mathbf{n}$) is not perfect in this sample.

A slow additional process, which was already present for the 0.05 g cm^{-3} sample, becomes much stronger for the 0.15 g cm^{-3} sample. This slow process is shown as a dash–double-dotted curve in Figs. 5(b) and 5(c). The characteristic frequency of the slow process is about two decades lower than the main process. This process can be fitted with a Cole-Cole process with α increasing with aerosil concentration. Slow processes, similar in relaxations times, have also been observed for 7CB and CB15 in their (chiral) nematic as well as their isotropic phase dispersed with hydrophilic Aerosils [13,14]. It is also seen in the isotropic, nematic, and smectic phases of 8CB [40]. The characteristics of the slow relaxation process are similar in all phases and are more or less independent of the phase. The fitting parameters of the spectra shown in Fig. 5 are given in Table I.

In the case of LCs dispersed with aerosil concentrations of 0.05 g cm^{-3} and higher, we could see another very slow relaxation process with the maximum around 1 kHz and lower. In Figs. 5(b) and 5(c) this process is represented by dotted curves. The relaxation time of this process does not

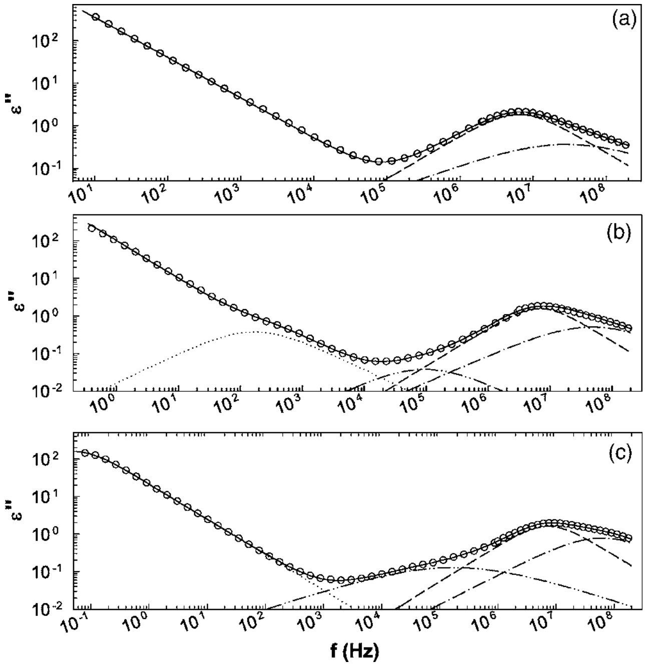

FIG. 5. Log-log plot of ϵ'' vs frequency for 5CB at $T=30$ °C (circles) filled with (a) $0.01\ \mathrm{g\,cm^{-3}}$, (b) $0.05\ \mathrm{g\,cm^{-3}}$, and (c) $0.15\ \mathrm{g\,cm^{-3}}$ hydrophilic aerosils. Solid lines show fitting according to Eq. (2); dashed lines represent the separated relaxation processes where dash-dotted line is the librational process, dashed line is the process due to rotation around short axis, and dash–double-dotted line is a surface process. Dotted lines represent a Maxwell-Wagner type process. See Table I for the fitting parameters.

have a clear concentration dependence. This process could be a Maxwell-Wagner-type ionic one [41].

The temperature dependence of the relaxation times of the main processes—libration and rotation around the short axis—are presented in Fig. 6 together with the corresponding results for the bulk and Anopore-confined casees.

The librational process is more or less similar to the bulk process as can be observed from the overlap of symbols in the figure. The exception was for $0.01\ \mathrm{g\ cm^{-3}}$ where the process is slightly faster. This is probably not a real effect as the process was weak and hence fitting was performed on the very weak shoulder observed on the main relaxation. It can be seen from Fig. 6(b) that the process due to the rotation around the short axis has relaxation times very similar to the bulk process. As such the activation energies were also comparable. However, on careful inspection we find that the process becomes systematically faster as a function of aerosil concentration. We see that the molecular rotation process in the 5CB-aerosil system moves with increasing ρ_s towards the process obtained in Anopore. The effect is also seen for the isotropic phase in Fig. 6(b), but is less pronounced in this phase. As will be shown in the next section, the whole trend reverses as we confine the LC-aerosil composites in cylindrical Anopores. With a fixed cylindrical confinement, on increasing the aerosil concentration inside, the molecular rotation process moves from an Anopore-like relaxation towards bulklike relaxation.

The temperature dependence of the relaxation times of the process due to the rotation of molecules in surface layers is also included in Fig. 6. The relaxation times are much slower in comparison to the bulk process. In addition to that, this process seems only slightly affected by the phase transition. The relaxation times have an Arrhenius-like temperature dependence typical for a surface process [14].

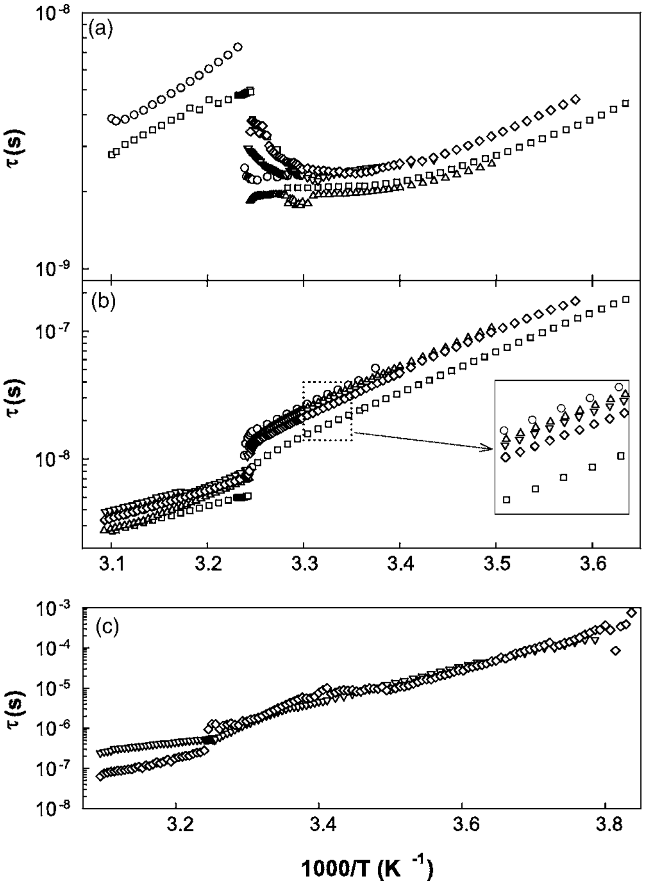

FIG. 6. Temperature dependence of relaxation times for (a) librational processes, (b) rotation around short axis, and (c) surface process for 5CB dispersed with aerosils for concentrations of $0.01\ \mathrm{g\,cm^{-3}}$ (up triangles), $0.05\ \mathrm{g\,cm^{-3}}$ (down triangles), and $0.15\ \mathrm{g\,cm^{-3}}$ (diamonds). For comparison corresponding bulk relaxation times (circles) and relaxation observed in Anopore membranes (squares) have also been included. The inset in (b) shows the enlarged area represented by dotted lines.

IV. DIELECTRIC PROPERTIES OF AEROSIL-DISPERSED 5CB IN ANOPORES

A. Dielectric spectra of aerosil-dispersed 5CB in Anopores

Typical spectra obtained for aerosil dispersed 5CB embedded in Anopores are presented in Fig. 7 for different concentrations. Apparently, the main relaxations due to the librational motion of molecules and the rotation of molecules around the short axis exist for all concentrations. The librational process is, however, rather weak for the $0.01\ \mathrm{g\,cm^{-3}}$ concentration. This process has a wide distribution of relaxation times for all concentrations. The other process, which is due to the rotation of molecules around the short axis, is observed prominently for all concentrations. We can see by

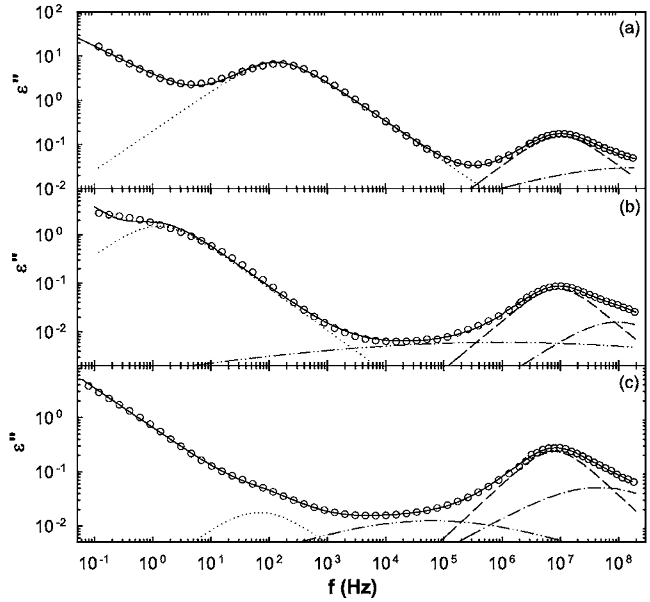

FIG. 7. Log-log plot of ϵ'' vs frequency for aerosil-dispersed 5CB embedded in Anopores at $T=30.0\ °\mathrm{C}$ (circles) at concentrations (a) $0.01\ \mathrm{g\,cm^{-3}}$, (b) $0.05\ \mathrm{g\,cm^{-3}}$, and (c) $0.15\ \mathrm{g\,cm^{-3}}$. Solid lines show fitting according to Eq. (2); dashed lines represent the separated relaxation processes where dash-dotted line is the librational process, dashed line is the process due to rotation around short axis, and (dash–double-dotted line) is the surface process. Dotted lines represent a Maxwell-Wagner type process. See Table I for the fitting parameters.

comparing the frequency of the maxima of the process that it becomes systematically slower as we increase the aerosil concentration inside the Anopores. This dependence is opposite to that observed for the LC-aerosil composite that is outside the Anopores.

In addition to the main processes, we also see the systematic emergence of a slow process around 50 kHz. This slow process is of similar origin as observed for 5CB dispersed with aerosils. The increase in prominence of this process with increasing aerosil concentration can be seen from Fig. 7. The process could not be observed for the $0.01\ \mathrm{g\,cm^{-3}}$ samples. This process is absent in bulk and has only been detected for LC-aerosil composites, which means that the process is a property of the composite.

B. Temperature dependence of relaxation times

The temperature dependence of the relaxation times is shown in Fig. 8. The process due to librational motion of molecules has more or less a similar dependence as observed for bulk. Due to the weakness in dielectric strength of this process here, there is a lot of scatter in the temperature dependence of the relaxation times. The process due to the rotation of molecules around the short axis is much better defined as seen from the smooth temperature dependence of the relaxation times. The activation energy of this process is also quite similar to that observed for a bulk sample. The systematic increase of relaxation times with increasing aerosil particle concentration can also be observed. The relaxation times of the slow surface process are also shown in Fig. 8(c). For comparison the surface process observed for 5CB with $0.15\ \mathrm{g\,cm^{-3}}$ aerosil has also been included. We can see that the slow process has comparable relaxation times, corroborating the fact that the process can be expected to be of similar origin as observed for pure LC-aerosil composites. The scatter in the data is due to the weakness of the process.

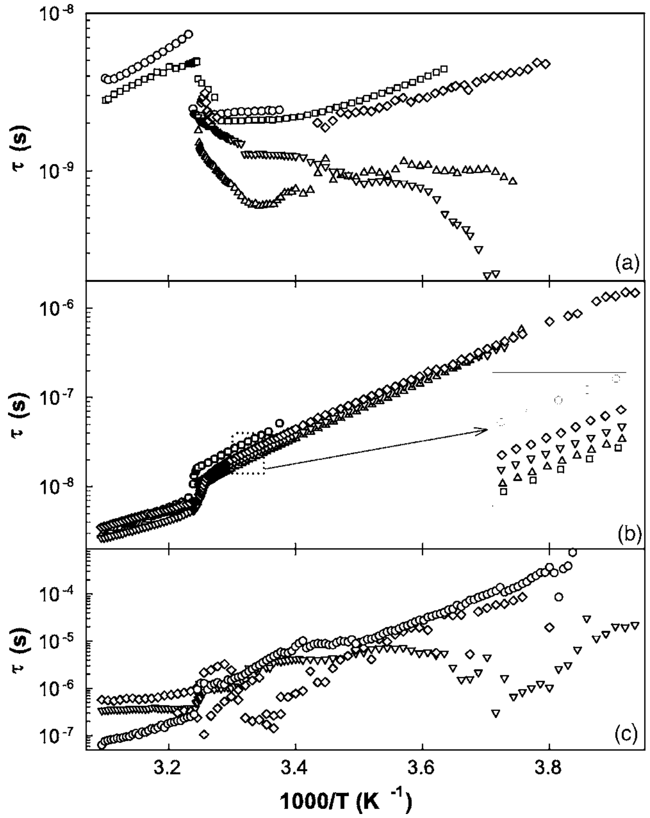

FIG. 8. Temperature dependence of relaxation times for aerosil-dispersed 5CB embedded in Anopores for concentrations for (a) librational processes, (b) rotation around short axis, and (c) surface process: $0.01\ \mathrm{g\,cm^{-3}}$ (up triangles), $0.05\ \mathrm{g\,cm^{-3}}$ (down triangles), and $0.15\ \mathrm{g\,cm^{-3}}$ (diamonds). For comparison corresponding bulk relaxation times (circles) and relaxation observed in Anopore membranes (squares) have also been included. The inset in (b) shows the enlarged area represented by dotted lines.

V. DIELECTRIC STRENGTH vs DISORDER

From various studies it is known that the presence of aerosils disorders the LC phase [18,19,42–45]. One such study which probed the orientational order parameter of 5CB dispersed with hydrophobic and hydrophilic aerosils used the electron-spin-resonance (ESR) technique [46]. The study also reports the changes in dynamics due to the reorientation of molecules around the short axis by considering the rotational diffusion coefficient D. In the case of dielectric measurements a similar parameter—related to the orientational order parameter—can be extracted from the temperature dependence of the dielectric strength of the process due to orientation of molecules around the short axis. For LCs with molecules having the dipole moment parallel to the molecu-

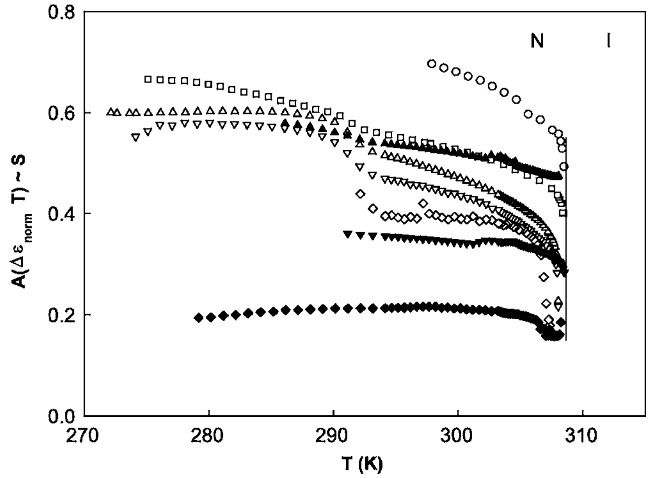

FIG. 9. Temperature dependence of the extracted orientational order parameter for bulk 5CB (open circles), 5CB embedded in untreated Anopores (open squares), aerosil dispersed in 5CB for concentrations 0.01 g cm^{-3} (solid up triangles), 0.05 g cm^{-3} (solid down triangles), and 0.15 g cm^{-3} (solid diamonds) and for aerosil-dispersed 5CB embedded in Anopores for concentrations 0.01 g cm^{-3} (open up triangles), 0.05 g cm^{-3} (open down triangles), and 0.15 g cm^{-3} (open diamonds).

lar long axis and with the director aligned parallel to the probing field, the dielectric strength $\Delta\epsilon=\epsilon_s-\epsilon_\infty$ has a relation with the order parameter given by the theory of Maier and Meier [47] as

$$\Delta\epsilon T \sim \frac{\mu^2}{k} S, \tag{3}$$

where μ is the dipole moment, k is the Boltzmann constant, and S is the order parameter. Therefore the product $\Delta\epsilon \times T$ is a measure of the temperature dependence of the orientational order parameter. In Fig. 9 we present the values extracted from the dielectric strengths of our measured samples. First of all, the dielectric strengths were normalized by their isotropic values to the bulk isotropic values to make a proper comparison of the magnitudes of $\Delta\epsilon$ of all samples. Second, the product of the normalized $\Delta\epsilon$ with T was divided by a common factor (A) that would equate the values of bulk 5CB to the order paramter values reported in literature.

For fluctuations of the dipole orientations with smaller amplitude—i.e., with lower order parameter values—the contribution of the dipole moment to the dipole polarization is minimal because the dipole moment is tilted away from the probing electric field. Therefore the dielectric strength, which is a measure of polarization, should be lower for higher disorder (higher concentration of aerosils) than for lower ones. That is the case as can be observed from Fig. 9 for all samples presented in the paper. The obtained values of the order parameter for 5CB dispersed with aerosils are very similar to the ones reported in Ref. [46]. We see that the changes in ordering are much higher in the pure LC-aerosil composites than those embedded in the Anopores. In summary, in Anopores, the disorder is lowest, whereas the acceleration of the process is highest. In the case of pure LC-aerosil composites, the disorder is highest, but the acceleration is the lowest. In the aerosil-dispersed 5CB embedded in Anopores the disorder is slightly greater than in pure Anopores and the acceleration is slightly lower than in Anopores.

VI. DISCUSSION AND CONCLUSIONS

In the previous sections we presented new dielectric spectroscopy results for pure bulk 5CB, 5CB embedded in 2000 Å cylindrical Anopore membranes, 5CB dispersed with 7-nm-diam hydrophilic aerosil spheres, and aerosil-dispersed 5CB in Anopore membranes. In this section we want to discuss some of the similarities and differences observed between the different systems.

A. Main relaxation times

In agreement with the well-established dielectric behavior of bulk alkylcyanobiphenyls (nCBs), two main dipolar relaxation processes are observed for bulk 5CB in the nematic phase: one for parallel alignment and another for perpendicular alignment of the director with respect to the probing electric field. For the parallel alignment, the process has characteristic frequencies around 5 MHz and is due to the rotation of molecules around their short axes. For the perpendicular alignment the main process around 70 MHz is due to librational motion of the molecules.

5CB embedded in untreated Anopore membranes orients mainly parallel with the cylinder axis and thus also parallel with the probing electric field. The main process in this case results in spectra which are very similar with those of the bulk process of 5CB for rotations around the short axis of the molecules. However, in Anopore this process is faster in all phases. We believe that this reduction of the relaxation times, which can be considered to correspond with a reduction of the effective rotational viscosity, is due to a (small) size effect. Although, as seen in Fig. 9, a lower overall orientational order parameter indicates disorder in comparison with bulk 5CB, the size effect seems to dominate. For the lecithin-treated Anopore matrix one induces homeotropic boundary conditions at the pore walls, resulting in molecules oriented perpendicular to the probing electric field. In this case the spectra as well as the relaxation times for the librational motion are very similar to the corresponding bulk 5CB situation.

In the case of 5CB dispersed with hydrophilic aerosils we found a systematic decrease of the relaxation times for the rotation of the molecules around the short axis with increasing aerosil concentration (see Fig. 6). This can be understood as the result of increasing disorder with aerosil concentration, resulting in an increased number of (small) nematic domains with deviating director orientation, macroscopically resembling a sample in the isotropic phase. This would then result in shorter main relaxation times as observed in Fig. 4 for the isotropic phase of bulk 5CB. On the contrary, for the librational motion, one would expect an opposite effect in the nematic phase induced by increasing disorder. Although less clear, the results in Fig. 6(a) point in this direction.

In the samples with aerosil-dispersed 5CB in the Anopore membranes we see an opposite evolution of the relaxation times with aerosil concentration for the main process of molecular rotation around the short axis. At low aerosil concentrations (e.g., 0.01 g cm^{-3}) we see a process almost as fast as for pure 5CB in Anopore (see Fig. 8). However, with increasing aerosil concentrations the process slows down and evolves in the direction of pure 5CB relaxation times. We believe this is the result of increasing disorder in the aerosil-dispersed 5CB in the pores of the membrane, much like in normal 5CB-aerosil samples: the disorder disturbs the size effect. The reduction of the overall order parameter value with increasing aerosil concentration, as seen in Fig. 9, is in accordance with this interpretation.

B. Aerosil-induced slow process

In the 5CB-aerosil systems also a slow process, about two orders of magnitude slower than the reorientation of the molecules around the short axis, is observed (see Fig. 5). This phenomenon, which increases with increasing aerosil concentration, has also been observed in other cyanobiphenyl systems [8,13,14]. This is generally interpreted as the result of restricted rotation in the aerosil surface layers. The cause could be the preference of the cyanogroup that is at one end of the elongated nCB molecules to form a hydrogen bond with the silanol groups present at the surface of the hydrophilic aerosil particles [8,13]. As already pointed out in the Introduction some other mechanism could be considered. In the liquid-crystalline phases defect mobility could be a possibility. However, the fact that the process is present with almost equal strength in the isotropic phase [see Fig. 6(c)] in our opinion rules out this possibility. Another possibility could be ion mobility, in which case one assumes that ions can travel along the interconnected aerosil network at a slow rate with a wide distribution of relaxation times due to the many hops they would have to make through many sites. Although this cannot be ruled out completely, we think this is, however, a rather unlikely process. One can expect this process to be stronger with the availability of many ions and thus in one way or another scale with the dc conductivity. However, the strength of the process increases with increasing aerosil concentration, but the dc conductivity decreases (see Fig. 5). In view of the fact that there is substantial hydrogen bonding between the OH groups at the strands and 5CB molecules, it is not clear where one could locate the hopping sites on the aerosil strands. Moreover, the observation at much lower frequency of a Maxwell-Wagner type of relaxation seems to set a much lower upper limit for ion mobility in the samples.

In aerosil-dispersed 5CB in Anopore membranes samples we also observe (Figs. 7 and 8) the same slow process as in the 5CB-aerosil samples outside the pores. The strength of it also increases with aerosil concentration, and it must have the same origin in both cases, as its features do not differ significantly between the two types of samples.

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