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The molecular dynamics of nematic liquid crystal confined in porous membranes treated by different surfactants

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ABSTRACT

The molecular dynamics of the well-known nematic liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl geometrically restricted in Anopore and Synpor porous membranes with various pore structure and treated by different surfactants (namely decanoic acid and lecithin) is compared. In the Anopore membrane the chosen surfactants induce the homeotropic orientation of the molecules on the walls of the cylindrical pores and observed corresponding relaxation processes (librational modes) are practically the same. The dielectric measurements of lecithin treated Synpor membranes reveals the reorientation of the molecules from planar to homeotropic on the complex multilayer structure present in their volume. The dielectric strengths of the observed two molecular processes (δ-process and librational mode) are inversed in the ratio compared to the untreated membranes. The observed differences in molecular dynamics results from the orientation of the liquid crystal molecules in untreated and treated membranes and the structure of the membranes themselves.

Introduction

The molecular and collective relaxation processes present in the liquid crystal (LC) mesophases confined in different porous materials and dispersed with nanoparticles are modified as results of surface interactions, finite-size effects or randomness effects [1]. The studies of the confinement effects on the different LC mesophases have been performed in porous filters [2–9], polymer matrices [10,11], various types of porous glasses [12,13], and in silica gels and aerosil nanoparticles [14–16]. The structure of the porous membranes can change from the well-oriented and well-defined cylindrical channels (e.g., aluminum oxide Anopore membranes) to the randomly distributed and interconnected porous voids (e.g., Synpor membranes) [2,5]. Especially, the cylindrical geometry of the Anopore membranes has produced a wide range of interesting studies ranging from determination of possible LC structures, effects on phase transition or wetting phenomena [17]. Moreover, the surfaces of the aerosil nanoparticles can be modified on this way that the particles stay hydrophilic or hydrophobic one [16]. Furthermore, the interesting LC systems with nano- and microparticles find in the last years the grate interest from the scientific and application point of view [18].

The surface effects alter the physical behavior not only the nematic LC (NLC) phases with one-dimensional orientational order but also the more complex LC phases such as cholesterics with long-range orientational evolution of the local nematic director or smectics with translational order [19]. Such studies are particularly important for LCs because their weak orientational and translational order is considerably influenced by the presence of surfaces [20]. A long-standing problem of significant scientific and technological importance is to improve the understanding of the geometry-dynamics correlations in porous materials.

The surface and confinement effects in various LC mesophases have been investigated in different porous systems and nanocomposites by a variety of techniques. The electron spin resonance (ESR) method has provided valuable information about variations in the spin probe order and dynamics with the temperature changes and the aerosil nanoparticles concentration [21]. The dynamic light scattering (DLS) technique enables to study the influence of boundary conditions and layer thickness of confined LC to cylindrical pores on phase transitions and relaxation of director orientational fluctuations [22]. The small angle neutron scattering (SANS) [23], X-ray scattering (XS) [24,25], and high resolution ac calorimetry (AC) [26,27] are convenient tools to investigate the influence of the size, the roughness, and the chemical composition of the pores on the modification of the structure and phase transitions in confined LCs. For example, a crossover between first and second order phase transition character for dodecylcyanobiphenyl (12CB) embedded in

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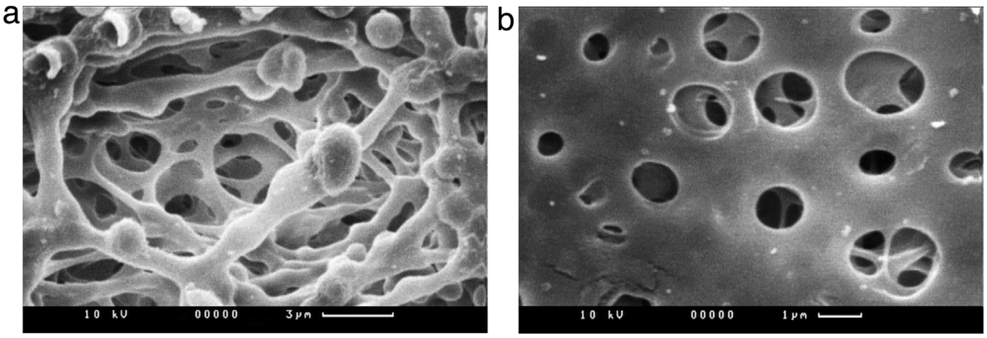

Fig. 1. The SEM photographs of the Synpor membrane with 0.60 µm pores: a) the upper membrane surface (magnification 10^4), b) the bottom membrane surface (magnification $6{\cdot}10^3$).

controlled-pore glasses with decreasing the pore radii was shown [26]. The optical methods allow to study the LCs orientation on the interface, the azimuthal and zenithal anchoring energies, the textures and topological defects, etc. [28].

Moreover, the deuteron nuclear magnetic resonance spectroscopy (DNMR) investigation of the deposited 5CB molecules on the inner cylindrical surfaces of Anopore membranes by the solvent-evaporation technique revealed the existence of the two different configurations of 5CB molecules: a bulklike one with parallel axial arrangement, and a surface one with planar radial arrangement dependent [29]. However, if the pores are primary treated with a lecithin there seems to be no indication for the presence of the molecular layer [30]. The existence of surface-induced discrete smectic order in the isotropic phase was shown for 12CB confined to Anopore membranes. A quantized smectic growth is induced by the pore surface when treated with an aliphatic acid of varying chain length. Nevertheless, the evolution of surface-induced smectic order in LC that have a nematic phase or in untreated or lecithin treated pores was not observed [31]. In other alkylcyanobiphenyl LCs new effects in confinement concerning specific-heat amplitudes, transition temperature shifts, broadening and rounding of phase transition were found [32]. The possibility of driving the weakly first-order SmA–N phase transition to second-order for 9OCB confined in Anopore membranes has been demonstrated [33].

The broadband dielectric spectroscopy (BDS) represents a particularly convenient tool for study the molecular and collective relaxation processes in LCs [34,35]. It covers a wide range of frequencies from mHz to GHz. In the GHz range LCs exhibit high frequency molecular processes corresponding to the rotation of the molecules around their short and long molecular axis [1]. In ferroelectric LCs specific modes in the range less than 1 MHz can be observed: the Goldstone mode and the soft mode [36]. In the low frequency range (hundreds of Hz) the effects connected with conductivity and the electrode polarisation dominate. Confinement can influence the dielectric strengths, relaxation times and shapes of relaxation processes as a sensor of interactions with the structure of the porous material [1,16].

In this study the BDS was applied to investigate the influence of the different surfactants on the dynamics of the molecular processes in confined NLC. The modification of the surfaces of the porous membranes by different surfactants induce the specific orientation of the NLC molecules on the surface of the pores. In these conditions the dynamics of the different relaxation modes can be investigated and some conclusions related to the structure of the porous membranes can be drawn.

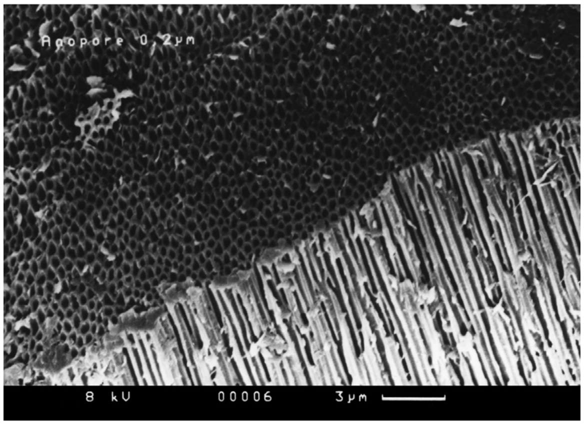

Fig. 2. The SEM photograph of the Anopore membrane with 0.2 µm cylindrical pores.

Experiment

The well-known nematic liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl (NLC 5CB) (Sigma-Aldrich Chemie GmbH) was used without any prior additional purification to investigate the molecular dynamics in confinement. The 5CB molecule is characterized by rather strong dipole moment (about 4D) related with the cyano group oriented nearly parallel to the long molecular axis. The molecules form dimers whose length reaches 25 Å while the lengths individual molecules are 18.7 Å. The nematic phase appear in the temperature range from 308 K to 295 K and can be easy supercooled up to 270 K.

Two kind of porous membranes were used to probe the influence of the surface treatment by different surfactants on the orientation and dynamics of the embedded NLC 5CB. The Synpor (Pragopor) membrane filters (Pragochema) are composed of pure cellulose nitrate films with interconnected pores and mean membrane thickness of about 80–120 µm. Figure 1 shows the scanning electron microscope (SEM) photographs of the Synpor membrane with 0.60 µm pores. The SEM reveals a very regular and uniform voids structure with broken up walls. The different filters are characterized by well-defined pore sizes which range from 0.23 to 0.85 µm and porosity which range from 60 % to 80 % [37]. The Synpor membranes are not hygroscopic and thermally stable even up to 473 K in an oxygen-free atmosphere.

The Anopore membranes (Whatman International Ltd) with honey-comb structure are composed of aluminum oxide film with cylindrical pores penetrating normally through its 60 μm thickness. The cylindrical channels of the Anopore membranes have a nominal diameter 0.02 μm, 0.1 μm and 0.2 μm with porosity which range from 25 % to 50 % [38]. Figure 2 shows the SEM photograph of the Anopore membrane with regular honey-comb structure of parallel and separated pores. In the untreated Anopore and Synpor porous membranes the 5CB molecules have tendency to orient homogeneously (planarly) on the walls of the channels or surfaces distributed inside the porous filters [2,5]. The inner surfaces of the porous membranes can be modified by different surfactants to achieve the homeotropic orientation of the molecules on the walls [39]. In the present experiment two different surfactants were used – the 1,2-dimyristoyl-sn-glycero-3-phosphatidylcholine (lecithin) and 1-nonanecarboxylic acid (decanoic acid). On the basis of the conclusion in Ref. 40 besides the lecithin the decanoic acid which contains a nine-carbon alkyl chain linked to a carboxylic group ($CH_3(CH_2)_8COOH$) was chosen to enforce homeotropic orientation of the 5CB molecules on the inner surfaces of the cylindrical channels of the Anopore membrane.

The empty Anopore membranes before filling with LC were annealed some hours in temperature of about 383 K in custom-made vacuum system to remove adsorbed water and other impurities. However, the Synpor membranes were annealed at a temperature lower than the Anopore using a Kofler hot-bench. The inner surfaces of porous membranes were also covered by different surfactants. The Anopore membranes were treated by temporary dipping in a 2 wt% solution of decanoic acid in spectral grade methanol and in a 1.5 wt% solution of lecithin in spectral grade ethanol. The thermal stability of the lecithin is about 473 K. However, the Synpor membranes were treated only with previously mentioned lecithin solution. The membranes were then heated at about 353 K and evacuated at about 80 Pa to remove the remaining solvents.

For the dielectric experiments, they were cut in the form of 5 mm diameter disks and filled with the mesogenic material in its isotropic phase by means of capillary forces. The excess of liquid crystal material from the outer surfaces was carefully removed by pressing the samples between the filter paper. Then, the filters were sandwiched between the gold-plated capacitor electrodes of the dielectric spectrometer.

To analyze the influence of the surface treatment and structure of the porous membranes on the dynamics of the molecular processes in NLC 5CB the dielectric spectroscopy in the frequency range from 10^7 to 10^9 Hz was applied. The HP 4191A impedance analyzer with custom-made cryos, which allows to adjust temperature between 280 K and 350 K by means of the nitrogen gas jet and temperature stability better than 0.5 K, was used.

The dielectric spectra were analyzed using superposition of the two Havriliak-Negami formula [41] and the conductivity contribution in the form:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \sum_{j=1}^{n} \frac{\Delta\varepsilon_j}{(1+(i\omega\tau_j)^{\alpha_j})^{\beta_j}} - i\frac{\sigma_0}{\varepsilon_0\omega^k}, \qquad (1)$$

where parameters α_j and β_j describe the broadening and asymmetry of the j-th relaxation process, respectively, $\Delta\varepsilon_j$ is the dielectric relaxation strengths, τ_j is the relaxation times, ε_∞ and ε_0 are the high frequency limit of the permittivity and the vacuum permittivity, respectively, σ_0 is the conductivity parameter, k is the fitting parameter, and $i = \sqrt{-1}$. Moreover, the all dielectric spectra were evaluated and analyzed using commercially available Novocontrol WinFit and Microcal Origin software. Additionally, the dielectric data were also analyzed using a self-written analysis software.

Table 1
Fitting parameters of the relaxation processes shown in Fig. 3.

Fitting parameters	Bulk 5CB	5CB in Anopore		
		untreated	decanoic acid treated	lecithin treated
$\Delta\varepsilon_1$	8.6	1.88	–	–
$\tau_1 \cdot 10^{-8}$ [s]	2.4	1.66	–	–
α_1	1	1	–	–
β_1	0.9	0.74	–	–
$\Delta\varepsilon_2$	0.92	–	1.06	1.07
$\tau_2 \cdot 10^{-9}$ [s]	1.93	–	3.8	2.8
α_2	1	–	0.78	0.77
β_2	0.68	–	0.77	0.88

Results and discussion

Figure 3 shows frequency dependence of the permittivity and the dielectric loss for 5CB bulk, 5CB confined in untreated and lecithin and decanoic acid treated Anopore membrane, and empty Anopore membrane. For better resolution, the data for 5CB bulk and in confinement are presented in different scales. The permittivity of empty Anopore membrane is practically frequency independent and takes the value of about 2.4 [Fig. 3a)], see the right-side axis of the graph). The permittivity of 5CB bulk and embedded in untreated and surfactants treated membrane indicate the presence of some relaxation processes. The 5CB permittivities measured in treated membranes by different surfactants only slightly differs each other in the value. Moreover, the permittivities measured in confinement are about three to four times smaller compared to the bulk. The anomalies visible especially in the high frequency border are related with the limitation of the BDS spectrometer in this range of frequency. The solid lines in Fig. 3 presents the best fitting of the Havriliak-Negami formula given by the Eq. (1) to the experimental points. The fitting parameters are collected in Table 1.

The frequency dependence of dielectric loss [Fig. 3b)] indicates the characteristic future. The empty Anopore membrane dielectric losses are very low and do not indicate any relaxation process in measured frequency range. In the isotropic phase of 5CB one relaxation process is observed due to the random reorientation of the molecules around the short molecular axis. However, in the nematic phase of bulk 5CB the two relaxation processes appear: the low frequency process assigned to the rotation of the molecule around the short molecular axis (δ-process) and the high frequency process related with libration of the long molecular axis around the direction of the director (librational mode).

In the untreated cylindrical pores of Anopore membrane only δ-process is observed. This behavior results from the perfect orientation of the long axes of the molecules parallel to the surfaces of the pores (axial orientation). In this geometry of the experiment only one relaxation process can be observed because the measuring electric field is parallel to both the pores axis and the long axis of the molecule. After treatment of the surfaces of the pores by lecithin or decanoic acid the situation is very different [2,42,43]. The lecithin forms the brush-like layers on the inner pore surfaces with the long alkyl chains pointing out of the surfaces. The nematic molecules fall into the gaps between the alkyl chains and orient homeotropically on the surface of the pores. As a result of the elastic forces, this orientation is transformed into the entire sample [44,45]. Moreover, the study of the aliphatic chain length effect of the aliphatic acid ($C_nH_{2n+1}COOH$) on the anchoring direction and orientational order at the surface of the cylindrical pores of the Anopore membrane shows that for $n \geq 7$ the homeotropic orientation is preferred but for $n \leq 6$ the planar orientation can be achieved [40]. In another words, the lecithin and decanoic acid molecules attached themselves in to the walls of the channels and induced homeotropic orientation of the 5CB molecules on the walls (radial orientation).

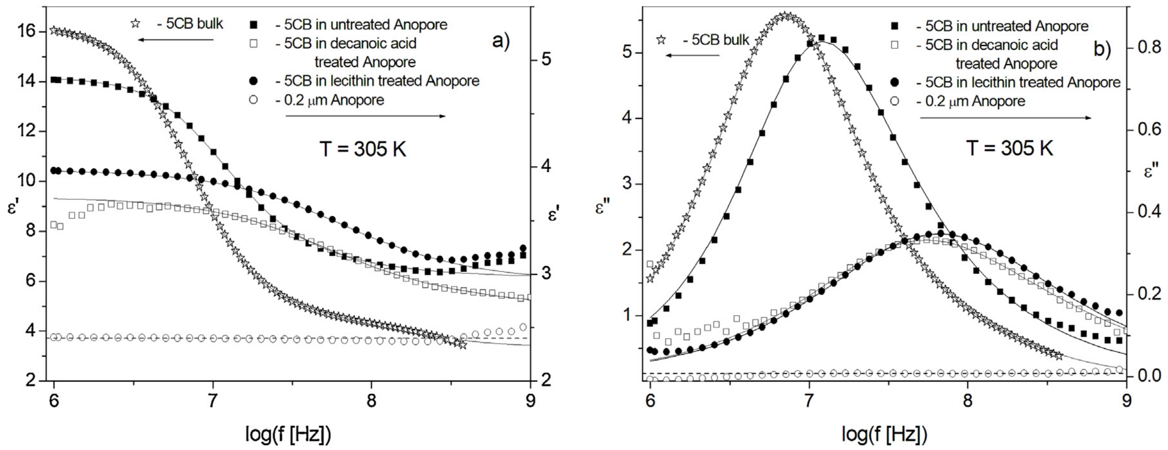

Fig. 3. Frequency dependence of the permittivity a) and the dielectric loss b) of the 5CB bulk, 5CB in untreated Anopore, 5CB confined in decanoic acid and lecithin treated Anopore and empty Anopore membrane. Please note, that the graphs for the 5CB bulk and in confinement are presented in different scales.

In this condition only the librational mode is active which is indicated in Fig. 3b) as a shift of the relaxation process to the higher frequencies. The separation of the δ-process and librational mode is also possible by proper orientation of the molecules in measuring cells and by applying magnetic field.

The presented measurements reveal that the used surfactants induce identical orientation of the molecules in the pores walls and show for the first time that the observed corresponding relaxation processes are practically the same - only a slight shift in the maximum frequency is observed. The solid lines present in the Fig. 3b) are fitted using Eq. (1). The fitting parameters are also presented in the Table 1. The relaxation time of the δ-process in untreated Anopore is slightly shifted to the lower values and more asymmetric compared to the bulk. However, the librational modes observed in the treated Anopore are broadened, asymmetric and slightly shifted to the higher values of the relaxation time compared to the bulk 5CB. The permittivity and the dielectric loss of the empty Anopore membrane shown in Fig. 3 were fitted by means of the linear function.

Figure 4 presents frequency dependence of the permittivity and the dielectric loss of 5CB bulk, 5CB confined in untreated and lecithin treated Synpor membranes, and empty Synpor membrane. The frequency dependence of the permittivity [Fig. 4a)] indicate presence of the two relaxation processes. The permittivity of the empty Synpor membrane is frequency independent and assumes the value of about 1.83. The values of the permittivities measured in confinement in the frequency of 10^6 Hz are much smaller compared to the bulk. The solid lines shown in the Fig. 4a) represent the best fit of Havriliak-Negami formula [Eq. (1) to the experimental data. The fitting parameters are summarized in Table 2. The permittivity and the dielectric loss of the empty Synpor membrane shown in Fig. 4 were also fitted by use of the linear function.

However, the frequency dependence of the dielectric loss of 5CB exhibit interesting behavior depending on whether it is placed in untreated or lecithin treated Synpor membrane [Fig. 4b)]. In untreated membrane the dielectric loss of the high frequency process is much higher than the low frequency one which suggest that the molecules are preferentially oriented perpendicular to the measuring electric field and anchored parallel to the inner walls of the membrane. It is advised that the inner structure of the membrane consists of the complex system of parallel and perforated surfaces distributed inside the membrane. It seems that this assumption supports SEM photographs of the membrane shown in Fig. 1. Moreover, in the lecithin treated membrane the dielectric losses related to the δ-process are more pronounced which suggests that the molecules are now preferentially oriented perpendicular to the inner surfaces of the membrane and parallel to the measuring field direction. These new results for the lecithin treated Synpor membranes are described and explained in more detail below.

Figure 5 shows the frequency dependence of the normalized dielectric loss for the 5CB confined in untreated and lecithin treated Synpor membranes with different pore diameters. The striking difference between frequency dependence of the normalized dielectric loss for untreated and treated systems is undeniable. In the 5CB-untreated Synpor system the librational mode dominates in the dielectric loss spectrum with the non-negligible contribution related to the δ-process. The dielectric strength of the librational mode is greater than dielectric strength of the δ-process. However, in the 5CB-treated Synpor system the δ-process dominates and depends slightly on the diameter of the pores. With decreasing the pore diameters, the librational mode is less pronounced in the spectrum. In the lecithin treated Synpor membranes the dielectric strengths of the both observed relaxation processes are reversed comparable to the untreated membranes. A very likely explanation of the observed behavior may be as follows. The surfactant induces the homeotropic orientation of the 5CB molecules on the inner surfaces distributed in the membrane and on average the most molecular long axis stays parallel to the measuring electric field. This results in greater dielectric strength of the δ-process. Moreover, the obtained results allow to formulate the conclusions regarding the membrane structure. The Synpor membrane consists of the complex structure of the parallel surfaces more or less distributed in its volume. The parallel surfaces are perforated by holes and interconnected by supporting strands and filaments (see Fig. 1). From the small angle X-ray scattering experiment done using a Siemens two-dimensional detector HI-STAR with CuKα radiation of a wavelength of 0.154 nm and a resolution of 0.03° it is known that the spatial structure of the Synpor membrane is not entirely isotropic and a kind of preferred axis for orientation of the LC exists inside the porous matrix [46]. Moreover, the previously performed analysis of the dielectric data for the Synpor-5CB system based on the effective medium approximation also suggests the presence of some kind of layered structure in the Synpor-5CB composite [47].

The fitting parameters of the solid lines presented in Fig. 5 are also summarized in Table 2. The relaxation times of the δ-process and librational mode shows comparable tendency as for Anopore confinement namely the relaxation time of the δ-process is lower but the librational mode is higher comparable to the bulk. The observed changes in the relaxation times can be related to the dependence of the liquid crystal order parameter on the temperature and geometric constraints. The broadening and asymmetry parameters of the δ-process observed for the 5CB in untreated and

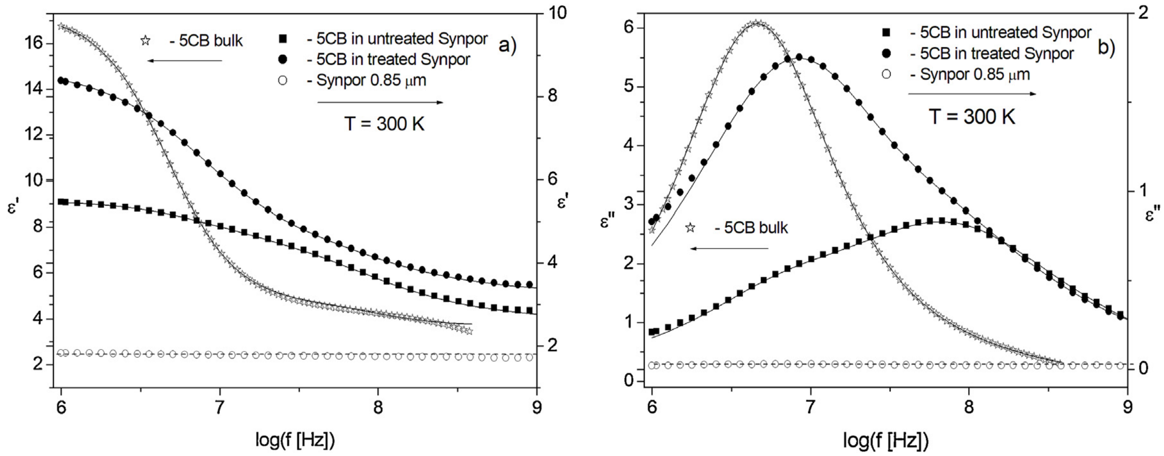

Fig. 4. Frequency dependence of the permittivity a) and the dielectric loss b) for the 5CB bulk, 5CB in untreated Synpor, 5CB confined in lecithin treated Synpor and empty Synpor membrane. Please note, that the graphs for the 5CB bulk and in confinement are presented in different scales.

Table 2
Fitting parameters of the relaxation processes shown in Figs. 4 and 5.

Fitting parameters	Bulk 5CB	5CB in untreated Synpor [μm]				5CB in lecithin treated Synpor [μm]			
		0.23	0.40	0.60	0.85	0.23	0.40	0.60	0.85
$\Delta\varepsilon_1$	12.08	1.65	0.90	0.79	0.69	5.23	4.45	4.22	4.43
$\tau_1 \cdot 10^{-8}$ [s]	3.48	3.17	2.12	2.08	2.44	2.67	2.39	2.34	2.04
α_1	1	0.9	0.84	0.86	0.9	0.79	0.85	0.8	1
β_1	1	0.4	1	1	1	1	1	1	1
$\Delta\varepsilon_2$	0.79	1.34	2.1	2.04	2.21	4.5	1	0.9	1.1
$\tau_2 \cdot 10^{-9}$ [s]	1.84	2.15	2.74	2.39	2.28	2.53	3.83	2.36	2.29
α_2	0.75	0.9	0.87	0.85	0.79	0.39	1	0.65	1
β_2	1	0.79	0.67	0.75	0.9	0.1	0.2	0.3	0.5
$\Delta\varepsilon_1/\Delta\varepsilon_2$	15.3	1.2	0.4	0.4	0.3	1.1	4.5	4.7	4

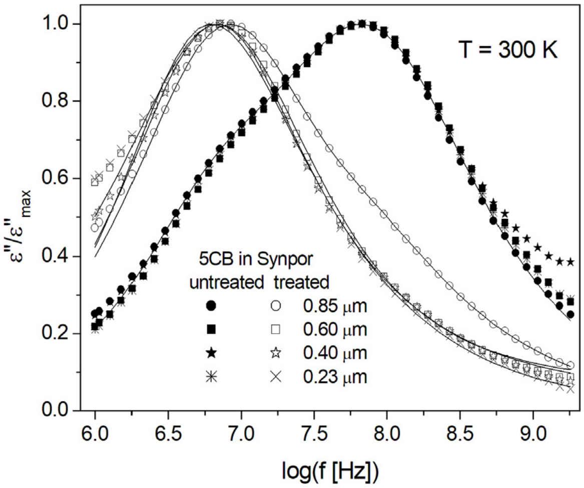

Fig. 5. The frequency dependence of the normalized dielectric loss for the 5CB confined in untreated (solid symbols) and lecithin treated (open symbols) Synpor membranes with different pore diameters.

treated membranes practically do not change with diameter of the pores in comparison to the bulk (Debye or Cole-Cole type). Surprisingly, the values of the fitting parameters for the librational mod suggest that the relaxation process in confinement is less broadened but more asymmetric in comparison to the bulk. The ratio $\Delta\varepsilon_1/\Delta\varepsilon_2$ of the dielectric strengths of the δ-process and librational mode clearly shows that in untreated Synpor membranes the librational mode dominates but in lecithin treated Synpor membranes the δ-process is more pronounced. The changes of $\Delta\varepsilon_1/\Delta\varepsilon_2$ ratio reflects the changes in the orientation of the liquid crystal molecules inside the structure of the Synpor membrane caused by the surface interactions modified by the surfactant molecules.

Conclusions

In the untreated Anopore membranes only one relaxation process is observed which reflects the structure of the membrane and geometry of the experiment. In this case the 5CB molecules orients parallel to the axes of the cylindrical pores and parallel to the measuring electric field direction (axial orientation). However, in treated membranes both with lecithin and decanoic acid the orientation of the molecules changes on the homeotropic and relaxation process related with libration of the molecules around direction of the director stay active (radial orientation). In this condition the separation of these two relaxations processes is possible. The drawing an unambiguous conclusion on the influence of the surfactant type on the dynamics of the relaxation processes is too premature in this case and requires further investigations.

In the untreated Synpor membranes two relaxation processes are observed with inverted dielectric strength compared to the bulk sample. These results suggest that the inner structure of the membrane consists of the more or less parallel planes with the LC molecules oriented planarly. However, after lecithin treatment of the membranes the dielectric strength of these two relaxation processes becomes again reversed compared to the untreated membrane. The reason of this behavior lies in the homeotropic orientation of the 5CB molecules on the membrane inner layered structure as a result of surfactant. The conclusions regarding the structure of the membrane drawn on the basis of the molecular dynamics studies are supported by the SEM photographs of the membrane structure, small angle X-ray scattering experiment and the effective medium approximation analysis.

Ethical statement

Not applicable.

Funding body

Not applicable.

Declaration of Competing Interest

Not applicable.

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