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Structure and dynamics of ferroelectric liquid crystals under random geometrical restrictions

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The dynamics of ferroelectric liquid crystals confined in porous nitro-cellulose membrane (Synpor) are investigated by broadband dielectric spectroscopy, and a characterization of the mesomorphism is achieved by DSC and X-ray scattering. The complex inner membrane structure of random interconnected voids can be treated as a frozen random defect disorder in the mesophases. Its influence on the molecular dynamics of the confined mesogens is negligible. However, Goldstone and soft modes of DOBAMBC (2-methylbutyl 4-(4-decyloxybenzylideneamino)cinnamate) are suppressed by the confinement and not detected dielectrically. In the short pitch and high spontaneous polarization material C7, 4-(3-methyl-2-chloropentanoyloxy)-4'-heptyloxybiphenyl, confinement has a minor influence on the soft mode, and the Goldstone mode is clearly present, although with reduced strength, broadened with respect to the bulk, and shifted to higher frequencies by more than one decade. The results are interpreted as effects of random confinement on the length scale of the helical pitch.

1. Introduction

Ferroelectric liquid crystals in restricted geometry represent an area of growing interest. The spatial confinement considerably influences the thermodynamic, optical and electro-optical properties of ferroelectric mesophases. The phase transition temperatures as well as the character of phase transitions can also be affected by geometrical restrictions [1]. Moreover, the helical superstructure in the SmC* phase can be strongly influenced and distorted due to surface interactions and can be unwound at a certain critical thickness [2]. The fast switching and promising application in ferroelectric liquid crystal (FLC) displays attracts attention to the understanding of physical mechanisms of surface-induced ordering and geometrical confinement on FLCs. The orientational order of mesophases can be stabilized, e.g. by polymer networks in the sample [3], or LCs can be encapsulated in polymers during phase separation processes [4]. In such composite systems, surface interactions and characteristic sizes and shapes of the confining structures become important.

Adsorption of LCs in a porous matrix represents an alternative method of preparation of composite systems. During recent years, various adsorber materials have been studied to probe the influences of surface interaction, shape and finite-size effects on LC mesophases: Anopore and Nuclepore membranes with submicrometer sized regular, well separated cylindrical pores [5]; Millipore and Synpor filters with a complex inner structure of interconnected voids [1, 6]; porous glasses with narrow pore size distributions, but random orientation of cavities [7]; silica aerogels with irregularly shaped cavities and a broad size distribution [8].

For the study of confinement effects on LCs, various experimental methods have been applied, such as photon correlation spectroscopy [9], AC calorimetry [10], NMR spectroscopy [5] and dielectric spectroscopy [6–8, 11–13]. Dielectric spectroscopy covers a broad range of frequencies from mHz to GHz, and represents a convenient tool for the study of molecular and collective relaxation processes. Confinement can influence dielectric relaxation strengths, relaxation times and shapes of relaxation processes which act as sensors of interactions with the structure of the porous material.

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The chiral molecules in the FLC phase form a helical structure which is very sensitive to the influence of external electric fields, as well as to surface induced effects. In samples of sufficient thickness, d.c. electric fields can deform and unwind the helix, an effect of the linear coupling between the electric field and the spontaneous polarization of the smectic material [14, 15]. A low frequency a.c. electric field can cause comparable effects to those of a d.c. electric field, but the quadratic effects connected with the induced polarization dominate with increasing frequency and several new phenomena can be observed [16]. The strong influence of surface induced order on the helical structure has been reported before; with decrease in sample thickness, an increase in the helical pitch was observed [17, 18]. For a certain critical thickness of the sample, the helix can be unwound [2] and the surface stabilized ferroelectric liquid crystal cell is formed, which plays an important role in display technology.

The dynamics of such FLCs is closely related to molecular motions and reorientation of collective assemblies of molecules. In the MHz range, the FLC exhibits two high frequency molecular processes corresponding to the rotation of the molecules around the short and the long molecular axes, and two other specific modes are found in the range below 1 MHz: the Goldstone and soft modes. The Goldstone mode is attributed to fluctuations of the azimuthal angle, describing the orientation of the tilt plane of the molecules. This mode exists only in the low temperature, ordered phase (SmC*). The soft mode is attributed to the fluctuation of the amplitude of the tilt angle of the molecules with respect to the normal to the smectic layers. The amplitude mode exists in both the ferroelectric and paraelectric phases (SmC* and SmA); in the SmA phase it is conventionally referred to as soft mode. In FLCs with high spontaneous polarization \mathbf{P}_s , the structural parameters can be influenced by \mathbf{P}_s under certain conditions (a new domain structure with different periodicity in the bulk and at the surface has been proposed) [19–21]. In the dielectric spectrum, characteristic relaxation processes connected with the formation of these two domain structures have been described. The influence of one-dimensional spatial confinement on dielectric processes in FLCs has been studied both theoretically and experimentally [22], and significant influences on the dielectric strength and relaxation rates of collective dynamic processes have been reported for surface stabilized FLC sandwich cells of a few micrometers in thickness.

In preceding dielectric studies [6, 7, 23], it has been shown that other confining geometries can also substantially influence dynamic processes in FLCs. Apart from specific interactions of the molecules with the surface of the adsorber material which influence orientational

order and molecular dynamics in some boundary layers and impose boundary conditions on the director field, the length scales and geometrical shape of the cavities are of crucial importance. Roughly one can distinguish between microporous adsorbers with pore sizes on the nanometer scale where phase transitions of the confined material are altered and the character of confined mesophases is influenced, and macroporous adsorbers with characteristic cavity sizes from about 0.1 μm to several micrometers where the thermodynamics of the confined mesophases is practically unchanged with respect to the bulk. In this study, we will focus on the analysis of such macroporous confinement effects. It can be assumed (and will be confirmed in the experiments below) that the adsorber does not influence the molecular orientational order parameter and dynamics in the pores, irrespective of possible effects in boundary layers of the confined mesogen. However, the adsorber has a global influence on the director configuration and layer arrangement, and consequently on collective dynamic processes and electro-optic properties. In ferroelectric smectic materials, the helical pitch provides some natural length scale for the estimation of the effectiveness of boundary effects on the orientational configuration and collective dynamic processes of the material. Pitch lengths of materials investigated in previous studies [6, 7, 23] ranged between 1 and 3 μm . The diameter of the membrane pores used in these experiments was 0.2 μm for inorganic Anopore filters, and somewhat larger for Synpor cellulose membranes. The investigation of the dielectric relaxation of the standard FLC material DOBAMBC confined by these Synpor membranes revealed the complete disappearance of collective dynamic processes [6]. In these experiments, the mesomorphism itself was not studied, so the reason for the unexpected dynamic behaviour remained unclear. Although it seems unlikely that the smectic mesomorphism itself is affected by the random character of the confining cavities on length scales of micrometers, we note that a sensitive influence of frozen random disorder on smectic layer arrangement has been predicted theoretically [24] and cannot be excluded *a priori*.

It has been shown in previous experiments that in the Anopore membrane filters, the disappearance of the Goldstone mode in the dielectric spectra is not related to an absence of the corresponding collective dynamic modes of the mesogen [7]. In these composite systems, the experimental geometry chosen (filter plates in-plane with the electrodes), in connection with the perfect orientation of smectic layers in the cylindrical pores with the helical axis parallel to the pore axes, prohibits direct dielectric observation. Because the measuring electric field is also parallel to the channels, the Goldstone and soft modes are dielectrically inactive in this geometry. However, with a special preparation technique it was

shown that a Goldstone mode is present, and is shifted to lower frequencies compared with bulk samples [7]. It should be noted that this geometrical explanation does not hold for the interpretation of experiments in cellulose membranes with random pore orientations [6].

In order to understand the physical mechanisms leading to the reduced dynamic behaviour of smectic mesogens in random porous material, the potential effects of confinement have to be evaluated and analysed in the experiment. It has to be established whether the mesomorphism is preserved, whether the smectic layer structure and, in particular, the different smectic modifications are formed in the random cavities, and which other effects can be responsible for the suppression of collective dynamic modes of the mesogen. The strategy of this paper is to exploit differential scanning calorimetry (DSC) to reveal the phase transitions of the confined material, and to analyse the smectic polymorphism by means of X-ray small angle scattering experiments. After establishment of the mesomorphism of the confined smectogen, we discuss the role of geometric restrictions on the formation of the helical structure and the influences of the ratio of helical twist to pore dimensions. We test our assumptions with a short pitch material (C7) with a high spontaneous polarization and compare the results obtained for this compound with those from the experiments with DOBAMBC.

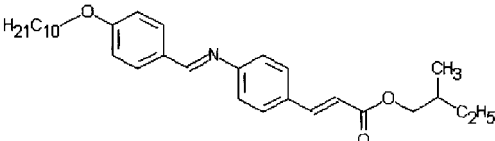
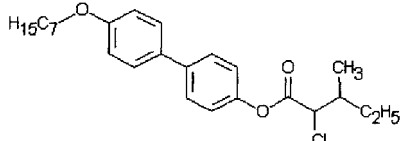
2. Experimental

Since we consider the effects studied in this paper to be general for the ferroelectric smectic C^* phase independent of the specific chemical composition of the

material, two standard ferroelectric liquid crystals have been chosen. DOBAMBC, 2-methylbutyl 4-(4-decyloxybenzylideneamino)cinnamate, is a well characterized chiral mesogenic material; historically it was the first compound known to exhibit a ferroelectric smectic phase [25]. Being a Schiff's base, it is probably not the best choice from the aspect of chemical stability. Phase transition temperatures, conductivities and critical parameters may differ between individual preparations or samples, but on the other hand, the substance is commercially available and many material parameters are available from the literature. The material employed here was obtained from Sigma Aldrich and used without further purification. DOBAMBC is characterized by a comparably large helical pitch (on the pore size scale), ranging from 1.7 to 3 μm [26, 27] and a low spontaneous polarization $P_s = 3.7\text{--}4.75 \text{ nC cm}^{-2}$ [28].

In addition, the mesogen C7 with short pitch p of about 300 nm [29] in the SmC^* phase has been studied. C7 is the heptyloxy homologue of the series of (*S,S*)-4-(3-methyl-2-chloropentanoxy)-4'-alkoxybiphenyls with alkyl chain lengths in the range from 5 to 10 carbons [30]. The value of the helical pitch is important in the context of the discussion of the confinement effects. For C7 it is considerably smaller than for DOBAMBC, and smaller than the pore sizes of the matrices studied here. The material shows a spontaneous polarization P_s ranging from 130 to 290 nC cm^{-2} [29–31] in the temperature region of the SmC^* phase; this is much higher than that of previously investigated materials like DOBAMBC or CE8 [28, 32]. The chemical compositions and mesomorphism of the materials investigated are given in table 1.

Table 1. Chemical structure and mesomorphism of the materials investigated.

	DOBAMBC $P_s = 3.7\text{--}4.75 \text{ nC cm}^{-2}$ $p = 1.7\text{--}3 \mu\text{m}$
2-Methylbutyl 4-(4-decyloxybenzylideneamino)cinnamate $\text{Cr } 347.6 \text{ K} \leftrightarrow (\text{SmI}^* 335 \text{ K} \leftarrow) \text{SmC}^* 367 \text{ K} \leftrightarrow \text{SmA } 390 \text{ K} \leftrightarrow \text{I}$	
	C7 $P_s = 130\text{--}290 \text{ nC cm}^{-2}$ $p \approx 300 \text{ nm}$
4-(3-Methyl-2-chloropentanoxy)-4'-heptyloxybiphenyl $\text{Cr?} \leftrightarrow \text{G}^* 316 \text{ K} \leftrightarrow \text{SmC}^* 328 \text{ K} \leftrightarrow \text{SmA } 335 \text{ K} \leftrightarrow \text{I}$	

As substrate, nitro-cellulose membranes (Synpor) characterized by an interconnected structure of voids with diameters from 0.23 to 0.85 μm (nominal) were chosen. These membranes were obtained from Pragochem. Electron microscopy shows that the structure of the matrix is very complex, consisting of a sponge-like structure with entangled cellulose strands. The actual average dimensions of the pores are higher than the nominal values for the membranes which give the size of the smallest particles that are not able to pass through the membrane (figure 1). The Synpor matrices investigated are dielectrically inactive in the frequency range studied here.

The phase transition temperatures and the character of the phase transitions have been examined using DSC which monitors the heat uptake of samples during a thermocycle and is a powerful technique for the characterization of the phase transitions in LCs confined to porous materials [10, 33]. The DSC measurements were performed using a Perkin Elmer calorimeter DSC 7 in the temperature range 303–403 K at a rate of 2 K min^{-1} and with stabilization of the temperature to about ± 0.1 K. The Synpor membranes were evacuated and annealed at about 393 K for 24 h to remove water and other impurities from the matrix. After this procedure, the filters were filled by capillary action with liquid crystal in the isotropic phase. Finally, about 20 mg of small pieces of the composite material were stacked in the aluminium capsule used for the DSC measurements.

In addition, basic information about the layer structure of the smectic phases in a confined geometry can be obtained from small angle X-ray scattering experiments [33]. Such X-ray measurements were done using a Siemens two-dimensional detector, HI-STAR, with CuK_α radiation of wavelength 0.154 nm and resolution

$\pm 0.03^\circ$. The samples were oriented with the filter sheet plane perpendicular to the X-ray beam which had a diameter of about 0.5 mm. The measurements were performed in the temperature range 323–398 K with a temperature stabilization of about ± 1 K. The random orientation of the smectic layers in the porous matrix yields a powder pattern. The transition between SmA and SmC* phases is characterized by the change in the tilt angle connected with a change in the smectic layer distance. Thus, the SmA to SmC* transition can be identified from the change in the smectic layer reflection at the transition temperature.

Broadband dielectric spectroscopy was applied to investigate the molecular and collective dynamic processes. The dielectric measurements were carried out in the frequency range 10^{-2} – 10^9 Hz to follow molecular as well as collective processes present in the FLC. To cover the broad range of frequency, the Solartron-Schlumberger frequency response analyser FRA 1260, a Novocontrol active sample cell BDC-S and a Hewlett Packard impedance analyser 4191A were used. The superposition of n Havriliak and Negami [34] relaxation functions was applied for a quantitative interpretation of the dielectric spectra, in order to determine the corresponding relaxation time distributions and dielectric strengths of the relaxation processes:

$$\varepsilon''(\omega) = \sigma/(\varepsilon_0 \omega) - \sum_{k=1}^n \text{Im} \{ (\Delta\varepsilon_k) / [1 + (i\omega\tau_k)^{\alpha_k}]^{\gamma_k} \} \quad (1)$$

where the parameters characterizing the k -th relaxation process are the relaxation time τ_k , the relaxation strength $\Delta\varepsilon_k$ and the shape parameters α_k and γ_k which describe broadening and asymmetry of the relaxation time distribution. The first term in equation (1) describes the conductivity contribution to the dielectric spectrum which dominates in the low frequency range where σ is the Ohmic conductivity and ε_0 is the vacuum permittivity.

3. Results and discussion

3.1. Dielectric properties of bulk DOBAMBC

For bulk measurements we have used samples sandwiched directly between the brass electrodes of the capacitor without special surface treatment. Naturally, the samples in the mesophases are not well oriented with respect to the electrode plates, although a preference for a largely normal (homeotropic) orientation at the brass surfaces is found. In the smectic phases, a broad distribution of layer orientations exists with dominating contributions from in-plane layers (layers normal to the electric field). In general, however, all orientations are present in the samples, and we observe dielectric processes which are effective for an electric field orientation along the layer normal, as well as processes characteristic

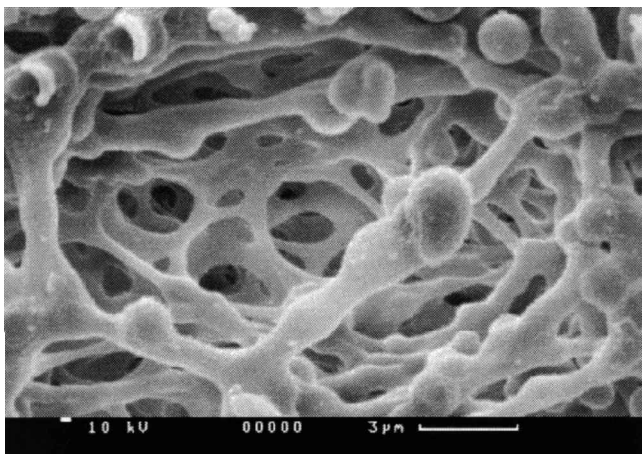


Figure 1. Electron microscope image of an empty 600 nm (nominal size) cellulose membrane. The image size is $20 \times 13 \mu\text{m}^2$.

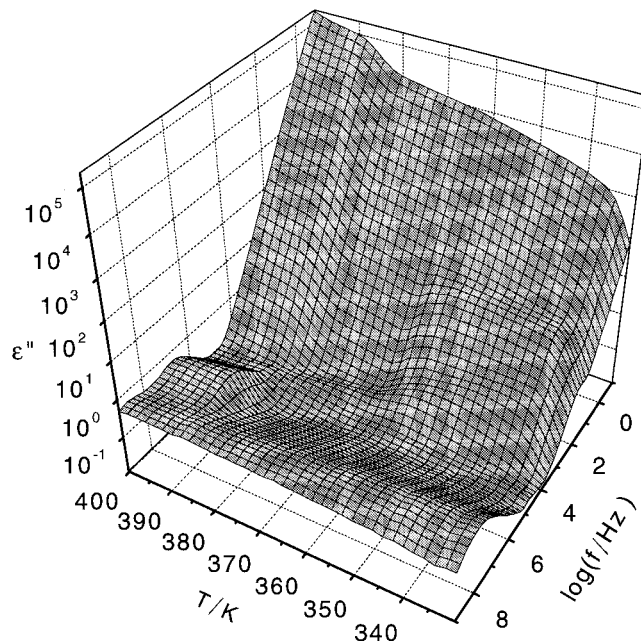
for an electric field in the layer plane. If one is interested in an exact quantitative comparison of dielectric strengths, it is certainly easy to obtain oriented spectra by special surface treatments. Within this study, the bulk spectra serve only as a standard for the identification and proper assignment of the individual processes for which the chosen geometry is sufficient.

Figure 2(a) shows the 3D-plot of the temperature and frequency dependence of dielectric losses for the chiral mesogen DOBAMBC. In the isotropic phase, two relaxation processes are observed: the β -relaxation and the δ -relaxation (figure 3). The thermally activated β -relaxation process was observed in all liquid and liquid crystal phases of DOBAMBC and has not revealed any significant changes at the phase transition temperatures. Its molecular assignment is a fast reorientational motion around the molecular long axis, which changes the effective molecular dipole moment perpendicular to the long axis. The δ -relaxation process reflects a molecular reorientation around the short axis which influences the effective dipole moment along the molecular long axis. It exhibits a discontinuity at the phase transition from the isotropic (I) to the SmA phase (figure 4). The dielectric relaxation strength of the δ -relaxation process is slightly lower than for the β -relaxation process.

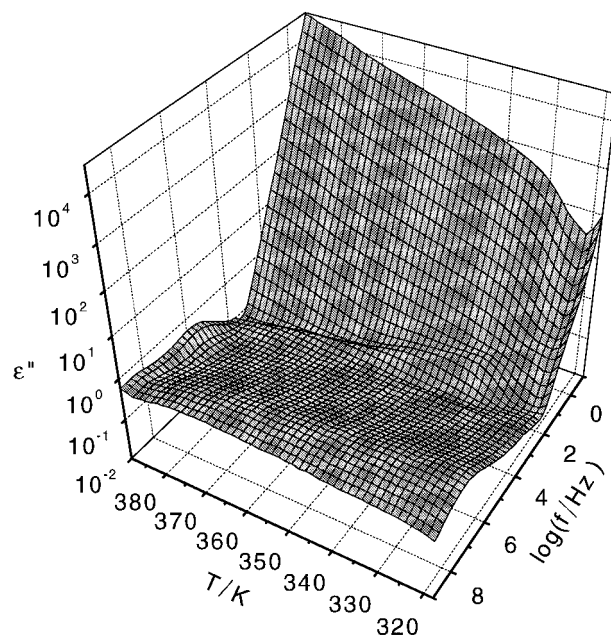
In the SmC* phase, the Goldstone mode dominates, figure 5(a). It reflects the fluctuations of the azimuthal angle of the c -director in the helical structure (phason). The relaxation rate of this process is practically temperature independent. However, the dielectric strength exhibits a characteristic maximum related to the maximum in the helical pitch near the phase transition region. Near the transition from SmA to ferroelectric SmC* the existence of a soft mode is expected, which is connected with the fluctuations of the director tilt with respect to the smectic layers (amplitudon). However, due to the apparently low dielectric strength of this mode (compared with the Goldstone mode) even close to SmC*, this process was not detected in our measurements, and in addition the process is dielectrically not very efficient in the particular sample geometry involved. It is completely covered by other relaxation processes and in the smectic A phase, the molecular δ -relaxation process is dominant. This confirms a preferred homeotropic rather than planar orientation of the mesogen, as discussed above. In the SmC* phase, the intense wing of the GM masks potential soft mode contributions.

3.2. DOBAMBC in Synpor matrices

In the Synpor-DOBAMBC system, the molecular dynamics are practically the same as in the bulk sample, figure 2(b). The dielectric spectra are practically equivalent for all pore sizes, and therefore we present spectra for the 850 nm membranes as representative for the other



(a)



(b)

Figure 2. 3D plot of temperature and frequency dependence of the relaxation losses for (a) the bulk mesogen DOBAMBC and (b) DOBAMBC confined in an 850 nm Synpor membrane.

membranes. The orientational state in the mesophase now reflects a random spherical powder distribution with all directions equivalent (although slight deviations from spherical isotropy are indicated in the X-ray

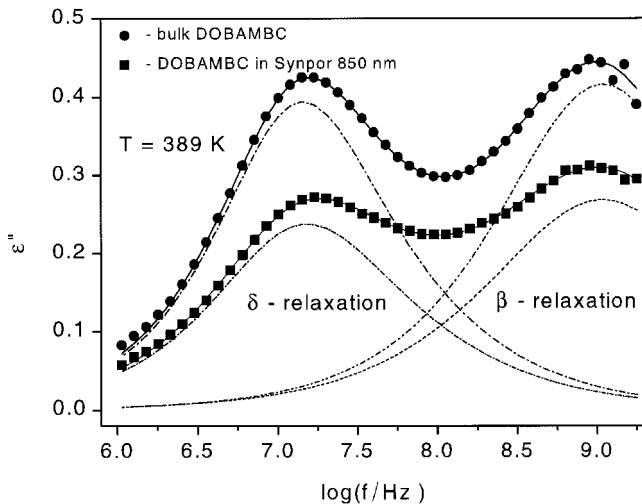


Figure 3. Comparison of relaxation processes in the isotropic phase of DOBAMBC in the bulk and in the Synpor membrane. Two molecular processes are present: β -relaxation and δ -relaxation.

patterns—see below). Comparison of the δ -relaxation processes in bulk and in confinement reveals significant broadening of the molecular process in the restricted geometry, figure 5(b). This may be partially explained by the existence of boundary layers of liquid crystal in the vicinity of the cellulose strands. Another feature is the slight increase in conductivity. This is a consequence of minor amounts of ions present in the membrane material and these are dissolved in the LC during filling. These impurities are responsible not only for an increasing Ohmic conductivity contribution, but presumably also for the slight shift in the phase transition temperatures in the confined LC as discussed in the context of the DSC measurements below. The most striking difference between the bulk and confined samples is the disappearance of the Goldstone mode in the confined mesophase, figure 5(b). No collective processes are present in the spectra of the confined material. On the basis of this observation, we will check the following possible interpretations: (1) Reactions of the smectogen with the network material, dissolution of components of the network in the LC material or physical interactions of the mesogen with the random network of cellulose strands leading to the suppression of liquid crystalline phases. This assumption seems rather unlikely; it can easily be tested by DSC experiments. (2) The introduction of defects in the director and layer structure by the random disorder of the cellulose matrix suppresses the formation of smectic order in the membranes. Such behaviour has been predicted (on a smaller length scale) by Radzihowsky and Toner [24]. This assumption will be probed for our systems on the basis of the X-ray measurements.

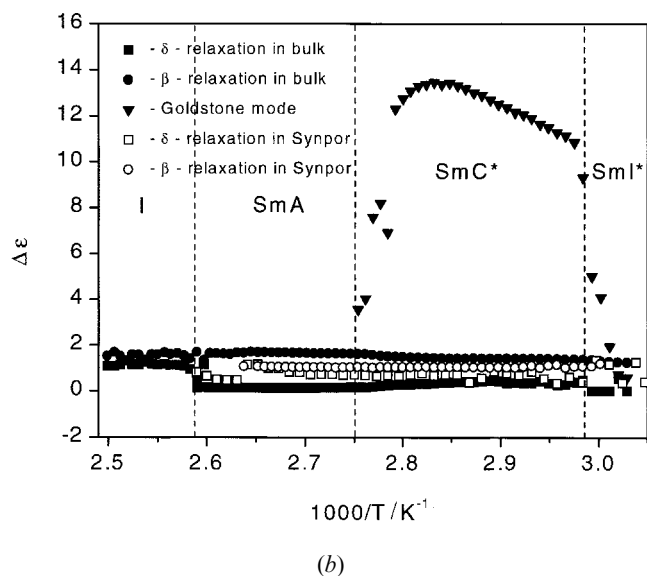
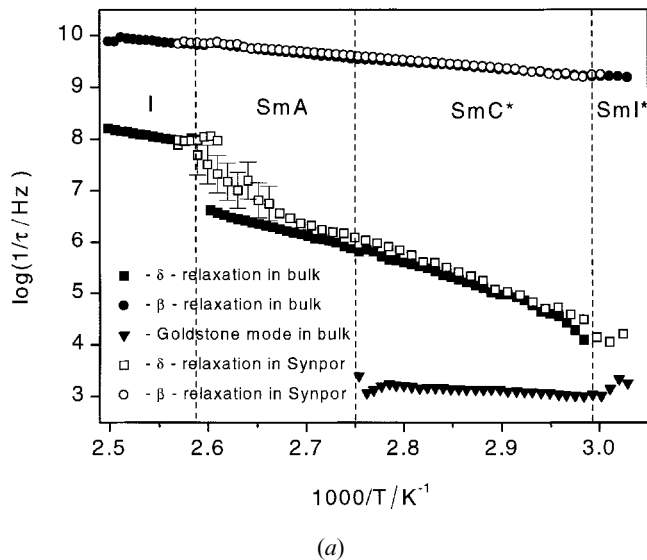
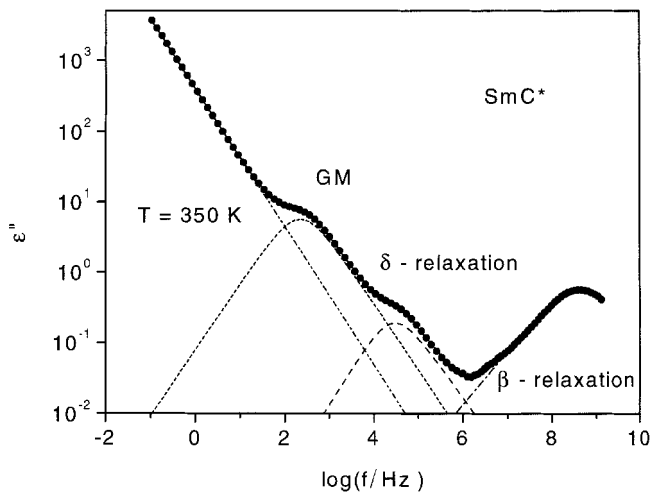


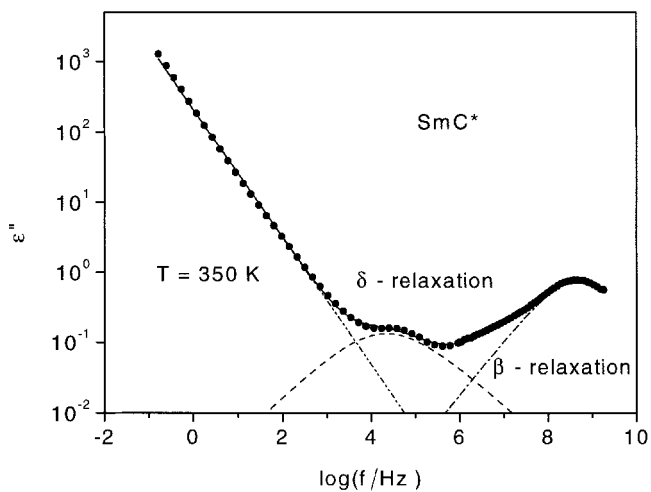
Figure 4. Comparison of (a) relaxation rates and (b) dielectric strengths of relaxation processes observed in the bulk and Synpor confined DOBAMBC.

3.3. DSC measurements

The DSC measurements for DOBAMBC presented in figure 6 confirm the existence of all the LC phases and the phase transition temperatures. For both bulk and confined samples we have measured DSC curves during heating from room temperature to about 393 K, and subsequent cooling to room temperature. During heating, the phase sequence was $Cr \rightarrow SmC^* \rightarrow SmA \rightarrow I$ in good agreement with literature data [35, 36], although there are systematic deviations of a few Kelvin in the phase transition temperatures which are not unusual for this type of material (see § 2). On cooling, the sequence



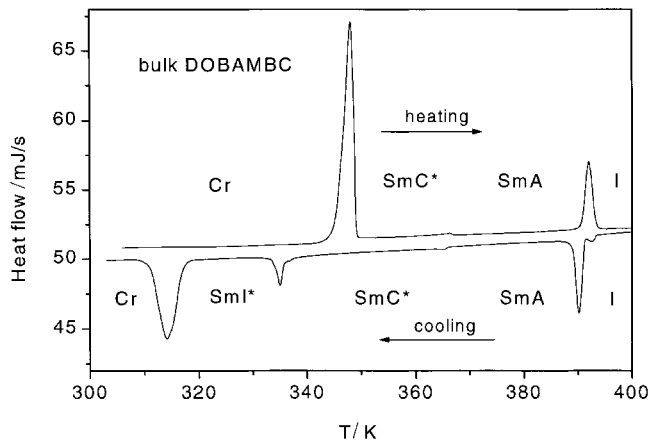
(a)



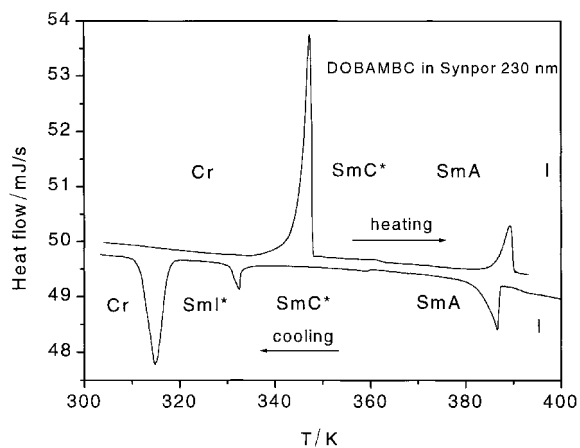
(b)

Figure 5. Relaxation for bulk and confined DOBAMBC observed in the SmC* phase and fitted processes according to equation (1). (a) Three relaxation processes in the bulk sample: β -relaxation (fitting parameters $\Delta\varepsilon = 1.58$, $\tau = 3.39 \times 10^{-10}$ s, $\alpha = 0.76$, $\gamma = 1$), δ -relaxation ($\Delta\varepsilon = 0.40$, $\tau = 5.98 \times 10^{-6}$ s, $\alpha = 1$, $\gamma = 0.87$) and Goldstone mode ($\Delta\varepsilon = 12.5$, $\tau = 7.18 \times 10^{-4}$ s, $\alpha = 0.94$, $\gamma = 1$); (b) two processes in the Synpor-DOBAMBC system: β -relaxation ($\Delta\varepsilon = 2.17$, $\tau = 3.49 \times 10^{-10}$ s, $\alpha = 0.77$, $\gamma = 1$) and δ -relaxation ($\Delta\varepsilon = 0.54$, $\tau = 8.15 \times 10^{-6}$ s, $\alpha = 0.60$, $\gamma = 0.93$).

of the phases was $I \rightarrow SmA \rightarrow SmC^* \rightarrow SmI^* \rightarrow Cr$. The transition enthalpies extracted from the DSC curves, obtained by integration over the transition peaks, are given in table 2. In confinement, the same sequence of peaks appears with slightly changed phase transition temperatures. All transitions are systematically shifted to lower temperatures. This effect can be explained by slight contamination of the Synpor membranes. Small



(a)



(b)

Figure 6. DSC curves for (a) bulk DOBAMBC and (b) confined DOBAMBC in Synpor 230nm membrane. The characteristic peaks for the different phase transitions can be observed. The slight hysteresis of the heating/cooling curves is systematic at a scan rate of 1 K min^{-1} .

amounts of impurities present in the cellulose matrix lower the mesophase transition temperatures. It should be noted in particular that a small peak marks the SmA to SmC* transition indicating a weak first order transition. This peak is shifted in the confined material about 4 K downwards, significantly more than the other transition temperatures. This indicates a particular sensitivity of this transition to the random confinement effects.

In both DSC measurements, the cooling and heating rates chosen lead to a slight hysteresis in the detected phase transition temperatures. For the DSC measurements in the composite LC/Synpor system, it was not possible to determine directly the exact amount of LC

Table 2. Phase transition temperatures and enthalpies extracted from the DSC curves for bulk and confined DOBAMBC.

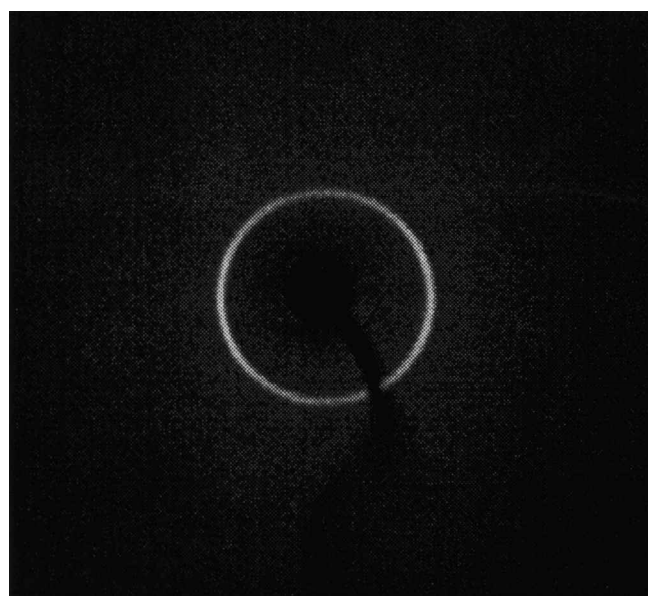
Sample	Phase transition	T/K	$\Delta H/J\ g^{-1}$	$\Delta H/\Delta H_{\text{bulk}}$
Bulk DOBAMBC	Cr \rightarrow SmC*	348.0	58.2	
	SmC* \rightarrow SmA	366.4	0.74	
	SmA \rightarrow I	392.1	13.9	
	I \rightarrow SmA	390.2	12.4	
	SmA \rightarrow SmC*	365.2	0.87	
	SmC* \rightarrow SmI*	335.0	4.5	
	SmI* \rightarrow Cr	314.2	31.2	
DOBAMBC in Synpor membrane pore size 230 nm	Cr \rightarrow SmC*	347.3	15.5	0.27
	SmC* \rightarrow SmA	361.0	0.35	—
	SmA \rightarrow I	389.3	3.57	0.26
	I \rightarrow SmA	386.6	3.36	0.27
	SmA \rightarrow SmC*	358.9	0.44	—
	SmC* \rightarrow SmI*	332.5	1.37	0.30
	SmI* \rightarrow Cr	314.8	10.6	0.34

mesogen contained in the membranes, and the measured transition enthalpies per mass refer to the composite system. The factor of about 0.3 for the average ratio of total latent heats accounts for the filling factor of the membranes of about 0.3, and within the experimental uncertainty it is in good quantitative agreement for all observed transition peaks (except for the SmA–SmC* transition peak which is very small and affected by a large relative error). The conclusion from these measurements is that the complete smectic mesomorphism is preserved in the confined samples, and slight temperature shifts (which also vary between individual membrane

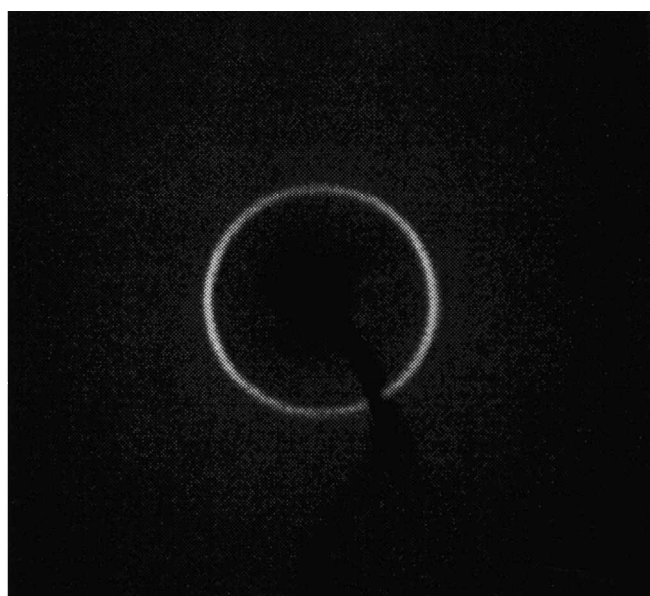
sheets) are caused by impurity effects which do not influence the phase dynamics. This is consistent with the dielectric data for the molecular processes. Even for the membranes with the smallest nominal pore size, the thermodynamic behaviour is practically that of the bulk phase.

3.4. X-ray measurements

The X-ray diffractograms presented in figure 7 show a rather sharp halo characteristic for non-oriented samples, where local smectic layer orientations are distributed at arbitrary angles with respect to the beam



(a)



(b)

Figure 7. X-ray diffraction patterns of DOBAMBC confined in Synpor 400 nm cellulose membranes: (a) diffraction halo in the SmA phase at 378 K, (b) diffraction halo in the SmC* phase at 348 K. The different ring diameters correspond to layer thicknesses of 3.3 and 3.1 nm, respectively.

direction. The images in figure 7 display only the small angle reflection belonging to the smectic layer structure and not the diffuse halo at larger angles reflecting correlations between the molecules within individual layers. The diffractogram in the SmA phase does not show qualitative differences from that of SmC* phase. However, the diameter of the diffraction halo increases with decreasing temperature near the phase transition temperature. This effect can be explained by the change of the smectic layer thickness due to the tilt of the molecules in the SmC* phase. The tilt angle depends on the temperature and for DOBAMBC changes from 0° to about 21° have been reported [15, 27]. Since the material is not aligned in the random matrix, direct access to the tilt angle from the respective orientations of the layer reflections and the molecular halo of the X-ray pattern is not possible. An indirect estimation of the tilt is possible if one assumes a simplified model which equates the layer thickness in smectic A with a molecular length parameter and the layer thickness in SmC* with the projection of that parameter due to the molecular tilt θ . This approximation yields the relation $\theta = \arccos[d(\text{SmC}^*)/d(\text{SmA})]$. Thus from the temperature dependence of the smectic layer thickness of figure 8, an estimate of the tilt angle can be calculated, although we note that this model is probably oversimplified because it neglects interdigitation and other steric effects. The result is in satisfactory agreement with results from previous conoscopic measurements [15]. We have considered the change of 4 K in the SmA–SmC* mesophase transition temperature for the Synpor membranes with respect to the bulk material by making a

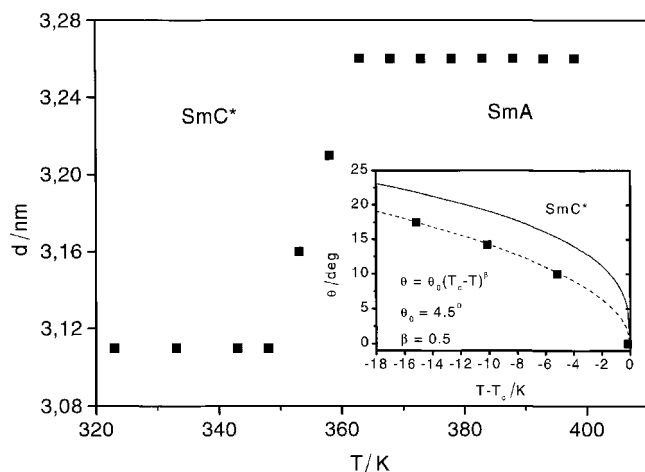


Figure 8. Temperature dependence of the thickness of the smectic layers obtained from the small angle X-ray scattering experiment. The dashed curve is a fit with the parameters given in the inset, using the simple cosine model (see text); the solid tilt angle curve is taken from [15], shifted by 4 K to lower temperatures.

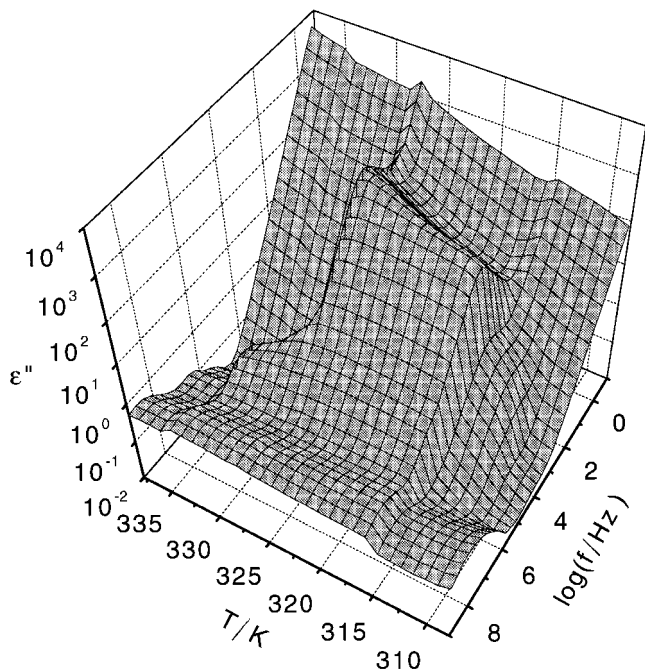
corresponding shift of the bulk curve. The X-ray data presented in figure 8 support the conclusion that both SmA and SmC* phases exist in the porous membrane under investigation, and the phase transition temperature differs from the bulk by only a few degrees downward.

Finally, it has to be mentioned that the distribution of the diffracted X-ray intensity in the halo is not homogenous and is more pronounced in the horizontal axis of the picture. This suggests that the cellulose membranes are not completely isotropic in their spatial structure, a kind of slight preference axis for the orientation of the smectic layers exists inside the porous matrix. However, the effect is of the order of a few percent; the influence on the interpretation of the dielectric spectra is negligible and is not quantitatively discussed further.

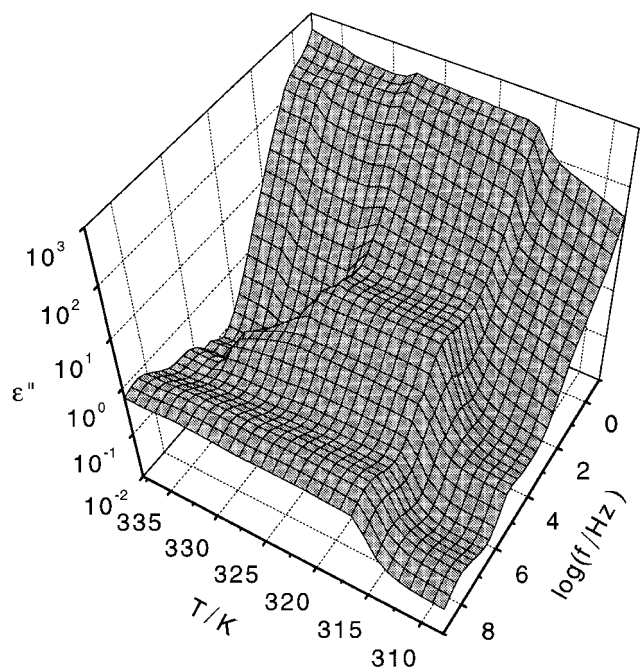
After it has been undoubtedly established that the random porous matrix leaves the phase sequences intact, one has to conclude that the strong anchoring and introduction of defects in the director structure at the confining matrix leads to the suppression of collective modes. Since the value of the helical pitch of the material gives some natural length scale for discussion of structural influences of the boundaries on the smectic c -director, a possible test of this interpretation could be the systematic change of the pitch versus pore size ratio. However, the range of pore sizes of the available Synpor matrix material is limited and the helical pitch in DOBAMBC is larger than the pore diameters of the Synpor membranes used. The helical structure is therefore distorted by confinement in all composite samples and no qualitative pore size dependence has been detected in the experiments. The GM process is absent in DOBAMBC in all membranes investigated from 0.23 to 0.85 μm nominal pore size. We note that the same result has been obtained for other ferroelectric materials with comparable pitch lengths [6, 23]. A test to probe the influence of pitch to pore size ratio is the choice of a short pitch material; this was available with C7, having a pitch about one order of magnitude smaller than the above-mentioned samples. The results of dielectric measurements made using C7 are dealt with in the following section.

3.5. Dielectric behaviour of C7 in bulk and confinement

Figure 9(a) shows a 3D plot of the temperature and frequency dependence of the dielectric losses for the bulk mesogen C7 for a broad range of frequencies. The general bulk dielectric behaviour of the relaxation processes in C7 is comparable to that described for DOBAMBC. In the isotropic phase, two high frequency modes exist which are related to the dynamics of individual molecules and assigned to rotations around the short (δ -process) and long (β -process) molecular axes (figure 10). The β -process observed in all mesophases exhibits Arrhenius-like behaviour of the relaxation time,



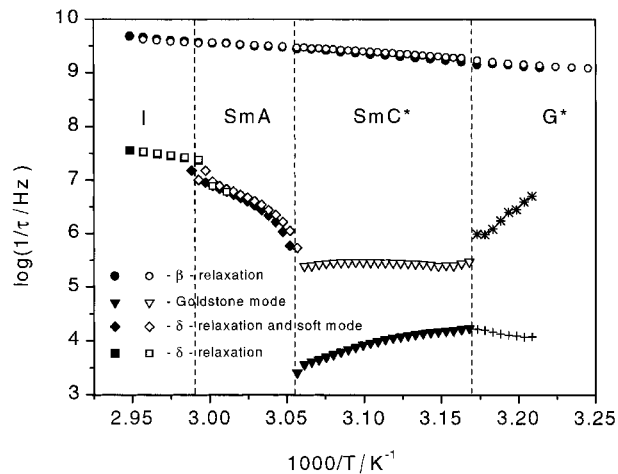
(a)



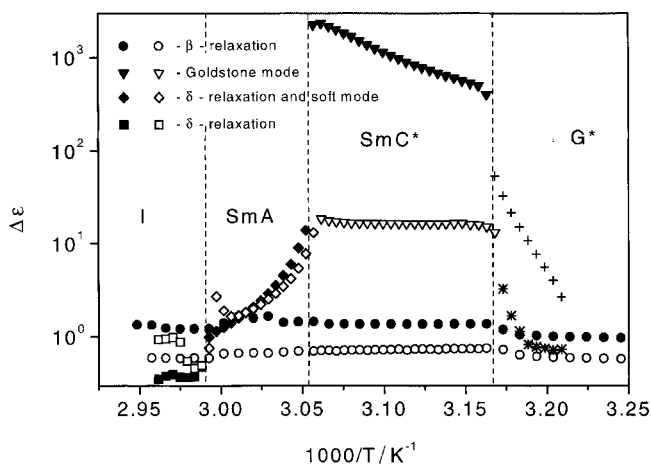
(b)

Figure 9. 3D plot of the temperature and frequency dependence of relaxation losses in (a) bulk C7 and (b) the 850 nm Synpor/C7 composite.

and no peculiarities at the phase transitions. The δ -process slows down at the phase transition from isotropic to SmA due to the molecular orientational order in the



(a)



(b)

Figure 10. Temperature dependence of (a) the relaxation frequencies and (b) dielectric strengths of the processes observed in the bulk and confined C7. Filled symbols represent the bulk data and open symbols the measurements in 850 nm confinement. The soft mode in the bulk FLC and Synpor/FLC systems is present in the SmA phase. In the SmC* phase the Goldstone mode in Synpor is broadened and shifted by more than one decade compared with the bulk. The δ -relaxation process is covered by the soft mode in the SmA phase and the Goldstone mode in the SmC* phase. Crosses and asterisks mark processes in the G* phase which are not analysed here.

SmA phase. With decreasing temperature, the increasing intensity of the soft mode covers this process. The observed strength of the soft mode is related to the comparably high value of the spontaneous polarization in the ferroelectric mesophase. Near the phase transition from SmA to the ferroelectric smectic C* phase, the characteristic behaviour of the soft mode, a critical slowing down at the phase transition, is observed. Within

the SmA phase, the relaxation frequency decreases, while the dielectric strength increases with decreasing temperature. The theoretical description predicts a Curie–Weiss dependence of the inverse dielectric strength on temperature with the slope in the SmA phase half that in the SmC* phase [37]. In the SmC* phase, the second strong collective relaxation process, the Goldstone mode (GM), appears in the spectra (figure 11). It covers the soft mode which also exists in this phase. The dielectric

relaxation strength of the GM is two to three orders of magnitude higher than that of the molecular and soft modes. The dielectric rate of this process is nearly temperature independent. However, one observes a decreasing relaxation time due to the presence of the soft mode (from the SmC* side) and an increasing dielectric strength near the smectic phase transition due to the maximum in helical pitch reached in the SmC* phase. In the G* phase dielectric losses are also observed, but not discussed here. In principle, it is possible to suppress the GM if one is interested in studying the soft mode behaviour within the ferroelectric phase. However, within this study, which focuses on confinement effects, this experiment has not been attempted.

In accordance with the assumptions discussed in the previous section, the influences of random confinement are much less drastic for C7 than for the large pitch DOBAMBC. The dielectric behaviour of the Synpor-FLC composite is comparable to that of the bulk FLC, with basically quantitative differences, but no qualitative changes. Figure 9(b) shows a 3D plot of temperature and frequency dependence of the dielectric relaxation losses for C7 confined in a Synpor membrane—for comparison see the corresponding DOBAMBC spectra in figure 2(b). The high frequency molecular β -process has a temperature behaviour comparable to the bulk. In the confined SmA phase, the soft mode is observed at slightly higher relaxation frequencies than in the bulk, figure 10(b). The same effect would be observed if the temperatures of the bulk and confined samples differed by about one Kelvin. As has been discussed already, unavoidable contamination by small amounts of impurities lowers the phase transition temperatures of the mesogen in the composite system, the observed tendency of the soft mode is in accordance with such a small lower temperature shift of the mesomorphism. The dielectric strength of the soft mode in confinement has the same characteristic temperature dependence as in the bulk. Two counteracting effects, (a) the higher dielectric efficiency of the process due to the random layer arrangement, and (b) the filling factor of the pores and probably a partial suppression of the soft mode in the confining matrix, almost cancel each other. In the SmC* phase, the Goldstone mode is also present, in contrast to DOBAMBC. The strength of this mode is lowered by almost two orders of magnitude compared with the bulk process. The relaxation frequency is shifted to higher frequencies by more than one decade (figure 11). The process exhibits all typical features of the GM process such as the temperature characteristics of the relaxation frequency and dielectric strength (figure 10). However, the process itself is slightly broadened with respect to the bulk GM, the parameter α changing from 0.95 to 0.70. This is certainly a consequence of the polydispersity of

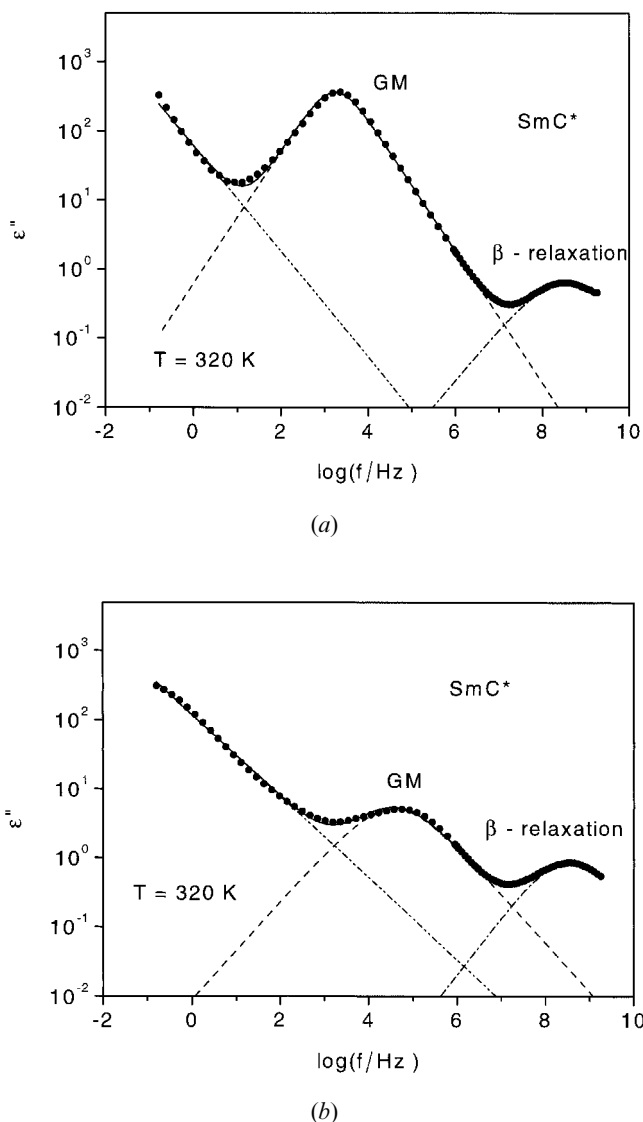


Figure 11. Relaxation processes observed in C7 (a) in the bulk and (b) confined in Synpor in the SmC* phase. Two relaxation processes visible in the bulk C7 were fitted to equation (1) with the following fitting parameters: Goldstone mode ($\Delta\epsilon = 780$, $\tau = 9.16 \times 10^{-5}$ s, $\alpha = 0.95$, $\gamma = 1$) and β -relaxation ($\Delta\epsilon = 2.17$, $\tau = 7.66 \times 10^{-10}$ s, $\alpha = 0.76$, $\gamma = 0.66$). In the confinement, the parameters were: Goldstone mode ($\Delta\epsilon = 16$, $\tau = 3.83 \times 10^{-6}$ s, $\alpha = 0.70$, $\gamma = 1$) and β -relaxation ($\Delta\epsilon = 2.69$, $\tau = 9.28 \times 10^{-10}$ s, $\alpha = 0.87$, $\gamma = 0.53$).

the pore sizes which is reflected here in an inhomogeneous broadening of the GM relaxation peak. Since the C7 helix is much smaller than the pore size and the helical structure can exist in the confinement, the helix is probably distorted by defects and partially unwound. The influence of anchoring of the director field at the cavity walls is reflected in the shift of the GM relaxation frequency. From the existence of soft and Goldstone modes, it is obvious that the smectic layer structure still exists in the highly inhomogeneous pore structure of Synpor membranes and additional confirmation by X-ray and DSC measurements is unnecessary.

4. Conclusions

Collective relaxation processes observed in the confined ferroelectric liquid crystals DOBAMBC and C7 show remarkable differences from bulk behaviour. The modifications of relaxation frequencies, dielectric strengths and shapes of the processes depend on the matrix structure and surface interactions. We have verified by DSC and X-ray measurements that the mesomorphism is preserved in the random macroporous confinement, except for slight shifts (~ 1 K) of phase transition temperatures. These shifts can be attributed to weak contamination of the mesogenic material with impurities contained in the cellulose membranes. An exception is the SmA to SmC* transition, with a shift of about 4 K.

In the long pitch material DOBAMBC, we observe the complete disappearance of the Goldstone mode. In the short pitch material C7, the GM is shifted about one decade to higher frequencies, is slightly broadened with respect to the bulk GM and the dielectric strength of the mode is reduced considerably. It cannot be excluded that in the confined DOBAMBC samples, a GM is also present with considerably reduced dielectric relaxation strength. If such a process is present and its dielectric strength is reduced by the same amount as in the C7 material, it would be hardly detectable, since the conductivity wing would cover it.

We attribute the described dynamic behaviour to the geometrical effects of anchoring of the liquid crystal material at the Synpor cellulose strands, which imposes an effective force on the director structure, damping the free reorientation on the tilt cone. Panarin and co-workers [22] have shown in an investigation of ferroelectric mesophases in sandwich cells that the correlation time for the reorientation on the tilt cone decreases continuously with decreasing cell gap. They found an agreement of experimental and theoretical data in the micrometer range. Although the results of that calculation cannot be directly transferred to a system with random three-dimensionally inhomogeneous confinement, the general trend of decreasing correlation times

of the collective reorientation process with decreasing dimensions of the 'cage' is in good coincidence with the observations presented here for Synpor confined material. Also, the predicted decreasing dielectric relaxation strength with decreasing cavity sizes [22] is in agreement with the measurements for C7 in the random cellulose matrix.

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