Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006

To cite this article: Ch. Cramer, Th. Cramer, M. Arndt, F. Kremer, L. Naji & R. Stannarius (1997): NMR and Dielectric Studies of Nano-Confined Nematic Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 303:1, 209-217

To link to this article: http://dx.doi.org/10.1080/10587259708039426

Mol. Cryst. Liq. Cryst., 1997, Vol. 303, pp. 209–217
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NMR AND DIELECTRIC STUDIES OF NANO-CONFINED NEMATIC LIQUID CRYSTALS

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Abstract

Orientational order and mobility of nematogens adsorbed in nanoporous glass are investigated by ^{1}H and ^{13}C NMR and broadband dielectric spectroscopy. For the mesogen 5CB, we detect local nematic order in cavities of 2.5, 5.0 and 7.5 nm diameter. Quantitative measurements of the order parameter are reported. The nematic-isotropic transition temperature is lowered by approximately 16K compared to the bulk phase. The N-I transition is smooth, of second or weakly first order. At low temperatures, order parameters of ≈ 0.7 are reached. Crystallisation (N-Cr) is suppressed considerably, at least to below 220K. A surface layer of mesogenic molecules at the pore walls with considerably retarded molecular dynamics is detected.

INTRODUCTION

Orientational order of liquid crystal molecules at solid surfaces and the influences of restricting geometries on the formation of a nematic phase are of considerable academic and practical interest. Among the various adsorbate systems that have been investigated in the past are organic and inorganic filters with highly parallel and well defined pores like ANOPORE or NUCLEPORE membranes (see, e.g. [1]), polymer dispersed liquid crystals, PDLC (see, e.g. [2]) with nematic inclusions of spherical or ellipsoidal geometry, porous glasses with random pores and narrow pore size distributions (see, e.g. [3]), and other systems like aerogels (see, e.g. [4]) with broad pore size distributions and irregular shapes of the cavities.

In particular, porous sol-gel glasses provide systems with huge inner surfaces and a high porosity. They are transparent, dielectrically inactive, thus being well suitable for optical investigations and dielectric spectroscopy. It is advantageous for NMR spectroscopy that the matrix does not contain carbons or hydrogens and therefore does not contribute to the background signal in ^{1}H or ^{13}C NMR spectra.

The basic goal of this study is the investigation of the influences of nano-confinement on the molecular mobility of the nematogens, the measurement of local orientational order and the characterisation of the nematic-isotropic phase transition. Previous dielectric [5] and ^{2}H NMR [3] measurements of nano-confined nematics in porous

glass have been published and demonstrated the power of these methods. Dielectric measurements are particularly useful for study of molecular mobility in the different thermodynamic phases. The relaxation processes can be directly assigned to molecular reorientation dynamics. Information on orientational order is not as easily extracted from the dielectric data. On the other hand, NMR measurements provide information on local orientational order but are less efficient in the characterisation of molecular mobility. Proton NMR is a rapid and easy to handle tool for order parameter measurements. It can provide absolute order parameter data. The more sophisticated ^{13}C NMR experiments can be used for a more detailed analysis, for example they give additional information on molecular diffusion in the pores. Within this work, we combine both dielectric and NMR techniques to yield a comprehensive picture of the confined nematic phase.

SAMPLE PREPARATION

We have used commercial porous glass from Geltech Inc., USA, with specific pore sizes of 2.5 nm, 5.0 nm, and 7.5 nm, a narrow pore size distribution and a huge inner surface of 520 to 610 m^2/g. For sample preparation, the porous glass is evacuated to 10^{-5} mbar at 570 K for 24 h to remove volatile impurities. Afterwards, the mesogenic substance is injected in the (closed) vacuum chamber by means of a syringe and the pores are filled by capillary wetting during 48 h at a temperature above the clearing point of the nematic.

In the NMR experiments, we have recorded ^{13}C spectra with a Bruker MSL 500 spectrometer ($B_0 = 11.7T$) using the simple $\pi/2$ pulse sequence in the carbon frequency channel and broadband proton decoupling during sampling. Proton spectra were measured with a 100 MHz Bruker MSL spectrometer.

For the dielectric experiments, 0.2 mm thick disk slices were cut from the glass cylinders by means of a diamond string saw. The faces of these disks were covered with aluminium foil (thickness 800 nm) and subsequently the samples were mounted between gold plated brass electrodes of the capacitor. Dielectric measurements were performed in the frequency range 10^{-2} - 10^9 Hz using a Solartron-Schlumberger frequency response analyser FRA 1260 with a Novocontrol active sample cell BDC-S (10^{-2} Hz - $3 \cdot 10^6$ Hz) and a Hewlett Packard impedance analyser 4191A (10^6 Hz - 10^9 Hz). Temperature control was achieved with a stability better than $\pm$ 0.05 K.

The mesogen used in the experiments was 4-n-pentyl-4'-cyanobiphenyl (5CB, MERCK). Its clearing point T_{NI} is 35°C. This standard sample has been extensively investigated in the past by means of ^2H, ^1H and ^{13}C NMR. Carbon chemical shielding tensor data are well known (e.g. [6, 7]).

DIELECTRIC EXPERIMENTS

Figure 1 presents two example dielectric curves of the nematogen in 5.0 nm porous glass. We show only the dielectric loss curves, that is the imaginary part $\epsilon''(\omega)$ of the complex dielectric function $\epsilon^* = \epsilon' + i\epsilon''$. We describe the isothermal data of the dielectric loss $\epsilon''(\omega)$ with a superposition of N Havriliak-Negami [8] model functions and a conductivity contribution

$$\epsilon'' = \frac{\sigma_0}{\epsilon_0} \cdot \frac{1}{\omega^s} - \sum_{k=1}^{N} \mathrm{Im}\left[\frac{\Delta\epsilon_k}{(1+(i\omega\tau_k)^{\alpha_k})^{\beta_k}}\right] \tag{1}$$

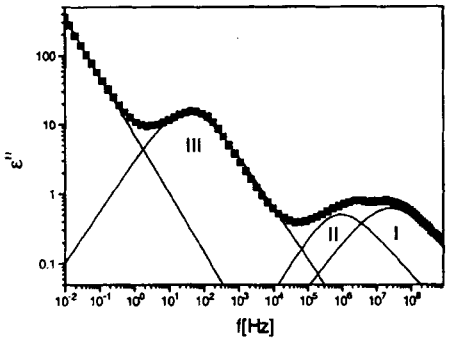

Fig.1a) *Typical dielectric loss spectrum $\epsilon''(\omega)$ in the isotropic phase (T=310K) of 5CB in 5nm porous glass together with the three dielectric processes and the conductivity contribution obtained from the fit.*

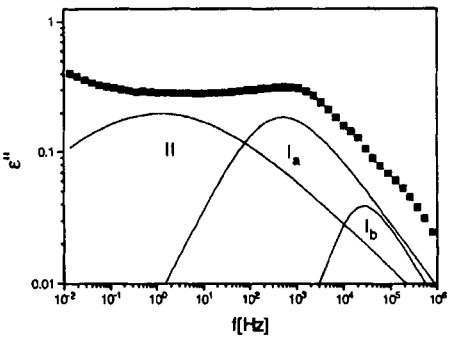

Fig.1b) *Dielectric loss $\epsilon''(\omega)$ in the nematic phase (T=220K) of 5CB in 5nm porous glass and the contributions of the individual fit functions (process III omitted).*

ϵ_0 is the vacuum permittivity, σ_0 a conductivity parameter, $\Delta\epsilon$ the dielectric strength and τ the mean relaxation time. The index k refers to the different processes which contribute to the dielectric response. α and β describe the symmetric and asymmetric broadening of the relaxation processes, which can be interpreted as symmetric and asymmetric broadening of a distribution of Debye relaxators. When β is close to 1, the relaxation rate τ corresponds to the maximum of this relaxation time distribution. The first term on the right hand side of Eq. 1 is caused by free charge carriers, with s=1 for *Ohmic* behaviour. Deviations ($s < 1$) can be caused by electrode polarisation. One can clearly discriminate three dielectric processes in the high temperature spectra (Fig. 1a), and four processes at low temperatures (Fig. 1b). As the parameters α_k, β_k are in the vicinity of 1 for all processes, we can disregard the broadening of the dielectric peaks in the following discussion and consider only the pronounced temperature dependence of the relaxation rates τ_k (Figure 2).

The assignment of the individual dielectric processes is possible on the basis of a comparison with bulk experiments and previous investigations of 5CB in micropores

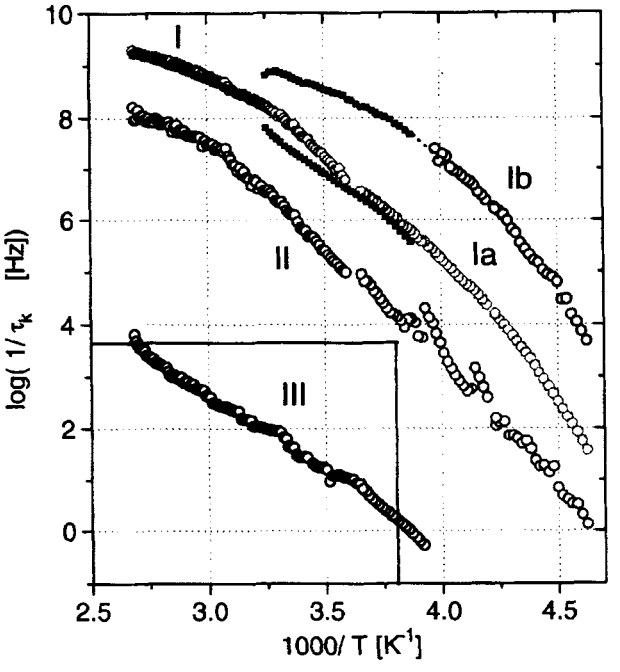

Figure 2)
Dielectric relaxation rates of 5CB in 5nm porous glass. Bulk data (solid symbols) are added for comparison. The square in the lower left corner visualises the "NMR window", that is the temperature and frequency range covered by our NMR experiments. The molecular dynamic processes are all fast on the NMR time scale and the NMR experiment measures only time averaged quantities.

[9]. The dielectric measurement of 5CB in ANOPORE filters (having parallel, well ordered channels of 200nm diameter and 60μm length) show the same dynamics as the bulk mesophase. In the isotropic phase ($> 308K$), one observes one single dielectric loss process originating from an isotropic reorientation of the molecular long axis, its relaxation rate is in the range of $10^6..10^8$ Hz. At the transition to the nematic phase, this dielectric loss peak splits into two processes. The slower of them is attributed to reorientations of the molecules about their short axes (180° flips) in the nematic potential. As the molecular dipole moment (along the $C \equiv N$ bond) is roughly parallel to the molecular long axis, this process influences mainly the polarisation along the nematic director. The faster relaxation process originates from fluctuations of the molecular long axis around the director $\vec{n}$, it changes basically the polarisation components perpendicular to $\vec{n}$. With increasing nematic order, the separation between both relaxation frequencies increases, but the changes are too insensitive to draw quantitative conclusions on the order parameter. In Fig. 2, relaxation frequencies measured in the free nematic phase [9] are indicated by solid symbols.

Knowing the molecular assignment of the bulk relaxation processes, we can now discuss the dielectric measurements of 5CB in nanoporous confinement. It is evident that the high frequency process (I) at high temperatures coincides with the isotropic reorientation process of the bulk phase, and it is also evident that the molecular dynamics is not changed with respect to the bulk phase. We can conclude that there is a

large portion of molecules in the pore centres which still have the dynamic properties of the free bulk molecules and do not sense wall effects. There is no change in the dielectric relaxation rates at the bulk T_{NI} but a smooth change in the temperature curve is indicated approximately 12..18K below the bulk phase transition. It is very likely that the isotropic reorientation process splits there into the two processes (Ia,b) as in the bulk nematic phase, but the high frequency process (Ib) cannot be resolved in the high frequency wing of (Ia). With decreasing temperature, the separation of processes (Ia,b) evolves much more gradually than in the nematic bulk sample, indicating a smooth transition from the isotropic to the nematic phase. At temperatures far below the bulk T_{NI}, one can clearly discriminate the fast process (Ib) from the slower process (Ia). The ratio of the relaxation frequencies becomes as large as in the bulk sample, and one can estimate that the nematic potential and consequently the nematic order parameter is roughly of the same order. It is also evident that the nematic phase can be supercooled considerably. In fact, we have not observed a crystallisation of the mesogen in the temperature range down to 220K, that is far below the crystallisation of the supercooled nematic bulk sample.

Parallel to the bulk like molecular reorientation processes described, we observe an additional dielectric relaxation peak at a frequency retarded by nearly two orders of magnitude compared to (I). It is well known that in adsorbate systems one often encounters a surface layer of partially immobilised molecules, and we can therefore assign this process (II) to 5CB molecules directly attached to the walls of the cavities. As the process is present in all phases of the mesogen and at all temperatures, it seems not to be connected with the formation of the nematic volume phase and not noticeably influenced by the nematic potential.

Finally, the spectra show a large relaxation peak (III) at very low frequencies. The large dielectric strength as well as the frequency range clearly characterise this process as a Maxwell-Wagner polarisation effect, that is polarisation generated by the restricted motion of ionic charge carriers in the cavities of the porous material. It is not directly connected to molecular dynamics of the mesogens and we exclude this process in the further discussions.

Figure 3 compares the dielectric relaxation rates measured in glasses of different pore sizes. It is evidently seen that no pronounced differences exist, that is the relaxation rates of both the free and surface bound molecules do not depend significantly upon pore sizes down to 2.5nm.

The dielectric strengths connected with processes (I) and (II) are of comparable magnitudes. The sum of processes (Ia) and (Ib) roughly totals that of (I), and the temperature dependence of the individual dielectric strengths is very weak. From the exact knowledge of the relative intensities, one could determine the thickness of the surface layer. However, the exact quantitative determination of the strength of the surface

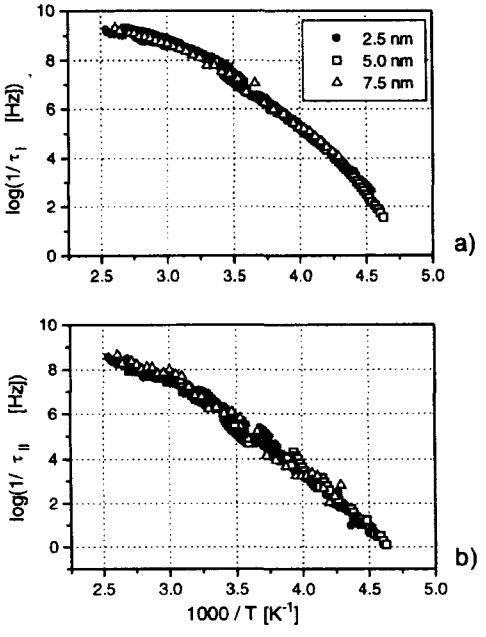

Fig.3) *Comparison of the dielectric relaxation rates of the free (a) and surface bound (b) sub-phases of 5CB in porous glasses of different pore sizes.*

layer process (II) is affected by a large uncertainty because it is masked in part by the large conductivity wing. One can conclude at least that the contributions from the surface layer (II) are consistent with the assumption of a monomolecular coverage of the channel walls in all phases.

NMR EXPERIMENTS

The ^{1}H and ^{13}C NMR experiments are described in detail in [7]. We recollect the principles of the order parameter measurements here and discuss the results, comparing them with the dielectric experiments.

Dipolar spin-spin interactions of the protons and chemical shift determine the line shapes of proton NMR spectra. Figure 4a shows the temperature dependence of the proton spectra. At high temperatures, dipolar couplings are averaged out and an isotropic spectrum is observed. Its resolution is limited by magnetic field inhomogeneity. With decreasing sample temperature, dipolar interactions which are a direct measure of the order parameter broaden the spectrum continuously, as is shown in the figure. The order parameter was calculated from the proton NMR powder pattern as follows: We measure the spectrum of the nematic bulk sample, which aligns perfectly to the $\mathbf{B_0}$ field and yields absolute nematic order parameters from the dipolar splitting of the two wings formed by the ortho ring protons. Using the well known scaling relation for

dipolar interactions of a sample with order parameter S in orientation Φ to $\mathbf{B_0}$

$$f_{(\Phi,S)}(\nu) = \frac{1}{P_2(\cos\Phi)\cdot S} f_0\left(\frac{\nu}{P_2(\cos\Phi)\cdot S}\right), \tag{2}$$

where $f_0(\nu)$ is a "master" line shape, we simulate the proton powder patterns for given order parameters and determine S from the fit to the experimental proton NMR spectra of Fig. 4a. We neglect here line shape averaging by molecular diffusion along the channels which has been found to influence the ^{2}H and ^{13}C NMR spectra considerably [10, 3, 7] but will be much less effective for the *Lorentz* like proton spectral patterns.

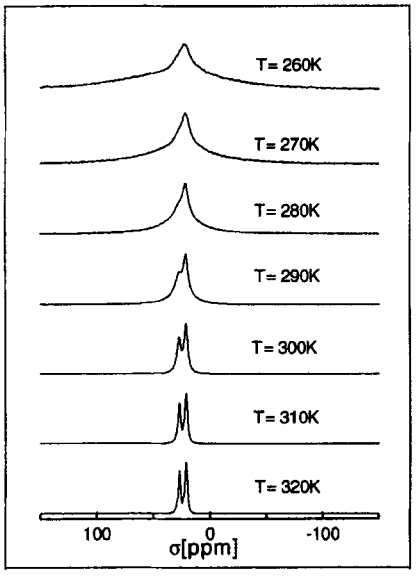

Fig.4a) *100 MHz ^{1}H NMR spectra of 5CB in porous confinement of 7.5nm channels.*

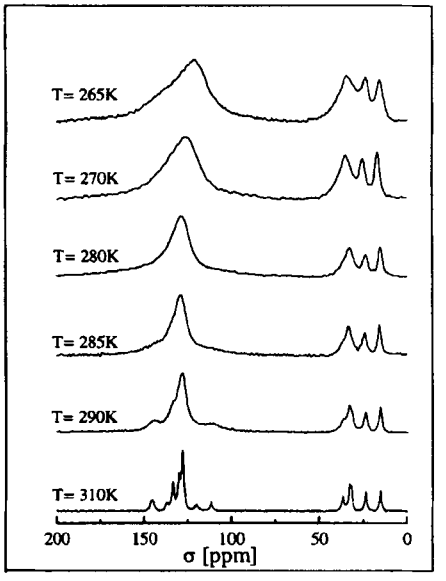

Fig.4b) *Typical ^{13}C NMR spectra of 5CB in porous confinement of 5nm channels.*

A characteristic feature of all spectra is that each spectrum can be described by an average order parameter, and there is no evidence that a different order parameter has to be introduced to describe the molecules in the surface layer. In addition, the proton T_1 relaxation curves give no indication of a two-layer system. Therefore, molecular exchange between surface and free molecules must be fast on the NMR time scale.

Carbon NMR spectra reveal much more detailed information on molecular order and mobility. Nematic orientational order manifests in the chemical shift anisotropy in these spectra. A mathematical approach to determine order parameters and diffusion effects from ^{13}C spectra has been described in [7]. The results of both proton and carbon NMR experiments are shown in Fig. 5. They are in agreement with data of

5CB in randomly oriented Vycor glass which have been determined by deuterium NMR [11].

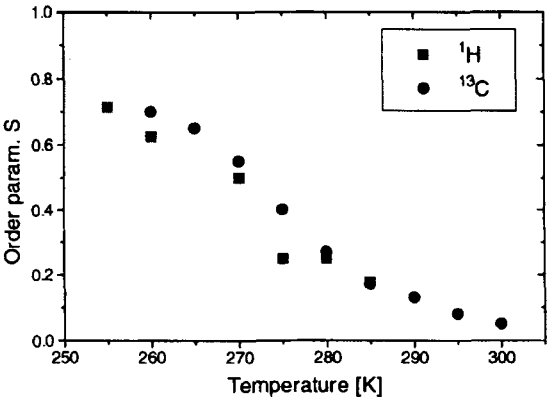

Fig. 5 *The nematic order parameter as determined from proton and carbon NMR.*

SUMMARY

We can summarise the results of the dielectric experiments as follows: The molecular dynamics of the free molecules in the nanopores are in the same order of magnitude as those in the free bulk. It is astonishing that there is still a remarkable amount of molecules with a bulk-like dynamics. The transition from the isotropic into the nematic phase is indicated by a weak change in the temperature characteristics of the relaxation rate. The transition seems to be lowered by about 12..18K, and the changes are smooth compared to the effects observed in the bulk at T_{NI}. The nematic phase persists down to at least 220K. The temperature dependence of τ_k deviates from Arrhenius behaviour and can be described by the Vogel-Fulcher-Tammann equation. The corresponding dynamic glass temperature has been determined to be about 200K. At low temperatures, the large ratio between the two dielectric processes of the free molecules in the pore centres (Ia,Ib) indicates that the order parameter reaches a magnitude comparable to the bulk phase, (≈ 0.7). The molecules directly attached to the surface of the cavities show a dynamic behaviour retarded by nearly two orders of magnitude compared to the free molecules. The thickness of the surface layer can be estimated as follows: If one assumes that the 5nm cavity walls are covered by a monomolecular layer of 5CB molecules, the ratio between free and bound molecules should be roughly 2:1. The relative dielectric strengths are given mainly by the ratio of the number of molecules in the subsystems. The ratio of dielectric strengths of processes (I) and (II) (and that of (Ia+Ib)/(II)) should be 2:1 as well. This ratio is consistent with the observations in the dielectric spectra, although an exact evaluation is not possible.

The NMR experiments give information on the nematic order parameter in the confined geometry. Molecular diffusion within the channel cross section and exchange between surface bound and free molecules are both fast on the NMR time scale, and NMR determines only an average local nematic order. As the exchange rate of surface layer and free molecules is fast on the NMR time scale but slow for the dielectric experiments, we can fix the upper and lower limits for this process, given by the frequency of process (II) in the dielectric spectrum and the inverse of the largest splitting in the NMR experiments, $\approx 10^{-4}s$. Possibly the molecular exchange rate coincides with the rate of (II).

The decrease of T_{NI} and suppressed order parameter found in the NMR experiments is compatible with the dielectric results. The transition starts approximately 15K below the bulk T_{NI} continuously from the isotropic into the ordered state. The order parameter reaches 0.7 at low temperatures and a crystallisation of the sample is completely suppressed in the temperature range of the NMR experiments.

The authors are indebted to H. Schmiedel and S. Grande for fruitful cooperation. This work was supported in part by the Sonderforschungsbereich 294.

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