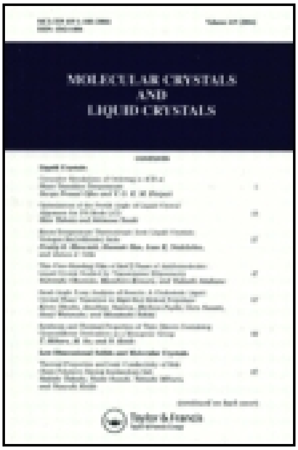

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

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To cite this article: Betzaida Batalla, Ghanshyam Sinha & Fouad Aliev (1999): Dynamics of Molecular Motion of Nematic Liquid Crystal Confined in Cylindrical Pores, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 331:1, 121-128

To link to this article: http://dx.doi.org/10.1080/10587259908047508

Mol. Cryst. Liq. Cryst., 1999, Vol. 331, pp. 121-128
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Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Dynamics of Molecular Motion of Nematic Liquid Crystal Confined in Cylindrical Pores

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Broadband dielectric spectroscopy was applied to investigate the influence of confinement on the dynamics of dielectric modes in MBBA, dispersed in porous matrix with parallel cylindrical pores, 200 Å in diameter. Both molecular modes due to the molecular rotation around its short and long axis were observed in the pores. The confinement results in the modification of the bulk-like modes and of the temperature dependencies of the relaxation times. Two low frequency modes due to relaxation of interfacial polarization (collective mode) and reorientational dynamics of molecules at liquid crystal-pore wall interface (surface mode) were observed. The relaxation time of the surface mode has strong glasslike temperature dependence.

Keywords: dielectric spectroscopy; liquid crystals; confinement

INTRODUCTION

Dielectric spectroscopy is a powerful method for characterization of porous materials in general, and for investigation of condensed matter confined to porous matrices[1,2] in particular. Previous applications of dielectric spectroscopy to confined liquid crystals (LCs)[3-7] were focused mainly on the investigations of the dynamics of the reorientational molecular motion in alkylcyanobiphenyls–liquid crystals with positive dielectric anisotropy. Other investigations[8] of the influence of the confinement on different physical properties of LCs were also performed on LCs with positive dielectric anisotropy. The alignment of these LCs in cylindrical pores with untreated pore surfaces is axial. In LCs with negative dielectric anisotropy, if the angle between the molecular dipole and the long axis of molecule is not equal to 90°, two molecular relaxation processes should be observed. These processes are due to the reorientational motion of molecules about their short and long axes. If the alignment in the pores is radial, i.e. the director is oriented perpendicular to the pore walls, then the influence of the pore wall-LC interface on the properties of the surface layer should be stronger than in the case of axial orientation. In these systems, the difference between the dynamical behavior of the molecules belonging to the surface layer and molecules farthest from the wall should be clearer than for confined alkylcyanobiphenyls.

We have investigated the dynamical properties of 4-methoxybenzylidene-4′-butylaniline (MBBA), a LC with negative dielectric anisotropy, confined to parallel cylindrical by broadband dielectric spectroscopy.

EXPERIMENTAL

We used Anopore membranes with cylindrical pores 200 Å in diameter and impregnated with MBBA. The parallel cylindrical pores are uniformly aligned[9] in these matrices. These matrices are widely used[8,9] for investigations of influence of confinement on properties of liquid crystals because of its simple structure. The bulk MBBA has a nematic phase in the temperature range 43 to 23 °C.

Measurements of the real (ϵ') and the imaginary (ϵ'') parts of the complex dielectric permittivity in the frequency range 10^{-3} Hz to 1.8 GHz were performed using a computer controlled Broadband dielectric spectrometer that is based on the following instruments: Schlumberger Technologies 1260 Impedance/Gain-Phase Analyzer + Novocontrol Broadband Dielectric Converter with active sample cell, HP 4291A rf Impedance Analyzer, and Novocontrol Quatro four circuit high precision temperature control system with cryostat. There is provision for application of an external electric field (d.c. bias voltage) up to 40 V. The temperature stabilization was better than 0.01°C. For the quantitative analysis of the dielectric spectra the Havriliak-Negami function[10] has been used. For the case of more than one relaxation process, taking into account the contribution of the dc conductivity to the imaginary part of dielectric permittivity, the Havriliak-Negami function[10] is given by

$$\epsilon^{*} = \epsilon_{\infty} + \sum_{j} \frac{\Delta\epsilon_{j}}{[1 + (i2\pi f\tau_{j})^{1-\alpha_{j}}]^{\beta_{j}}} - i\frac{\sigma}{2\pi\epsilon_{0}f^{n}}, \qquad (1)$$

where ϵ_{∞} is the high-frequency limit of the permittivity, $\Delta\epsilon_{j}$ the dielectric strength, τ_{j} the mean relaxation time, and j the number of the relaxation process. The exponents α_{j} and β_{j} describe the symmetric and asymmetric distribution of relaxation times. The term $i\sigma/2\pi\epsilon_{0}f^{n}$ accounts for the contribution of conductivity σ, with n as fitting parameter. The errors in determination of the characteristics of the dielectric process are mainly determined by the quality of the experimental data and are less dependent on the algorithm (Gauss or Newton algorithm) used for optimization of the fitting curve. Maximal error in determination of the parameters does not exceed 10 % and the accuracy is much better for relaxation time.

CONFINED MBBA AT T > 267 K

Bulk MBBA has two dielectric dispersion regions[11] when the director is parallel with respect to electric field. The characteristic frequencies are about 5 MHz and 160 MHz. The faster process has been found to be more prominent and is due to the restricted rotation of the molecules about their long axis. When the director is perpendicular to the electric field, MBBA has a dielectric process around $f \sim 170$ MHz. We found out that the dielectric properties of confined MBBA are very different to those in the bulk. Figure 1 gives a general picture of the broadband dielectric spectrum of MBBA confined in cylindrical pores at the temperature corresponding to the bulk nematic phase. From Fig. 1 one can see that for MBBA confined in 200 Å pores, at least five dispersion regions could be identified: a low frequency dispersion around $10^{-1} - 10$ Hz, a clear broad process ($10 - 10^{5}$ Hz), a third process in the frequency range $10^{5} - 10^{7}$ Hz, a low amplitude process around 10 MHz and the last one, which is clear without analysis, in the frequency range 100 MHz $< f <$2 GHz. Analysis of the data shows

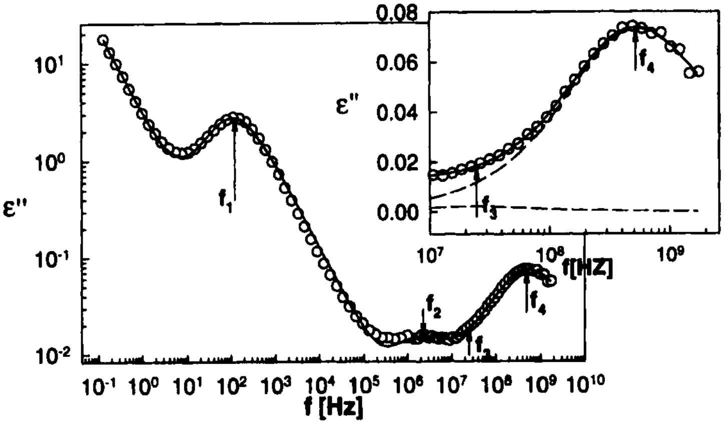

FIGURE 1: Imaginary part of the dielectric spectrum for MBBA in 200 Å pores for $T = 306$ K. Open circles: experiment; solid line: fitting. Inset: high frequency part of the spectrum. Dashed lines: decomposition of bulk like processes. The arrows indicate the characteristic frequencies of different relaxation processes.

that the frequency dependence of ϵ'' for $f < 10$ Hz is mainly due to Ohmic conductivity. The remaining processes are of relaxation origin that can be quantitatively described by the Havriliak-Negami formula. We found that all relaxation process are independent of the applied d.c. bias voltage. It is very important to note that the bias field did not influence the low frequency process (both the characteristic frequency and dielectric strength) at all. If this process was due to ion adsorption at the interface then there would be clear influence of external bias field. We suggest that the low frequency process with characteristic frequency f_1 (Fig. 1) is the relaxation of the interfacial polarization arising at the pore wall-liquid crystal interface. There is another new relaxation process in the pores that does not exist in the bulk LC. The characteristic frequency of this process is identified as f_2 in Fig. 1. This relaxation is due to the rotation of molecules about their long axis, located in the surface layer that is formed at the pore walls. In the high frequency range the process due to the rotation of molecules about their long axis dominates. Since the origin of this mode as well as of the mode due to rotation of molecules about their short axis is the same as in bulk LC, we call these two modes as bulk-like. However this process cannot be described as a single process. Data analysis and the fitting procedure show that in this frequency range the second process, due to the rotation of molecules about their short axes should be taken into consideration. The decomposition of the broad high frequency relaxation into two molecular processes is illustrated in the inset of Fig. 1. All the relaxation processes were found to be of non-Debye-type. For the Anopore membrane with cylindrical pores, the applied electric field was parallel to the pore axis. Since at frequencies greater than 1 MHz the process corresponding to the rotation of the molecule around their long axis dominates, we conclude that the majority of the molecules are oriented perpendicular to the pore wall. However, because the process due to the rotation of molecules about their short axes cannot be neglected we assume that the suggested orientation is not perfect and that a small fraction of molecules have orientations deviating from perpendicular.

The temperature dependence of the relaxation times (τ) corresponding to the rotation of MBBA molecules around the long axis confined in 200 Å pores is presented in Fig. 2 for T > 267 K. In the presented tempera-

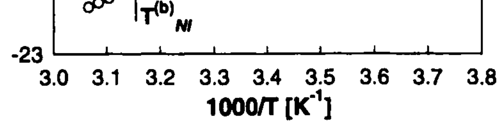

FIGURE 2: Temperature dependence of relaxation times of the process due to the rotation of MBBA molecules around long axis confined in 200 Å pores. Vertical lines: $T_{NI}^{(b)}$ and $T_{NC}^{(b)}$ indicate the bulk nematic-isotropic and nematic-crystal phase transition temperatures.

ture range, which also covers the temperatures corresponding to the bulk nematic phase, we see that the relaxation times smoothly increase as the temperature decreases and there are no sharp changes that can identify the phase transitions. This dependence obviously is not of the Arrhenius type. At temperatures below 296 K the relaxation processes due to molecular reorientation in bulk MBBA should be frozen because of crystallization. In confined MBBA the bulk-like processes were not frozen at least at 30 K below the bulk crystallization temperature. At temperatures below the bulk crystallization temperature, the dependence of the relaxation times deviates from the Arrhenius type behavior more strongly than at higher temperatures. This is accompanied by a decrease of the dielectric strength of the process. At temperatures below 266 K the contribution from bulk-like polarization is negligibly small and the two low frequency processes dominate.

SUPERCOOLED MBBA

Confined MBBA was supercooled without solidification to temperatures much below the bulk crystallization temperature. The process with characteristic frequency earlier identified as f_1 moves out of the measurement range at very low temperatures due to a glass-like slowing down. In the

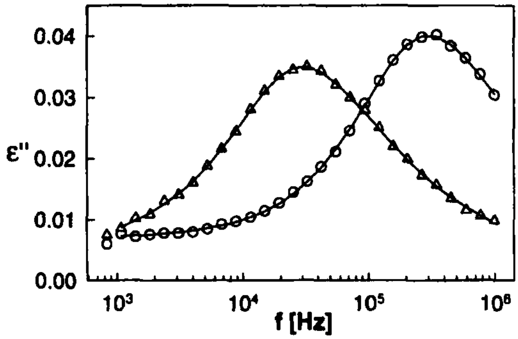

FIGURE 3: Dielectric spectra of the surface mode at different temperatures. Open circles: 249 K; open triangles: 219 K. Lines: fitting.

temperatures below 266 K, the dielectric relaxation due to the rotation of molecules in the surface layers around their long axis dominates. This process is observed to be present even at temperatures as low as 150 K. Figure 3 shows the frequency dependencies of ϵ'' for the surface mode of confined MBBA in the supercooled state. The characteristic frequency of this process in the supercooled state depends strongly on temperature. The corresponding temperature dependence (Fig. 4) of the relaxation times is described by the Vogel-Fulcher relation:

$$\tau = \tau_0 exp(B/(T - T_0)) \tag{2}$$

with the parameters as: $\tau_0 = 1.1 \cdot 10^{-12} s$, $B = 2680$ K and $T_0 = 43$ K. From this we conclude that there is evidence for glass-like dynamical behavior for confined MBBA in the supercooled state.

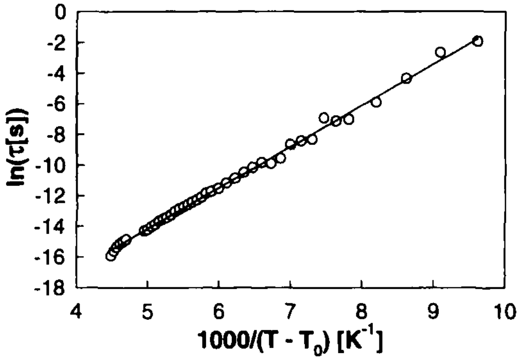

FIGURE 4: Temperature dependence of relaxation times of the surface mode. Symbols: experiment; line: fitting according to formula (2).

The confinement suppresses crystallization, and therefore liquid crystal in restricted geometry might be substantially supercooled below bulk crystallization temperature. The decreasing of the characteristic size of the system increases supercooling along with the tendency to form a glass. This causes glass-like behavior of LC in narrow pores although bulk liquid crystals do not have glassy properties either in anisotropic or in isotropic phases.

CONCLUSION

The influence of cylindrical confinement on liquid crystals with negative dielectric anisotropy has resulted in the appearance of two new processes of relaxation origin, which are observed in addition to the two modified bulk-like dielectric processes, and deep supercooling. In the supercooled state the surface mode shows glass-like behavior even though bulk MBBA is a non-glass-forming substance.

Acknowledgement

This work was supported by U.S. Air Force Grant No. F49620-95-1-0520 and DOE-EPSCoR grant DE-FG02-94ER75764. G. Sinha is grateful to the Organizing Committee of the 16th ILCC, Kent, USA for support.

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