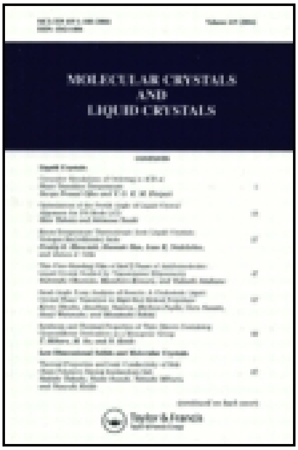

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

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Version of record first published: 24 Sep 2006

To cite this article: Zaira Nazario, Ghanshyam Sinha & Fouad Aliev (2001): Dynamics of Librational Mode of Nematic Liquid Crystal Confined in Cylindrical Pores, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 367:1, 333-340

To link to this article: http://dx.doi.org/10.1080/10587250108028653

Mol. Cryst. and Liq. Cryst., 2001, Vol. 367, pp. 333-340
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Printed in the USA

Dynamics of Librational Mode of Nematic Liquid Crystal Confined in Cylindrical Pores

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Dielectric spectroscopy was applied to investigate the dynamic properties of nematic liquid crystal – 5CB confined in 2000 cylindrical pores of Anopore membranes with the molecules oriented perpendicular to the pore wall with lecithin treated surface. This allows the investigation of the librational (tumbling) mode since the probing electric field is parallel to the pore axis. We found that the dynamics of the librational mode is totally different from the behavior observed in investigations of relaxation due to reorientation of molecules around their short axis. The interpretation of the temperature dependence of relaxation times in nematic phase needs the involvement of the temperature dependence of orientational order parameter. In the supercooled state, the temperature dependence of the librational mode did not follow the behavior observed in the nematic phase and shows a sharp increase while the temperature is decreased that is mainly determined by the variations of viscosity.

Keywords: confinement; relaxation; librational mode

INTRODUCTION

Alkylcyanobiphenyls such as 4-n-pentyl-4′-cyanobiphenyl (5CB) are liquid crystals which have been deeply investigated in the past. These materials are stable and have a large dipole moment (~ 5 D) oriented along the molecular long axis. The dielectric properties of the bulk alkylcyanobiphenyls have been studied extensively [1-7] and have been quite clearly understood. In the nematic phase of 5CB in a geometry in which the electric field **E** is parallel to the director **n**, i.e., **E**||**n**, [1-3] the real (ϵ') and imaginary (ϵ'') parts of the dielectric permittivity have a dispersion region with a characteristic frequency at about 5 MHz. This dispersion is of relaxation origin due to the restricted rotation of the molecules about their short axis and is of Debye type, i.e., it has a single relaxation time. The temperature dependence of the corresponding relaxation times obeys the empirical Arrhenius equation. For the geometry in which the electric field **E** is perpendicular to the director **n**, **E**⊥**n**, dielectric investigations were performed using the conventional frequency domain [2,3] and time domain spectroscopy for 8CB [4,5]. In this geometry the most prominent relaxation process with characteristic frequency about 70 MHz was observed. In a recent dielectric investigation of 5CB confined in cylindrical porous membrane [8] and random porous metrices [9] this process has been attributed to the librational motion of the molecules. The dielectric properties of alkylcyanobiphenyls in the isotropic phase are also well known. In this phase, the characteristic relaxation frequencies corresponding to the molecular rotation of 5CB are around 20 MHz.

To obtain a quantitative description of the librational mode, dielectric spectroscopy was applied to investigate relaxation properties of 5CB confined in 2000 Å cylindrical pores of Anopore membranes treated with lecithin. This treatment provides homeotropic boundary conditions for confined 5CB. Since pore axis is parellel to the probing electric field and molecular dipole moment is oriented perpendicularly to its direction, such a configuration makes it possible to investigate the dynamics of librational (tumbling) mode by dielectric method. Detection of relaxation process due to librational motion of molecules in samples with axial symmetry is principally impossible and the use of treated sample is the most effective way to investigate dynamics of this mode.

EXPERIMENTAL

We used Anopore membrane with cylindrical parallel pores 2000 Å in diameter as a matrix. Porous Anopore membrane was dipped inside a 3 % mass concentration solution of lecithin in hexane for one hour. The matricix was dried until complete evaporation of hexane from the pores. After that the matrix treated with lecithin was impregnated with 5CB from isotropic phase. Bulk 5CB has a nematic phase in the temperature range of 22.5 - 35.0°C.

Dielectric measurements were performed using the broad band spectrometer based on SI 1260, Novocontrol Broad Band Dielectric Converter with active sample cell and HP4291A. We focus on relaxation observed at frequencies above 1MHz that was investigated using high frequency part of the spectrometer. For the quantitative analysis of the dielectric spectra the Havriliak-Negami function [10] has been used:

$$\epsilon^* = \epsilon_\infty + \frac{\Delta\epsilon}{[1 + (i2\pi f\tau)^{1-\alpha}]^\beta}, \quad (1)$$

where ϵ_∞ is the high-frequency limit of the real part of the dielectric permittivity, $\Delta\epsilon$ - the dielectric strength and τ - the mean relaxation time. The exponents α and β describe the distribution of relaxation times.

RESULTS AND DISCUSSION

Figure 1 illustrates the difference in relaxation observed in bulk 5CB and 5CB confined in lecithin treated matrices (homeotropic orientation). The relaxation in bulk 5CB is due to reorientation of molecules around their short axis. It is clear that relaxation process in treated matrices is observed at much higher frequencies than in bulk sample and therefore cannot be assigned to the same mechanism. Since molecules of 5CB do not have component of dipole moment perpendicular to the long axis the only explanation of the observed high frequency relaxation in treated sample is to associate it with librational motion of molecules. This mode should be observed in 5CB if probing electric field is perpendicular to director as it takes place in treated sample. The lines in Fig. 1 represent the use of fitting analysis according to relation (1). For the bulk LC fitting line corresponds to Debye relaxation function ($\alpha = 0$, $\beta = 1$. The fitting line slightly deviates from experimental results at frequencies above 50 MHz indicating that there is deviation from a single process at higher frequencies due to imperfections in the alignment of bulk 5CB. The experimental results for liquid crystal in lecithin treated matrix could be easily fitted with a single relaxation process. The

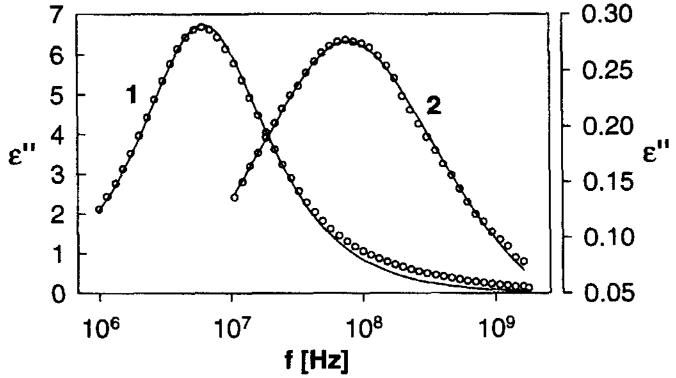

FIGURE 1: Dielectric spectra of: 1 - bulk 5CB (left axis) - relaxation due to the rotation of molecules around their short axis, T=303 K; 2 - 5CB confined in lecithin treated Anopore membrane (right axis) - librational mode, T = 305 K. Symbols: experiment, lines: fitting.

process for the librational mode observed in lecithin treated porous matrix is however of non-Debye type as the parameter $\alpha = 0.25$.

Figure 2 shows three types of temperature dependencies of dielectric spectra observed for confined 5CB in three temperature ranges.

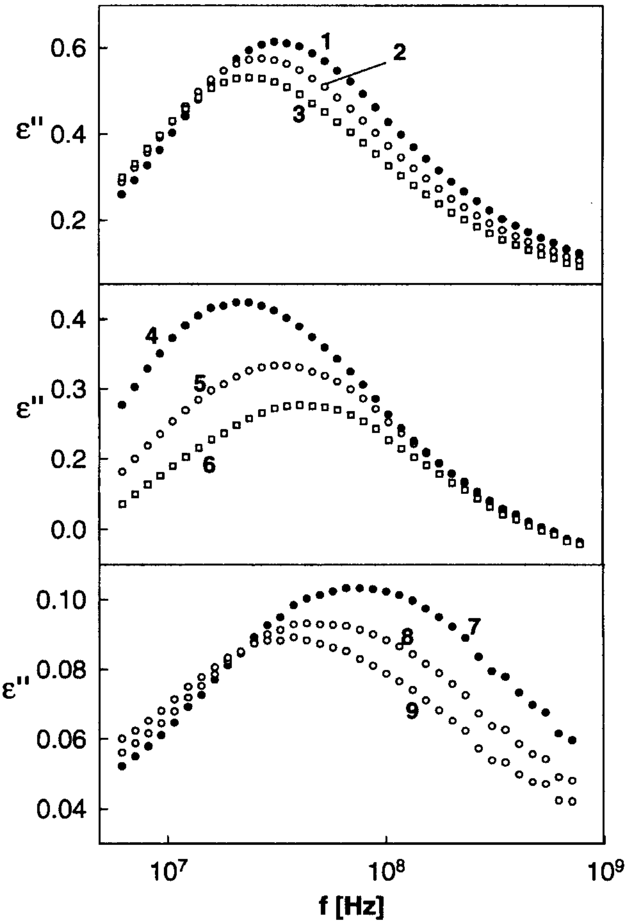

FIGURE 2: The frequency dependencies of the imaginary part of the dielectric permittivity (ϵ'') of 5CB confined in 2000 Å cylindrical lecithin treated pores at different temperatures: 1- 318.1 K, 2 - 314.1 K, 3 - 311.1 K (isotropic phase, mode due to the rotation of molecules around their short axis), 4 - 307.3 K, 5 - 306.9 K, 6 - 305.1 K (nematic phase, librational mode), 7 - 297.1 K, 8 - 288.1 K, 9 - 282.1 K (supercooled state, librational mode).

In the temperature ranges corresponding to the bulk isotropic phase (curves 1,2 and 3) and supecooled state (curves 7,8 and 9) the positions of ϵ'_m move to the lower frequencies with the decreasing the temperature. In nematic phase (curves 4,5 and 6) the positions of ϵ'_m move to the higher frequencies with decrease in the temperature indicating the faster relaxation rate at lower temperatures.

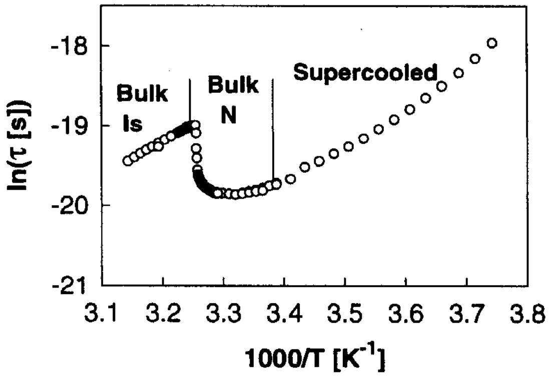

FIGURE 3: Temperature dependence of relaxation times of in 5CB confined in 2000 Å lecithin treated cylindrical pores.

The temperature dependence of the relaxation times obtained for 5CB confined in lecithin treated cylindrical pores is illustrated in Fig. 3. The temperature dependence of relaxation times of the librational mode is totally different from the behavior observed in investigations of relaxation due to reorientation of molecules around their short axis. The relaxation time of librational mode in the temperature range corresponding to the nematic phase increases upon increasing the temperature towards the nematic-isotropic transition temperature. In contrast, the temperature dependence of the relaxation times of the process due to reorientation around short axis decreases upon temperature increase in the same range of temperature. The interpretation of the results obtained in nematic phase needs the involvement of temperature dependence of orientational order parameter. The decrease of relaxation time in the temperature range from 308 K to 303 K for 5CB could be due to acceleration of process with increasing of order parameter. In the sample with homeotropic boundary conditions, in the case of perfect order (S=1) and taking into account that dipole moment of molecule is parallel to its long axis, the projection of dipole moment on the direction of the electric field that is along pore axis is minimal because the fluctuations of molecular orientations with respect to radial direction are very small. These fluctuations of the dipole moment (or molecular long axis) correspond to the librational motion of the molecule and the amplitude of the fluctuations determines the relaxation rate of dipole in the viscous media. At higher temperatures these deviations (fluctuations) are of greater amplitude (the order parameter is smaller) and this requires longer time to complete one librational cycle. As a result the relaxation rate is smaller for fluctuations of greater amplitude and vice versa. Such behavior has resulted in the particular temperature dependence of relaxation times observed for the librational mode in the nematic phase temperature range.

In the supercooled state the temperature dependence of relaxation times is mainly determined by the variations of viscosity.

CONCLUSION

The relaxation of librational mode in lecithin-treated cylindrical pores is observed in dielectric spectroscopy experiment. This is a proof of hometropic boundary conditions in this sample. The dynamics of the librational mode is totally different from the behavior observed in investigations of relaxation due to reorientation of molecules around their short axis. The interpretation of the temperature dependence of relaxation time needs the involvement of the temperature dependence of orientational order parameter and suggest that the better orientational order the faster the process due to libration of molecules. In the supercooled state the temperature dependence of relaxation times of the tumbling mode did not follow the behavior observed in the nematic phase and the sharp increase of the relaxation times upon decreasing the tempearture is mainly determined by the variations of viscosity.

Acknowledgement

This work was supported by NRO grant N00014-99-1-0558. F.A. acknowledges support from Japan Science and Technology Corporation, Tsukuba Research Consortium.

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