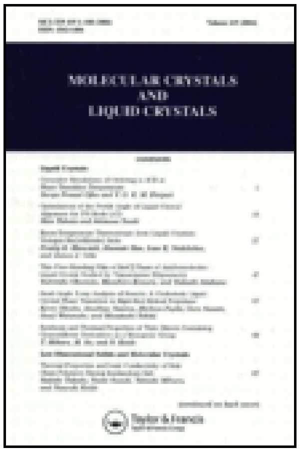

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DIELECTRIC RELAXATION OF NEMATIC LIQUID CRYSTAL CONFINED IN POROUS MATRICES

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Abstract Using dielectric spectroscopy in the frequency range 0.1 Hz-1.5 GHz, we investigated the dynamic properties of pentylcianobiphenyl (5CB) confined in porous matrices with randomly oriented, interconnected pores as well as in parallel cylindrical pores with different pores sizes. The confinement has a strong influence on the dielectric properties of LC which resulted in the appearance of a low frequency relaxational process ($f \leq 10$ KHz) absent in bulk and a strong modification of modes due to the molecular rotation around short axis and librational motion. From qualitative point of view the dielectric behavior of LC in random and cylindrical pores is similar. So we conclude that the finite size effect due to the confinement and existence of LC-pore wall interface have more influence on the properties of LC than the influence due to different porous structure.

INTRODUCTION

A variety of new properties and phenomena such as a modification of phase transitions, orientational order, elastic properties, director field, has been studied both experimentally and theoretically for liquid crystals confined in random and cylindrical pores (see a review articles[1-3] and the book[4]). Although great success in the understanding of physical properties of liquid crystals confined in porous media with different size, shape of pores and different structure of porous matrix was achieved, little work has been done to characterize the influence of confinement on different aspects of dynamical behavior of confined LC. In this paper we present the results of investigations of the influence of confinement and interface on the dynamic behavior of nematic liquid crystals (LC) dispersed in porous matrices, which have different pore structure, using broad-band dielectric spectroscopy. We used matrices with randomly oriented, interconnected pores (porous glasses with average pore sizes of 100 Å and 1000 Å) and parallel cylindrical pores (Anopore membranes with pore diameters of 200 Å and 2000 Å).

Since the volume of this paper is limited we restrict our consideration to the description of results obtained for 1000 Å random pores and we just mention observations for 100 Å random pores and cylindrical pores. Complete results of these investigations will be published separately.

EXPERIMENTAL

Measurements of the real (ϵ') and the imaginary (ϵ'') parts of the complex dielectric permittivity in the frequency range 0.1 Hz - 3 MHz were carried out at different temperatures using a computer controlled Schlumberger Technologies 1260 Impedance/Gain-Phase Analyzer. For measurements in the frequency range 1MHz - 1.5GHz we used HP 4291A RF Impedance Analyzer with a calibrated HP 16453A Dielectric Material Test Fixture. The samples were porous glass plates, of dimension $2 \times 2 \times 0.1 cm$ and Anopore membranes 60 μm thick impregnated with 5CB. The dipole moment of the 5CB molecule is $5D$, and it is parallel to the longitudinal axis of the molecule. The temperatures of phase transitions of 5CB in the bulk are T_{CN}=295 K and T_{NI}=308.27 K. Both matrices have practically negligible electrical conductivities, and their dielectric permittivities are independent of temperature and frequency over a wide range of frequencies.

RESULTS AND DISCUSSION

The dielectric behavior of confined 5CB is different from the behavior in bulk[5]. We observe at least three identified relaxational processes: low frequency (1 Hz - 10 KHz) which possibly overlaps with a hidden process in between 1kHz and 50 kHz, a very clear process in MHz frequency range and the last one in the frequency range f >30MHz. We call the process with the relaxation in MHz range as "bulk-like".

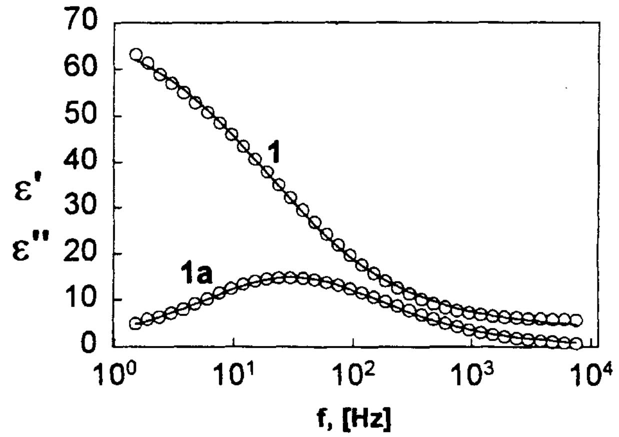

FIGURE 1 5CB in 1000 Å random pores, T= 19 °C. (1)-real and (1a)-imaginary parts of dielectric permittivity. Opened circles - experimental data, solid lines-fitting.

In this paper we will mainly consider the bulk-like relaxational process for 5CB in random pores of 1000 Å. We would like to mention that all observed processes were active up to 267 K in confined 5CB instead of being frozen as in the case of solid crystal, and the relaxation time of the first (slow) process in random pores shows glass-like behavior in a wide temperature range below bulk melting point. The examples of the low and the high frequency relaxations, are given in Fig. 1 and Fig. 2 which show frequency dependencies of the real and imaginary parts of the dielectric permittivity for 5CB in 1000 Å pores.

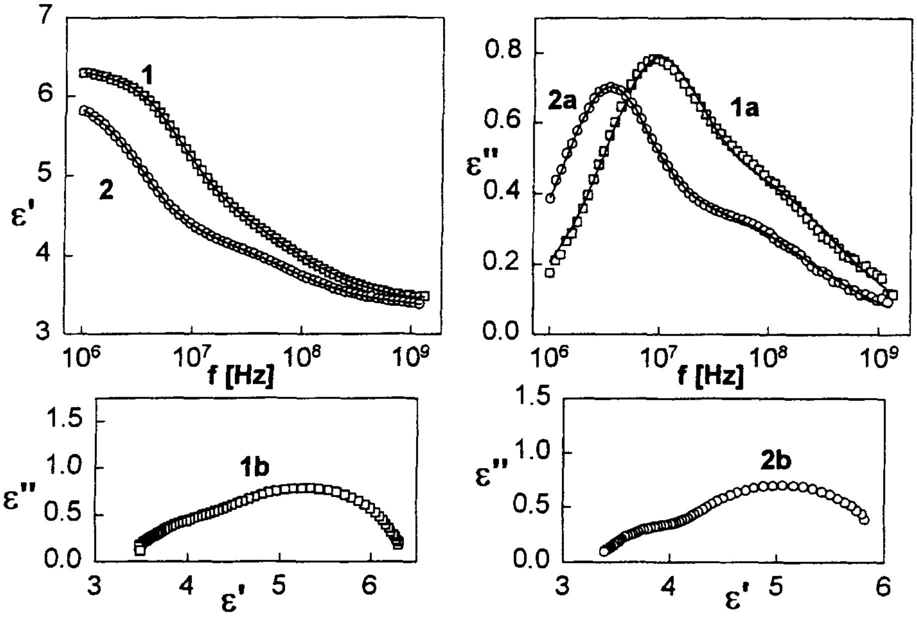

FIGURE 2 Frequency dependencies of ϵ' (1,2) , ϵ'' (1a), (2a) and Cole-Cole plots (1b), (2b) for 5CB in 1000 Å random pores. (1, 1a, 1b) - T = 31.6°C, (2, 2a, 2b) - T = 19.9°C.

The Cole-Cole plots were performed for all the samples and allows the use of the Debye equation for complex permittivity ϵ^*, modified by Cole and Cole[6].

According to Cole and Cole the frequency dependence of complex dielectric permittivity of a system which has more than one relaxational process is described by the equation:

$$\epsilon^* = \epsilon_\infty + \sum_{j=1}(\epsilon_{js} - \epsilon_\infty)/(1 + i2\pi f\tau_j)^{1-\alpha_j} - i\sigma/2\pi\epsilon_0 f^n, \qquad (1)$$

where ϵ_∞ is the high-frequency limit of the permittivity, ϵ_{js} the low-frequency limit, τ_j the mean relaxation time, and j the number of the relaxational process. The term

$i\sigma/2\pi\epsilon_0 f^n$ takes into account the contribution of a conductivity σ and n is fitting parameter ($n \simeq 1$). The solid lines in Fig. 1 and Fig. 2 represent the results of using formula (1) for the description of the observed dielectric spectra. In Fig. 1 the parameters discribing the low frequency relaxational process are: $\tau = 5.2 \cdot 10^{-3}s$, α=0.31. In Fig. 2 the parameters corresponding to lines 1, 1a are: $\tau_1 = 1.8 \cdot 10^{-8}s$, α_1=0.06, $\tau_2 = 1.1 \cdot 10^{-9}s$, $\alpha_2 = 0.26$, and for lines 2, 2a are: $\tau_1 = 4.9 \cdot 10^{-8}s$, α_1=0.02, $\tau_2 = 2.4 \cdot 10^{-9}s$, α_2=0.3. We believe that the relaxional process with $\tau \sim 10^{-8}s$ corresponds to the rotation of the molecule around the short axis[5]. The temperature dependence of relaxation times corresponding to the rotation of molecules around short axis for 5CB in 1000 Å random pores is presented in Fig. 3. The process with $\tau \sim (10^{-9} - 10^{-10})$s could be related to the librational motion of the molecules. This process was much more visible in random pores than in cylindrical pores.

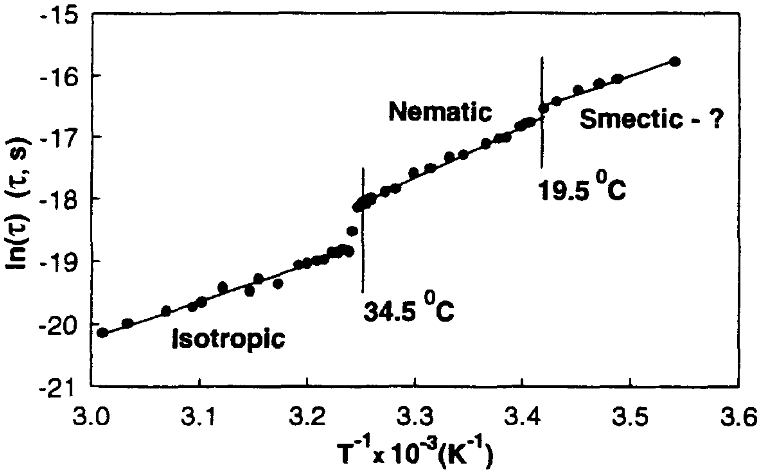

FIGURE 3 Temperature dependence of relaxation time corresponding to the molecular rotation around short axis.

The data analysis shows that the first (slow) relaxational process in 100 Å pores is slower than in 1000 Å pores, and the temperature dependence of these relaxation times in both random pores in the temperature interval (275-295) K for 1000 Å pores and in (275-305) K for 100 Å pores follow the Vogel-Fulcher law[7]: $\tau = \tau_0 exp(B/(T - T_0))$, which is characteristic of glass-like behavior. The parameters obtained by using this equation are: $\tau_0 = 1.7 \cdot 10^{-9}$ s, $B = 1240K$, $T_0 = 212K$ for 5CB in 1000 Å pores and $\tau_0 = 1.2 \cdot 10^{-5}$ s, $B = 627K$, $T_0 = 220K$ for 5CB in 100 Å pores. This along with the facts that relaxation times are strongly temperature dependent and there exists a spectrum of relaxation times suggests that the first relaxational process is probably not related to the low frequency dispersion given by the Maxwell-Wagner mechanism[6]. Possibly at low frequencies we observe the relaxation of interfacial polarization not due to Maxwell-Wagner effect but rather due to formation of a surface layer with polar ordering on the pore wall. In this case a new cooperative and slow process may arise. The relaxation times which we attribute to the molecular rotation around short axis in pores are of the same order of magnitude as in the bulk[5]. Howerver the temperature dependence of these relaxation times in pores (Fig. 3) is different from the bulk behavior. First of all in the temperature range corresponding to the anisotropic phase ($T < 34.5°\mathrm{C}$) in pores, $ln\tau$, is not a linear function of $1/T$. However if we consider the temperature regions $34.5°C < T < 20°C$ and $19.5°C < T < 9°C$ separately then $ln\tau = f(1/T)$ in each of these regions is resonably well approximated by a linear function and the corresponding activation energies are $U_1 = 0.74eV$ and $U_2 = 0.53eV$. The first activation energy U_1 is greater than the activation energy of bulk nematic phase ($U_b = 0.61eV$) but $U_2 < U_b$. We attribute the temperature range $34.5°C < T < 20°C$ to nematic phase. The activation energy in pores in nematic phase is greater because the pore wall imposes additional potential due to pore wall - molecule interaction. This potential is 0.13 eV ($2 \cdot 10^{-13} erg$), and taking into account that number of molecules per unit area is $(2-3) \cdot 10^{14} cm^{-2}$ we estimate surface potential of molecule-wall interaction $U_{surf} \sim 50 erg/cm^2$. The fact that $U_2 < U_1$ at the temperatures below 19.5°C is the evidence for smectic type order formation in this tempearture range. The change in relaxation time at nematic-isotropic phase transition in pores is not as sharp as in the bulk, and the relaxation time in pores at the transition does not change as much as in the bulk. The activation energy of isotropic phase of 5CB in pores is 0.51 eV. The retardation factor $g = \tau/\tau_{is}$ at nematic-isotropic phase transition temperature is $\simeq 1.8$, where as the corresponding typical value of g in bulk nematic liquid crystals is $\simeq 4$. Relatively smooth and small changes in τ at phase transition in pores suggest that the "isotropic" phase of LC in pores is not bulk like with complete disorder in molecular orientations, and some orientational order still persists.

The relaxational process at the frequencies $f > 50$ MHz was observed[8-11] in alkylcyanobiphenyls for an orientation of the electric field perpendicular to the director. One of the suggested explanations[9] of the origin of this high frequency relaxation was given in terms of librational motion of molecules. In random pores, there are always molecules oriented perpendicular to the electric field regardless of the molecular alignment inside pores. So we suppose that the mode observed in the frequency range $f > 30$ MHz has the same origin as earlier was found for bulk alkylcyanobiphenyls. The difference is that in our experiments, as it is clearly seen from Fig. 2, the existence of this mode is obvious even without deep analysis, where as for bulk alkylcyanobiphenyls the conclusion about high frequency relaxation was made on the basis of of fitting procedure. In 100 Å random pores the third procces was also clearly observed but it's amplitude was smaller than in 1000 Å pores. This is because the volume fraction of liquid crystal in 100 Å pores is smaller than in 1000 Å. It is surprising that this process was detected in cylindrical pores as well. 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 short axis dominates, we conclude that majority of the molecules are oriented along the pore axis and structure of 5CB in the cylindrical pores is axial. However due to the fact that the high frequency process (at f >30 MHz) is also detected we assume that small fraction of molecules presumably at the pore walls are tilted with respect to the axis direction. The relaxation time of the third mode does not depend on applied d.c. bias voltage up to 40 V, but it is temperature dependent.

CONCLUSION

From qualitative point of view the dielectric behavior of LC in random and cylindrical pores is similar. So we conclude that the size effect due to the confinement and existence of LC-pore wall interface have more influence on the properties of LC than the influence due to different porous structure.

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