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Finite Size and Interfacial Effects in Liquid Crystals Confined to Random Porous Matrices: Broadband Dielectric Spectroscopy Investigations

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The dielectric behavior of confined 8CB has been investigated by means of ultra broad-band dielectric spectroscopy. New features such as two relaxation processes with characteristic frequencies around (1–10) Hz and 100 kHz, which are absent in bulk liquid crystals, were observed in confined geometries. These processes arise due to the relaxation of interfacial polarization at pore wall-liquid crystal interface and the hindered rotation of the molecules near the interface respectively. Two other bulk like modes due to the rotation of polar molecules around their short axis and due to tumbling of molecules were also observed in confined geometries. We also investigated these processes in the supercooled state. All observed processes are non Debye like.

Keywords: dielectric spectroscopy; liquid crystals; confinement

INTRODUCTION

Dielectric spectroscopy contributes significantly to the overall characterization of porous materials in general, and investigations of condensed matter confined to porous media in particular. This method can be applied to investigate multiple aspects of the influence of confinement on the dynamic properties of LCs. Applications of dielectric spectroscopy to confined glass-forming liquids[1,2] and liquid crystals (LCs)[3–7] revealed new information on the changes in the molecular mobility, the broadening of the distribution of relaxation times, as well as changes in the glass and the phase transition temperatures.

In this paper we report the study of the dielectric properties of octylcyanobiphenyl (8CB) confined to random pores. Broadband dielectric spectroscopy in the frequency range 10^{-3} Hz-$1.5{\cdot}10^{9}$ Hz was applied to investigate the influence of confinement on the dynamical behavior of the 8CB in isotropic, nematic, and smectic-A phases, and in supercooled state.

EXPERIMENTAL

We used porous silica glasses with randomly oriented and interconnected pores as matrices with mean pore sizes of 100 Å and 1000 Å and volume fractions 27% and 40% respectively. These matrices were solid plates with dimensions 25 mm $\times$25 mm $\times$1 mm. The porous silica glasses have negligible electrical conductivity, and their dielectric permittivity is practically independent of frequency and temperature. We impregnated these porous glasses with liquid crystal 8CB at temperatures corresponding to isotropic phase. The bulk 8CB has a nematic phase in the temperature range of 40.8-33.5 °C and a smectic phase in the temperature range of 21.1-33.5°C.

Measurements of the real (ϵ') and the imaginary (ϵ'') parts of the complex dielectric permittivity in the frequency range 10^{-3} Hz to 1.5 GHz were performed using two sets of devices. In the range from 10^{-3} Hz to 3 MHz we used the Schlumberger Technologies 1260 Impedance/Gain-Phase Analyzer in combination with Novocontrol Broad Band Dielectric Converter and an active sample cell (BDC-S). The sample was mounted between two gold plated parallel plates and placed in the shielded cell. For measurements in the frequency range 1 MHz-1.5 GHz we used Hewlett-Packard 4291A rf Impedance Analyzer. The temperature stabilization was better than 0.01°C.

For the quantitative analysis of the dielectric spectra the Havriliak-Negami function 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 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.

BROADBAND SPECTRA OF CONFINED 8CB

The dielectric behavior of confined 8CB that we investigated is very different from its bulk behavior. Figure 1 represents the broadband dielectric spectrum for confined 8CB measured at 310 K. The figure is a typical example of the broadband dielectric spectra observed for confined LC. It is clear from Fig. 1 that for 8CB confined in 100 Å, at least five dispersion regions could be obviously identified: a low frequency dispersion around $10^{-2}-10^{-1}$ Hz, a clear broad process ($10^{-1}-10^{4}$ Hz), a third process in the frequency range $10^{4}-10^{6}$ Hz, a very clear process in MHz frequency range and the last one in the frequency range f >30 MHz. For 8CB confined in 1000 Å random pores the dielectric spectra are similar to that observed in 100 Å pores. The last two processes are observed to be clearly separated for 8CB confined in 1000 Å random pores. This has been presented in the inset of Fig. 1 for $T = 300$ K.

Data analysis and application of formula (1) show that the frequency dependence of ϵ'' for $f < 0.1$ Hz is mainly due to Ohmic conductivity. All the other four processes have relaxation origin and are quantitatively described by the Havriliak-Negami formula. All the relaxation processes are of non-Debye-type. We suggest that the low frequency process with characteristic frequency (the frequency corresponding to the maximum of ϵ'', and that in the simplest case of the Debye relaxation, is related to τ as $\tau = 1/2\pi f$) 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 pores that does not exist in bulk LCs. The characteristic frequency of this process is identified as f_2 in Fig. 1. This relaxation is due to the rotation of molecules, located in the surface layer formed at pore walls. This process

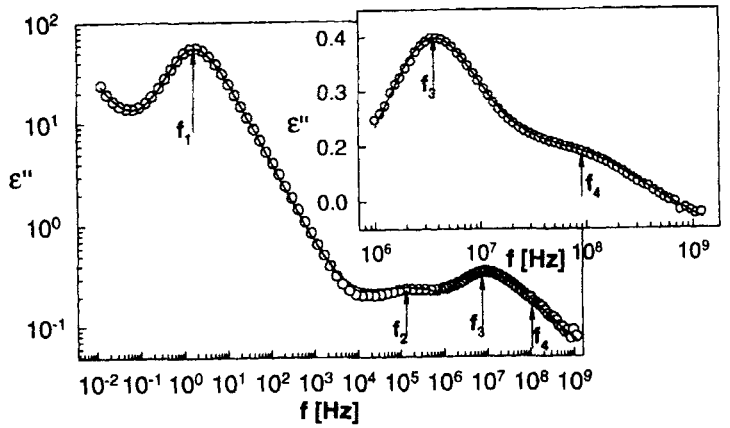

FIGURE 1: Imaginary part of the dielectric spectrum for 8CB in 100 Å pores for $T = 310$ K. Open circles: experiment; solid line: fitting. Inset: high frequency part of the spectrum for 8CB in 1000 Å pores, $T = 300$ K. The arrows indicate the characteristic frequencies of different relaxation processes.

is slower than the process due to rotation of molecules in bulk because the viscosity in surface layers is greater than the bulk viscosity.

The last two processes in MHz and 100 MHz frequency range observed for both matrices are "bulklike". The first one is due to the rotation of molecules about its short axis and the second one is due to the tumbling of the molecules about their molecular short axis. These two processes in pores, although having the same mechanism as in bulk, are strongly modified by confinement. First of all, in pores these processes are characterized by a spectrum of relaxation times instead of being the Debye type with single relaxation time. There are also marked changes in the temperature dependence of the relaxation times compared to the bulk behavior.

TEMPERATURE DEPENDENCE OF RELAXATION TIMES

The temperature dependencies of the relaxation times (τ) corresponding to the rotation of molecules around the short axis for 8CB confined in 100

and 1000 Å pores are presented in Fig. 2. These dependencies provide

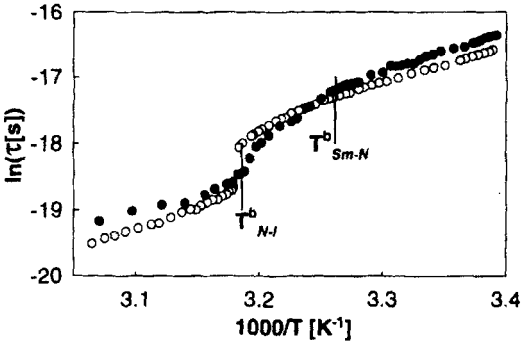

FIGURE 2: Temperature dependence of relaxation times of the process due to the rotation of molecules around short axis for confined 8CB. Closed circles: 100 Å; open circles: 1000 Å pores.

us with the information on the influence of confinement on the isotropic-nematic and the nematic-smectic-A phase transitions. In the temperature range corresponding to the liquid crystalline phases in pores, there are no abrupt changes in the relaxation times as it is for the bulk nematic-smectic-A phase transition. Instead, the relaxation times smoothly increase while the temperature varies from values corresponding to the nematic phase to that of the smectic-A phase. On the other hand the slope of the $\ln \tau$ versus $1/T$ (Fig. 2) slightly decreases in the temperature range corresponding to the smectic-A phase as for bulk LCs having nematic and smectic-A phases. These obsrvations are in agreement with previously made conclusion[8] that the smectic phase is still present in pores, however, the nematic-smectic-A phase transition is considerably broadened. We also observe that the changes in relaxation times at the isotropic-nematic phase transition in pores for both LCs are not as sharp as in bulk, and the relaxation times in pores at the transition do not change as much as in bulk. Relatively smooth and small changes in τ at isotropic-nematic phase transition in pores suggest that the "isotropic" phase of LCs in pores is not bulklike with complete disorder in molecular orientations, and some orientational order still persists.

The highest frequency process (due to molecular tumbling) was more visible in 1000 Å pores than in 100 Å pores. The pore size dependence of the dielectric strength of the process due to the tumbling motion suggests that in anisotropic phases 8CB in 100 Å pores macroscopically is less ordered than in 1000 Å pores. The influence of the disorder imposed by the random porous structure (geometrical disorder) affects the physical properties and phenomena that are mainly determined by the order at macroscopic scales.

CONFINED 8CB IN SUPERCOOLED STATE

Figure 3 shows the dependencies of the imaginary part of the dielectric permittivity ϵ'' versus frequency ($10^{-2} - 10^{6}$ Hz) and temperature (316.0-208.0 K) for 8CB confined in 100 Å pores. In the low frequency range the process

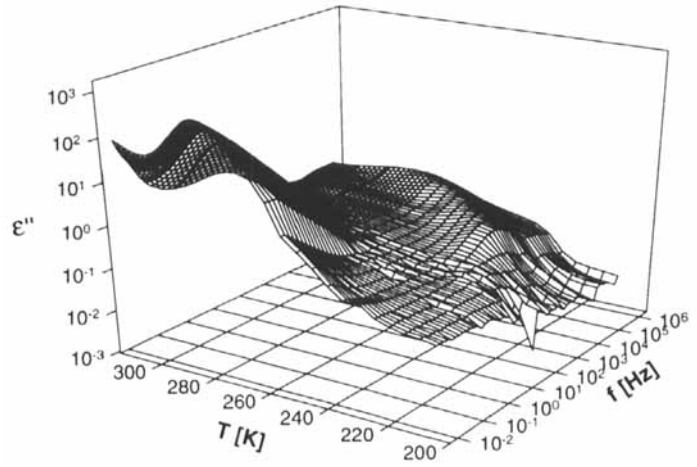

FIGURE 3: Three-dimensional plot of the frequency and the temperature dependence of the imaginary part of dielectric permittivity ϵ'' for 8CB in 100 Å pores.

earlier identified as f_1 is clearly visible and goes out of the measurement range in the very low temperature region due to glasslike slowing down. The surface molecular process is present in the whole temperature range but it is less visible because of its small amplitude. In the low temperature

region, the dielectric relaxation due to the rotation of molecules around the short axis shifts into the frequency range $10^{-2} - 10^{6}$ Hz. This process is observed to be present even up to 230 K. The process due to tumbling of molecules is also present at very low temperatures and can be seen in the high frequency region. In fact we found that all the observed relaxation processes were not frozen even at 60° below bulk crystallization temperature. To show dramatic changes in the rate of the relaxation process in supercooled state we have presented, as an example, the dielectric spectrum measured for the process due to the rotation of molecules around the short axis at two very different temperatures in Fig. 4. The dielectric process in the supercooled state is well described by the Havriliak-Negami function (1). The characteristic frequency (f_m) of this process in the supercooled state changes by more than 3000 times compared to f_m obtained at the temperature corresponding to the nematic phase.

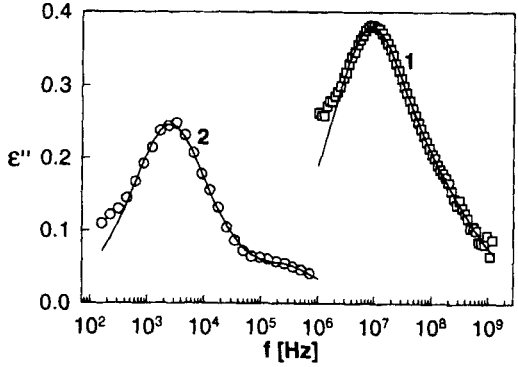

FIGURE 4: Frequency dependencies of ϵ'' for 8CB in 100 Å pores. 1: $T = 310$ K; 2: $T = 233$ K. Open symbols: experiment; lines: fitting.

We can see from Figs. 3 and 4 that all the four relaxation dispersions are strongly temperature dependent. Rigorous analysis shows that the temperature dependencies of the relaxation times follow the Vogel-Fulcher law: $\tau = \tau_0 exp(B/(T - T_0))$. From this we conclude that there is evidence for glass-like dynamical behavior for confined 8CB in supercooled state, although in bulk it does not show glassy properties. The small pore size

(surface effects) and random pore structure (geometrical disorder) stimulate partial disorder (at least at long scales) and prevent crystallization. Therefore LC supercooled in small random pores has properties typical for glass forming liquids.

CONCLUSION

The dielectric behavior of 8CB confined in porous matrices is very different from its bulk behavior. Two new processes with relaxation origin are observed in addition to the two modified bulklike dielectric processes. Confined 8CB can be supercooled up to 60° below bulk crystallization temperature. All the four relaxation processes are strongly temperature dependent and there is clear evidence for glasslike behavior.

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