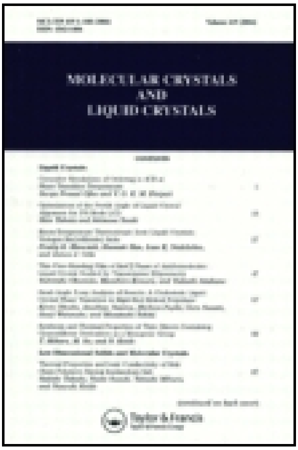

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Photon Correlation Spectroscopy of Confined Liquid Crystals in Isotropic, Nematic, and Smectic Phases

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Photon correlation experiments were performed to study the influence of confinement on the dynamic behavior of liquid crystals (LCs) in isotropic, nematic and smectic-*A* phases. In isotropic phase the only fast, single exponential decay due to the order parameter fluctuations is observed. While decreasing the temperature, but still above I-N phase transition in pores, the contribution from this decay decreases and second decay due to director fluctuations appears. The existence of this decay is the evidence for the formation of ordered (paranematic) phase preceding I-N transition in confined LCs. In nematic phase the decay due to order parameter fluctuations vanishes, the relaxation due to director fluctuations dominates, and slow process absent in the bulk LC appears. In smectic phase the director fluctuations are almost frozen.

Keywords: photon correlation spectroscopy; liquid crystals; confinement

INTRODUCTION

Studies of liquid crystals confined in porous media have been very useful in exploring both the fundamental physics of condensed matter and in applications. Although a great success[1] in the understanding of the physical properties of LCs confined in porous media with different size and shape of pores and different structure of porous matrix was achieved, little work has been done to characterize the influence of confinement on the dynamical behavior of LCs. Different aspects of the dynamical behavior of confined LCs can be investigated by photon correlation spectroscopy. Using this method has been shown[2–8] that different kind of confinement strongly influences dynamics of different fluctuations in LCs. In this paper we report on the investigations of the influence of the confinement on the dynamic behavior of alkylcyanobiphenyls (5CB and 8CB) confined in porous matrices by means of photon correlation spectroscopy. Investigations of LC in cylindrical pores together with studies in random porous matrices, makes it possible to separate the role of random structure from the contributions due to the existence of LC-solid pore wall interface and finite size effect in the dynamical behavior of LC.

EXPERIMENTAL

We performed photon correlation measurements using a He-Ne laser operating at wavelength λ=6328 Å, and an ALV-5000/fast digital multiple tau correlator (real time) operating over delay times from 12.5 ns up to 10^3 s. The depolarized component of scattered light was investigated. In the dynamic light scattering experiment, one measures the intensity-intensity autocorrelation function $g_2(t) = \langle I(t)I(0)\rangle/\langle I(0)\rangle^2$. The intensity-intensity autocorrelation function $g_2(t)$ is related to the dynamic structure factor $f(q,t)$ of the sample by $g_2(t) = 1 + kf^2(q,t)$, where k is a contrast factor that determines the signal-to-noise ratio and $q = 4\pi n \sin(\Theta/2)/\lambda$, ($n$ is the refractive index, Θ - the scattering angle). All the dynamic light scattering data discussed below were obtained at Θ=30°. 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). The matrices were impregnated with liquid crystals 5CB and 8CB. The bulk 5CB has a nematic phase in the temperature range of 295 - 308.18 K. 8CB has a smectic A phase in the temperature range of 294.2 - 306.72 K in addition to the nematic range of 306.72 - 313.85 K.

RESULTS AND DISCUSSION

Dynamic light scattering in bulk liquid crystals is well understood[9], and in the nematic phase the main contribution to the intensity of scattered light is due to the director fluctuations. If for simplicity we assume that six Leslie coefficients have the same order of magnitude and are $\sim \eta_{eff}$ (η_{eff} is the effective viscosity), and three elastic constants (bend, splay and twist) are equal to K_{eff} (K_{eff} is the effective elastic constant) then the relaxation time of director fluctuations is[9]

$$\tau = \frac{\eta_{eff}}{K_{eff}q^2}. \qquad (1)$$

The corresponding decay function is single exponential. The experiments show significant changes in the physical properties of confined LCs. The difference between the dynamic behavior of confined and bulk LC in nematic phase, observed in photon correlation experiments, can be seen by comparing curves (1) - (4) in Fig. 1. In nematic phase of bulk 5CB the observed relaxation process due to director fluctuations is single exponential (curve 1) in agreement with the theory[9]. Slow relaxation process which does not exist in the bulk LC and a broad spectrum of relaxation times appear for 5CB in both random and cylindrical pores if LC is in anisotropic phase (curves 2-4). It is clear from Fig.1 that the relaxation processes in 5CB confined in the both matrices are highly nonexponential, as it is usually observed in glasses and glass-like systems. The long time tail of the

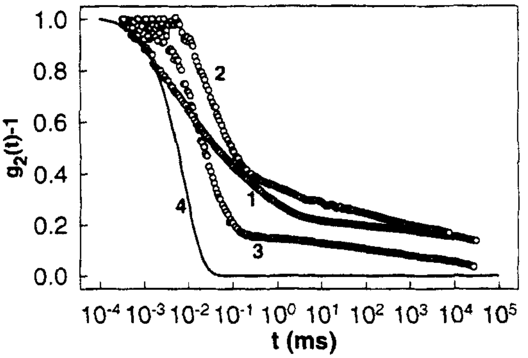

FIGURE 1: Intensity/intensity autocorrelation functions for 5CB: (1): bulk, T=301.1 K; (2): 100 Å random pores, T=295.8 K; (3): 200 Å cylindrical pores, T=301.8 K, (4): 2000 Å cylindrical pores, T=307.3 K.

relaxation process for 5CB in pores can not be described by using standard form of dynamical scaling variable (t/τ). It is reasonable for so slow dynamics to use[2] the scaling variable $(lnt/ln\tau)$.

We found that the decay function:

$$f(q,t) = a \cdot exp(-(t/\tau_1)^{\beta}) + (1-a) \cdot exp(-x^{z}), \tag{2}$$

where $x = ln(t/\tau_0)/ln(\tau_2/\tau_0)$, and $\tau_0 = 10^{-8}s$ provides suitable fitting for 5CB in pores. For 5CB in 100 Å random pores the second term in relationship (2) dominates, whereas for cylindrical pores and 1000 Å random pores the contribution from the first term is much more visible.

The relaxation time of slow process for 5CB in 100 Å pores strongly increases when temperature decreases from 300 K up to 270 K varying from 1.7×10^{-4} to 14 s. The data analysis shows that the temperature dependence of the relaxation times obeys the Vogel-Fulcher law $\tau = \tau_0 exp(B/(T - T_0))$ with parameters: $\tau_0 = 1.4 \cdot 10^{-11}$ s, B=847 K, and T_0=246 K. This behavior is typical for glass forming liquids.

The dynamical behavior of LCs confined in large pores (1000 Å and 2000 Å) was closer to the bulk behavior as we expected. However slow decay was observed in anisotropic phase. The dynamic behavior of LCs in cylindrical pores at different temperatures is illustrated in Fig. 2 and Fig. 3. Curve 1

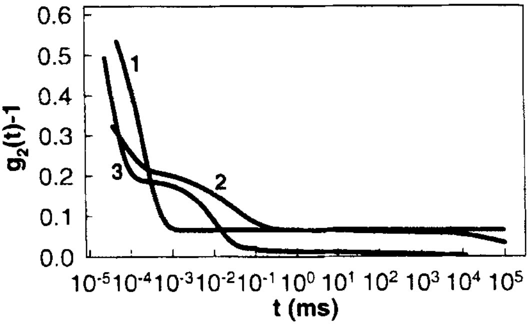

FIGURE 2: Intensity/intensity autocorrelation functions for 5CB in cylindrical pores: (1) and (2): 2000 Å, (3): 100 Å, (1): T = 307.9 K; (2): T = 307.7 K; (3): T = 307.05 K.

(Fig. 3) obtained for 5CB illustrates dynamical behavior of confined LCs in isotropic phase. In 2000 Å pores at T = 307.9 K (curve 1), which is below bulk T_{NI}^{b} but above T_{NI}^{p} in pores, only the fast decay due to the order parameter fluctuations is observed. This decay is single exponential with the relaxation time $\tau=3.8\cdot10^{-7}$ s. With decreasing the temperature (but still above T_{NI}^{p}) the contribution from order parameter fluctuations decreases and a visible second decay (curve 2 in Fig. 2) due to director fluctuations appears. The same behavior is observed in 200 Å cylindrical pores (curve 3). The existence of this process in the transitional temperature region is an experimental confirmation of the formation of ordered phase preceding isotropic-nematic phase transition in confined LC. This ordered (paranematic) phase has some features of nematic phase. However, the decay corresponding to the director fluctuations in confined LCs is not single but is stretched exponential. The superposition of single exponential and stretched exponential decays adequately describes experimental data in transitional temperature region. We determine the nematic-isotropic phase transition temperature for LCs in pores as the temperature above which there is no visible decay due to order parameter fluctuations. For 8CB confined in cylindrical pores bulk-like relaxation of director fluctuations is

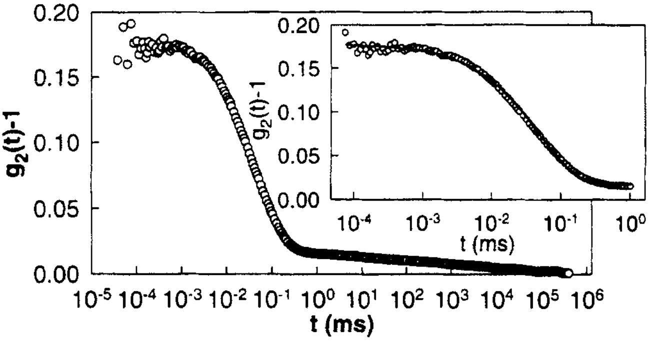

FIGURE 3: Intensity/intensity autocorrelation function for 8CB in 2000 Å cylindrical pores at T = 312.65 K. The inset shows the result of fitting. Open symbols-experiment, solid line - fitting.

also observed in nematic phase. But in pores this relaxation is a stretched exponential which is typical for glass forming systems. The first term in the formula (2) adequately describes the experimental data up to $t < 0.1$ s. The data presented in the inset of Fig. 3 have parameters $\tau = 0.11$ ms and $\beta = 0.76$.

The temperature dependence of the relaxation time of director fluctuations for 8CB confined in 2000 Å cylindrical pores in nematic phase, obtained by fitting of data in the restricted time window, is presented in Fig. 4. This figure also shows relaxation times of director fluctuations of bulk 8CB in nematic phase. The lower values of the relaxation times for confined 8CB compared to the bulk values can be explained as follows. The measurements are performed at wave number corresponding to the linear size $l = 2\pi/q \approx 7600$ Å. This size is larger than the pore size d=2000 Å. Therefore, for the confined liquid crystal (intrapore fluctuations) q should be replaced by $2\pi/d$ in the expression (1). In this case, the ratio of the bulk relaxation time (τ_b) to the relaxation time (τ_p) of LC in pores is ≈ 14.5. In the temperature range $307 < T < 313$ K (the flat part of temperature dependence or the relaxation times in Fig. 4) $\tau_b/\tau_p \approx 4.7$. It is natural to assume that the local orientational elasticity is not altered significantly by cylindrical pore. Then the only reason leading to much smaller changes,

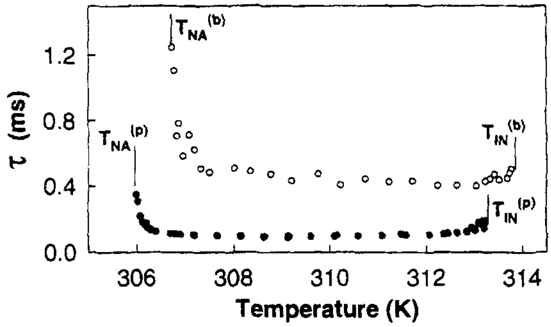

FIGURE 4: Temperature dependence of director fluctuations relaxation time for bulk and confined 8CB. Opened circles-bulk, closed circles-in 2000 Å pores.

than predicted by formula (1). in relaxation times of confined nematics is an increase in the effective viscosity of LCs due to the confinement. It follows from the above estimations that the effective viscosity of LCs in 2000 Å cylindrical pores is by factor 3 large than the bulk viscosity. This difference is reasonable because the thickness of the layer of LC in pores of 2000 Å diameter can not exceed 1000 Å. and the effective viscosity of confined LC is the surface viscosity that is larger than the bulk viscosity.

It should be noted that the slow relaxation process in confined LCs vanishes if the relaxation due to director fluctuations vanishes. and the slow process is connected to the existence of nematic (or nematic like) ordering. One of the possible explanations (together with the model suggested in [2,3] and the model based on slow motions of domains [4]) of the origin of the slow decay may be a formation of interfacial layers on the pore wall.

We found that at the nematic-smectic-A transition the amplitude of the decay due to the director fluctuations drastically decreases and the contrast ratio becomes less than 0.01. These changes in the autocorrelation functions are accompanied by the appearance of a significant noise in the smectic phase at the time window $t < 0.05$ ms. The quantitative analysis of the relaxation processes in smectic-A phase is very difficult. However. the long time tail of the slow decay at times scale $t > 1$ ms can be distinguished from the noise.

Temperature dependent changes in auotcorrelation functions allow to determine the shifts of phase transition temperatures due to confinement $\Delta T_{IN} = T^b_{IN} - T^p_{IN}$. and $\Delta T_{NA} = T^b_{NA} - T^p_{NA}$. where subscripts IN and NA identify isotropic-nematic and nematic-smectic-A phase transitions. and superscripts b and p identify temperatures corresponding to bulk LCs and LCs in pores respectively. For 5CB we obtain: $\Delta T_{IN} = 0.65$ °C in 1000 Å random pores. 0.55 °C in 2000 Å pores. and 1.15 °C in 200 Å pores. For 5CB confined in 100 Å random pores we found that there is no well defined phase transition from ordered phase to the phase in which long range order is completely absent. or opposite from disordered phase to the phase with perfect long range orientational order. For 8CB in 2000 Å the shifts of the phase transition temperatures are $\Delta T_{IN} = 0.55$ °C. and $\Delta T_{NA} = 0.77$ °C.

CONCLUSION

The photon correlation experiments show significant changes in the physical properties of confined LCs and suggest that there is some evidence for glass-like dynamical behavior, although bulk liquid crystals do not have glassy properties. Slow relaxation process which does not exist in bulk LC and a broad spectrum of relaxation times appear for LC confined in random and in cylindrical pores. Since both the slow relaxation process which does not exist in the bulk LC and the broad spectrum of relaxation times appear not only for LC in random pores but in cylindrical pores, we suggest that the differences in the dynamical behavior of confined LC from that in the bulk are mainly due to the existence of the LC-pore wall interface.

Acknowledgments

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