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DYNAMIC AND STATIC LIGHT SCATTERING AT PHASE TRANSITIONS IN LIQUID CRYSTAL CONFINED INTO POROUS POLYMER FILM

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Autocorrelation function $g_2(\tau)$ and intensity (I) of the depolarized scattered light were obtained at the study of a dynamic light scattering from the composite liquid crystal (LC) material, consisting of porous polyethyleneterephthalate (PET) film filled with octylcyanobiphenyl (8CB). The simultaneous analysis of these parameters made possible to extract the temperatures T_{IN} and T_{NA} of the isotropic liquid – nematic ($N-I$) and nematic – smectic A ($N-SmA$) phase transitions in LC samples confined into cylindrical pores of diameters in the range of 0.02 ... 2 μm . The dependences of T_{IN} and T_{NA} on the pore diameter were obtained and compared with the theoretical predictions. It was shown that simultaneous investigations of dynamic and static light scattering can be considered as a perspective approach for a study of phase transitions in LCs at strong confinement, which is typical for composite LC materials.

Key words: liquid crystals, porous films, phase transitions, dynamic light scattering, static light scattering.

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ДИНАМИЧЕСКОЕ И СТАТИЧЕСКОЕ РАССЕЯНИЕ СВЕТА ПРИ ФАЗОВЫХ ПЕРЕХОДАХ В ЖИДКОМ КРИСТАЛЛЕ, ПОМЕЩЕННОМ В ПОРИСТУЮ ПОЛИМЕРНУЮ ПЛЕНКУ

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Автокорреляционная функция $g_2(\tau)$ и интенсивность (I) деполаризованного рассеянного света были получены при исследовании динамического рассеяния света от композиционного жидкокристаллического (ЖК) материала, состоящего из пористой пленки полиэтилентерефталата (ПЭТ), заполненной октилцианобифенилом (8CB). Одновременный анализ данных параметров позволил получить температуры T_{IN} и T_{NA} фазовых переходов изотропная жидкость – нематик ($N-I$) и нематик – смектик А ($N-SmA$) в ЖК-образцах, ограниченных цилиндрическими порами с диаметрами в диапазоне 0,02 ... 2 мкм. Были получены, и сравнены с предсказаниями теории, зависимости T_{IN} и T_{NA} от диаметра пор. Показано, что одновременное исследование динамического и статического рассеяния может рассматриваться как перспективный подход для изучения фазовых переходов в жидких кристаллах при сильных пространственных ограничениях, типичных для композиционных жидкокристаллических материалов.

Ключевые слова: жидкие кристаллы, пористые пленки, фазовые переходы, динамическое рассеяние света, статическое рассеяние света.

Introduction

Photon correlation spectroscopy is a useful optical tool to study the behavior of liquid-crystalline systems with micron and submicron confinements (for example, plane layers of LC [1], liquid crystal emulsions [2], porous media [3], etc.) where traditional techniques are inapplicable. Such method provides measurements of droplets diameters in LC emulsions, temperature of phase transitions, anchoring strength, etc. on the basis of analysis of relaxation times of director fluctuations. Porous films with cylindrical cavities filled by LC are interested from the fundamental point of view and can be used, for example, in photonics [4–6] and microfluidics [7]. For the letter application, effective shear viscosity plays the essential role, as it determines the technical characteristics of LC electro-hydrodynamic pump [7]. In turn, the effective value of the shear viscosity depends on the orientational structure of LC, formed in porous film. Direct measurements of the shear viscosity of liquid crystals, flowing through the porous film [7, 8], confirmed the non-homogeneous type of such structure, which is in accordance with the previously obtained results [4–6]. It makes the problem of calculation of normal modes of the director fluctuations inside pores more difficult in the comparison with the case of homogeneous orientation, realized in plane layers of LC [1]. Nevertheless, analysis of correlation function in DLS measurements makes possible to get information about temperatures of phase transitions in LC confined to pores of polymer film [9]. One has to take into account that the

noise component in the autocorrelation scattering function increases with decreasing of the pore size. It reduces the accuracy of the phase-state analysis of the LC in the porous film. Here we present the results of complex studies of phase transitions in liquid-crystalline *octylcyanobiphenyl* (8CB) confined by anisotropic *polyethylene terephthalate* films with cylindrical pores of various diameters $d = 0.02...2 \mu\text{m}$, using the dynamic and static light scattering measurements. The final aim of such approach is the increasing of reliability at determination of the phase transition temperatures in liquid crystals at strong confinement, realized in porous PET films.

Experimental

In our experiments, a liquid crystal *octylcyanobiphenyl* produced by Merck without special purification, was filled in porous films of *polyethylene terephthalate* of thickness $h = 23 \mu\text{m}$. The cylindrical and randomly allocated pores of diameters $d = 0.02, 0.1, 0.2, 0.3, 0.5, 1$ and $2 \mu\text{m}$, were obtained by using a well-known technology [10, 11] of the track-etched membranes production (Fig. 1, *a, b*). Prepared samples were filled with 8CB at room temperature. Afterward the samples were wiped to remove parasite surface layers of LC. Photon correlation spectrometer (Photocor Complex, Russia) with Dyna LS software was used to study dynamic (DLS) and static (SLS) light scattering of 8CB from the porous PET films filled with LC. Geometry of experiment is shown at Fig. 1, *b*. The scattering angle θ was equal to 15° in all experiments described below.

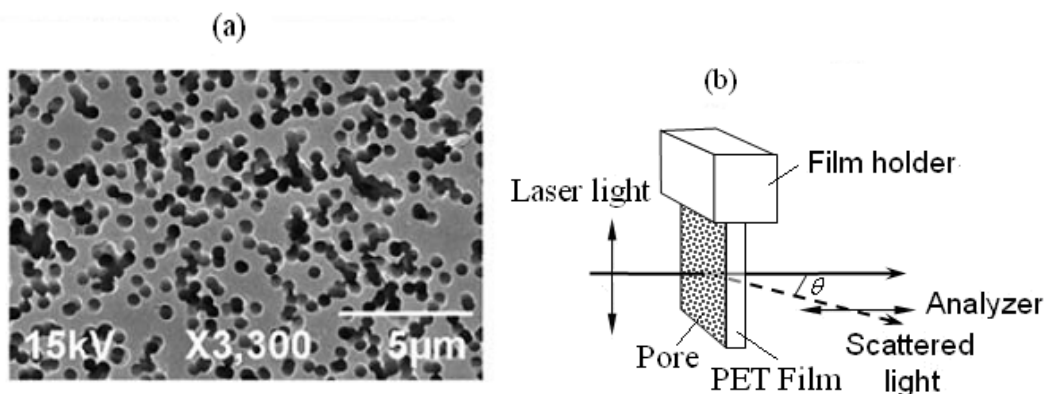


Fig. 1. Typical TEM images of porous PET film (*a*) and experimental geometry (*b*)

Results and discussion

The typical example of autocorrelation function $g_2(\tau)$ (a) and relaxation spectra of τ in nematic phase of 8CB are shown in Fig. 2.

The sharp peak of the spectra (Fig. 2, b) within the window 0.1..10 ms can be assigned to the thermal orientational fluctuations of the nematic ordering.

The temperature dependence of the effective

relaxation time τ , corresponding to the maximum of the above mentioned peak, is shown in Fig. 3, a for a fixed value of the pore's diameter $d = 2R$.

The arising of the mentioned above relaxation peak at cooling from isotropic to nematic phase and its further disappearance in smectic A phase can be used for determination of the temperatures of the isotropic-nematic (T_{IN}) phase transition and nematic-smectic A (T_{NA}) phase transitions.

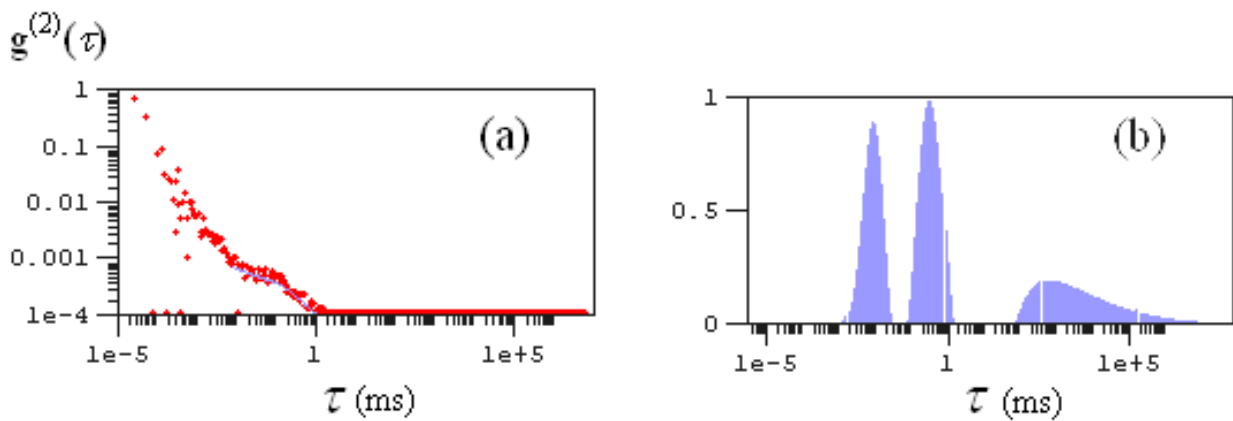


Fig. 2. Example of dynamic light scattering characteristics for 8CB-PET samples: autocorrelation function $g_2(\tau)$ (a) and relaxation spectra of τ (b) for pores diameter 500 nm at temperature 310.9 K, corresponding to N-phase

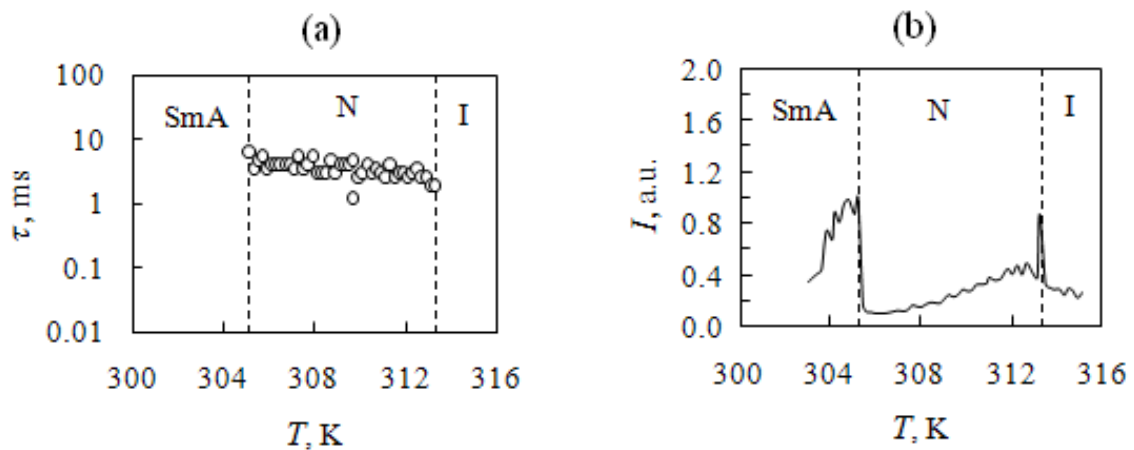


Fig. 3. The temperature dependence of dynamic and static light scattering parameters of 8CB-PET sample ($d = 500$ nm): the peak values of the relaxation time τ (a) and the intensity I (b) of light scattering

Table 1. The temperatures of phase transitions nematic – smectic A (T_{NA}) and isotropic – nematic (T_{IN}) in the 8CB-PET system for different values of pore diameter d

$d, \mu\text{m}$	Experiment number	DLS measurement		SLS measurement	
		T_{NA}, K	T_{IN}, K	T_{NA}, K	T_{IN}, K
0.02	1	301.8	309.5	–	–
	2	302.9	309.5	303.4	309.5
	3	301.8	309.6	304.0	309.1
0.1	1	304.6	312.0	301.9	309.7
	2	–	310.7	–	–
	3	303.7	309.8	304.5	–
	4	303.2	310.7	–	310.9
	5	302.4	309.6	303.4	310.1
0.2	1	305.5	312.5	305.8	312.2
	2	304.4	312.4	–	–
	3	303.0	310.4	302.4	310.4
0.3	1	304.5	311.9	–	312.0
	2	305.5	–	–	313.0
	3	305.5	311.9	–	312.0
0.4	1	304.4	311.7	304.3	311.3
	2	304.7	312.2	–	312.2
	3	305.5	309.9	–	–
	4	304.7	312.2	–	–
0.5	1	304.9	312.4	304.8	312.3
	2	305.4	312.8	–	312.8
	3	304.9	312.8	305.1	312.7
1	1	302.6	311.6	303.3	311.2
	2	305.1	313.3	305.3	313.2
2	1	303.7	311.7	303.5	311.3
	2	303.5	310.9	303.1	310.9
	3	303.7	311.5	303.5	311.5

The alternative way to get the information about phase transitions' temperatures is based on the analysis of the temperature dependencies $I(T)$ of the intensity of scattered light. The example of such dependences is shown in Fig. 3, *b*. One can observe sharp peaks in the vicinity of phase transitions, which are obviously produced by critical fluctuations of the tensor order parameter.

The experimental values of T_{IN} and T_{NA} , extracted from dynamic and static light scattering data, are presented in Table 1 for different pore diameters. The temperature shifts of the phase transition

temperatures induced by confinement are of the same order of magnitude as those obtained at calorimetric studies of 8CB-pore glass system [12].

The theoretical analysis of the obtained results can be made in the framework of the generalized Landau – de Gennes – Ginzburg type phenomenological approach presented in [9]. In particular, the shifts $\Delta T_{IN} = T_{IN}(R) - T_{IN}$ and $\Delta T_{NA} = T_{NA}(R) - T_{NA}$ of the phase transitions temperatures $T_{IN}(R)$ and $T_{NA}(R)$, imposed by confinement in 8CB-PET system, respectively to the values T_{IN} and T_{NA} for bulk samples can be expressed as:

$$\frac{\Delta T_{\text{IN}}}{T_{\text{IN}} - T_*} = g_e^{(n)} \left(\frac{\xi_n^{(\max)}}{R} \right)^2 + g_i^{(n)} \frac{(\xi_n^{(\max)})^2}{d_0^{(n)} R}, \quad (1)$$

$$\frac{\Delta T_{\text{NA}}}{T_{\text{NA}}} = -g_e^{(s)} \left(\frac{\xi_s^{(\min)}}{R} \right)^2, \quad (2)$$

where $d_0^{(n)} = K_{ii} / (WS_0)$ is the extrapolation length of the order parameter, K_{ii} is the elastic modulus, S_0 is the order parameter, and W is the anchoring energy, which can be estimated from the dependences of the relaxation time τ on the pore diameter d using the expression:

$$W_\phi = \frac{\eta}{2(\Delta\tau/\Delta d)}, \quad (3)$$

where η – the effective value of the shear viscosity coefficient, corresponding to the dominant mode of a director fluctuations, responsible for light scattering. The details of calculations can be found in [9].

The comparison between the theoretical and experimental dependencies $\Delta T_{\text{NA}}(R)$ and $\Delta T_{\text{IN}}(R)$, obtained by two methods, are presented in Fig. 4. The theory satisfactory describes the experimental data on the qualitative level. In our calculations we used material parameters of 8CB, obtained from independent measurements [13, 14] and considered a splay deformation as the dominant mode in dynamic light scattering.

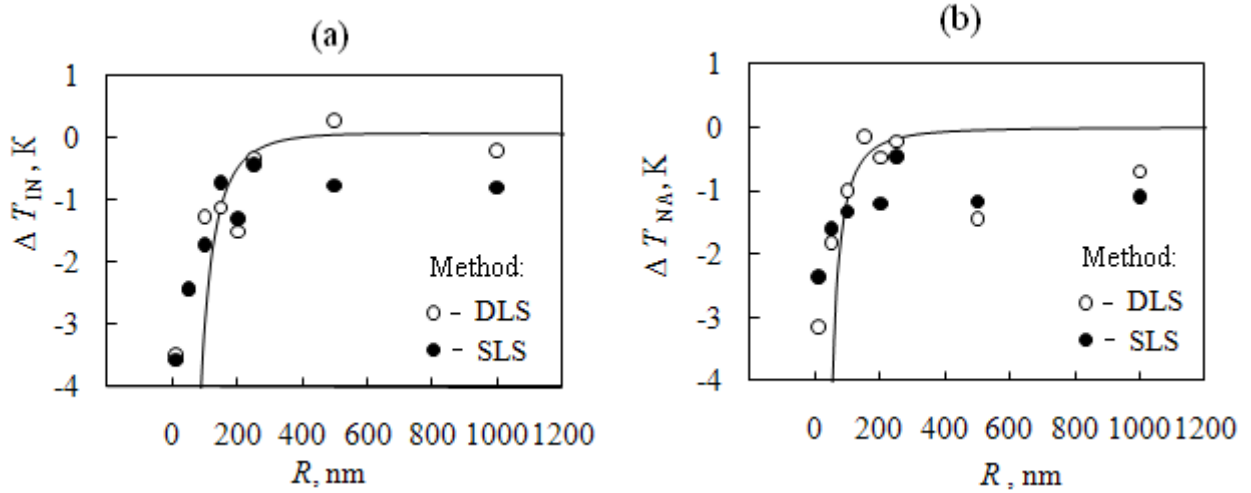


Fig. 4. The experimental results obtained by the DLS and SLS methods (circles) and the corresponding fits (line):

$\Delta T_{\text{IN}}(R)$ (a) (for splay director deformation) and $\Delta T_{\text{NA}}(R)$ (b) as a functions of pore radius R . Calculations are performed using the following values of material constants and parameters: $T_{\text{IN}} - T_* = 1$ K, $K_{11} = 5.2 \cdot 10^{-12}$ J/m², $W = 1.68 \cdot 10^{-5}$ N [13, 14], $S_0 = 0.8$, $\xi_n^{(\max)} = 200$ nm, $\xi_s^{(\min)} = 6$ nm, $g_e^{(n)} = g_i^{(n)} = g_e^{(s)} = 1$

Conclusion

Dynamic and static light scattering methods were applied to study isotropic-nematic and nematic-smectic phase transitions in LC 8CB confined to anisotropic films with micron and submicron cylindrical porous. The temperature dependencies of the relaxation time $\tau(T)$ and intensity of the scattered

light $I(T)$ were obtained and analyzed to extract the phase transitions' temperatures at different values of the pore's diameter. It was shown that both dynamic and static light scattering can be used to study phase state of nematic and smectic A liquid crystals in porous PET films. Our results qualitatively agree with the data obtained for the other confined systems (LC – pore glass [3] and LC micro-emulsions [2].

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