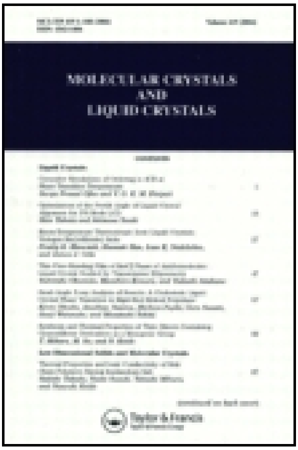

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Dynamics of Molecular and Collective Modes in Filled Nematic

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Dynamics of Molecular and Collective Modes in Filled Nematic

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The influence of filling of 5CB with hydrophilic and hydrophobic Aerosil particles on dynamics of molecular and collective modes has been investigated by broadband dielectric spectroscopy (BDS) and photon correlation spectroscopy (PCS). BDS provides information on reorientational motion of polar molecules while PCS probes dynamics of collective modes associated with director fluctuations. Two bulklike dielectric modes due to the rotation of molecules around short axes and the librational motion were observed in filled 5CB. We found that the properties of 5CB are considerably affected by the filling. A low frequency relaxation process and dispersion of dielectric permittivity due to conductivity were observed. The treatment of the surface of filling particles has strongest influence on the properties of the slow process and it is less important for molecular modes. PCS experiment shows that two new relaxation processes appear in filled 5CB in addition to the director fluctuations process in bulk.

Keywords: filled nematic; dynamical behavior; relaxation

INTRODUCTION

The heterogeneous systems based on liquid crystals (LC), such as liquid crystals dispersed in polymer matrices (PDLC) [1] and in inorganic porous matrices [2] are materials extremely important for both applications and fundamental physics of confined systems. Searches for new materials for electrooptic devices and particularly for displays has led to the creation of a new liquid crystal based heterogeneous material - filled nematics (FN) [3,4].

Filled nematics have attracted a great deal of attention as materials for display applications [3,4]. These materials are suspensions of highly dispersed silica in the nematic phase of a liquid crystal. Investigations have shown that the agglomeration of 2-3 volume percent of Aerosil particles in a nematic phase forms a three-dimensional network dividing the liquid crystal into LC domains with a linear size of approximately 250 nm [4] and with a random distribution of director orientation of each domain.

FN have some similarities with other types of liquid crystal based heterogeneous materials: PDLC [1] and LCs dispersed in inorganic porous matrices [2]. These systems are anisotropic (at least at short spatial scales) and heterogeneous materials characterized by a very developed interface. The main difference between the structure of LC confined in porous matrices and filled nematics is as follows: porous glass matrices or Anopore membranes have solid network whose structure is temperature independent while the particles in FN are capable of changing their mutual arrangement which results in changes of the network structure [4].

In contrast with PDLC and confined liquid crystals, the investigations of filled nematics are in the initial [5-10] stage and have been mainly concerned with static properties such as the influence of filling on the phase transitions [5-7] and optical properties [4,6]. The first attempts to investigate the dynamics of director fluctuations were made in Ref. [8] and the dielectric properties of filled LC in Ref. [9,10].

In this paper we present the results of investigations of 5CB - filled with Aerosil particles with hydrophilic and hydrophobic surfaces by broad band dielectric and photon correlation spectroscopies in the nematic phase and the supercooled state. These two methods provide complementary information on dynamical properties of material. Broad band dielectric spectroscopy is a powerful technique for investigations of condensed matter. Relaxation of different physical origin such as molecular reorientation, dynamics of collective or surface polarization modes, and conductivity can be investigated in different systems. Photon correlation spectroscopy applied to nematic liquid crystal provides information on the dynamics of director fluctuations determined by elastic and viscous properties of LC.

EXPERIMENTAL

We used liquid crystalline 5CB filled with Aerosil particles, both hydrophilic (A200) as well as hydrophobic (R974), as materials. Bulk 5CB has a nematic phase in the temperature range of 22.5-35°C. The volume concentration of the filling particles was 2.3 % for both samples. The hydrophilic particles are made of silica with OH-groups (1.4 - 2 groups per nm^2) on the surface. In the hydrophobic Aerosil particles, about 70 % of the surface hydrophilic groups are replaced by hydrophobic groups reducing the interaction with the liquid crystal molecules and between particles.

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). For measurements in the frequency range from 1 MHz to 1.5 GHz we used Hewlett-Packard 4291A rf Impedance Analyzer.

Photon correlation measurements were performed using a $\lambda = 0.6328 \mu m$ He-Ne laser and the ALV-5000/Fast Digital Multiple Tau Correlator (real time) operating over delay times from 12.5 ns up to

10^3 s with the Thorn EMI 9130/100B03 photomultiplier and the ALV preamplifier. The temperature stabilization in both experiments was better than 0.01°C.

BROADBAND SPECTRA OF FILLED 5CB

In the nematic phase of bulk 5CB there are two dielectrically active relaxation processes of molecular origin [11-15]. For a geometry in which the electric field **E** is parallel to the director **n** i.e. $\mathbf{E} \| \mathbf{n}$, the Debye type process due to the restricted rotation of the molecules about their short axis exists. The characteristic frequency of this process is $\sim$ 5 MHz and the temperature dependencies of the corresponding relaxation times obey empirical Arrhenius equation. For the geometry in which the electric field **E** is perpendicular to the director **n**, i.e. $\mathbf{E} \perp \mathbf{n}$, the most prominent relaxation process with a characteristic frequency about 70 MHz has been attributed to the tumbling of the molecules [16,17]. No dielectrically active collective modes are present in 5CB.

The broadband spectra of filled 5CB are different from spectra typical for bulk 5CB. Figure 1 represents the spectra in frequency range from 10 mHz to 1 GHz for both filled samples at T = 303 K. Two more relaxation processes in addition to two bulk-like processes as well as dispersion due to contribution from conductivity, were observed for both systems in the low frequency range ($f \leq 100$ kHz).

For the quantitative analysis of the dielectric spectra the Havriliak-Negami function [18] 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 complex dielectric permittivity, ϵ_∞ is the high frequency limit of the permittivity, $\Delta\epsilon_j$ the dielectric strength, τ_j the

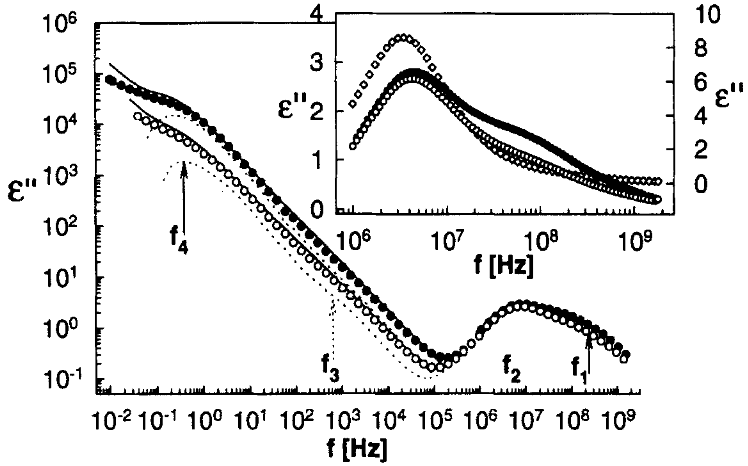

FIGURE 1: Broad band dielectric spectra of filled nematics at T = 303 K. Open circles: hydrophobic; closed circles: hydrophilic Aerosil - experiment, solid lines: fitting. Dotted lines have been plotted after subtraction of the contribution due to d.c. conductivity. The arrows identify characteristic frequencies of relaxation processes. Inset: high frequency dielectric spectra of bulk and filled 5CB at T = 297 K. Bulk 5CB - opened diamonds (right axis), 5CB filled with hydrophilic and hydrophobic particles (left axis).

mean relaxation time, f is frequency, 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.

The frequency dependencies of ϵ'' after the subtraction of the contribution from conductivity are represented by the dotted lines in Fig. 1. These dependencies have relaxation origin and are quantitatively described by the Havriliak-Negami formula. The contributions from conductivity is perfectly described by the second term in formula (1) and their values at T = 303 K are: $2.48 \cdot 10^{-9}$ $S \cdot cm^{-1}$ (hydrophilic) and $1.13 \cdot 10^{-9}$ $S \cdot cm^{-1}$ (hydrophobic). After subtraction of the contribution from conductivity we observe a clear maximum (f_4) at $f \approx 0.5$ Hz. We suggest that this low frequency process is the relaxation of the interfacial polarization arising at the Aerosil particle-liquid crystal interface. The relatively fast process is just a shoulder at $f \approx 1$ kHz (f_3) and is hard to analyze.

The difference between the molecular relaxation processes of bulk nematic 5CB and filled 5CB can be seen by comparing curves in the inset of Fig. 1 that represents the imaginary part of dielectric permittivity as a function of frequency measured at 297 K. In bulk 5CB the observed process is the relaxation due to the restricted rotation of the molecules about their short axis. This process is described by the Debye relaxation function ($\alpha = 0$ and $\beta = 1$ in formula (1)) with a single relaxation time. In filled nematics the characteristic frequencies of the main process are slightly changed from the bulk value and the contribution from the tumbling process in filled 5CB is clearly observed. This is due to the fact that filling of nematic liquid crystals with Aerosil particles introduces disorder with random orientation of the director of domains. Therefore in filled 5CB there are molecules oriented both parallel as well as perpendicular to the direction of probing electric field and both molecular modes are detected in the same experiment. The amplitude of the tumbling mode in hydrophilic sample is greater than in hydrophobic one.

It should be mentioned that all relaxation processes in filled 5CB are not frozen even 25 K below the crystallization point of bulk 5CB. Figure 2 shows the temperature dependence of the relaxation time of the bulk-like processes due to the flip-flop reorientation around the short axis and tumbling motion of molecules as well as the temperature dependence of relaxation times of the slow process.

The filling of 5CB with Aerosil particles as well as the modifi-

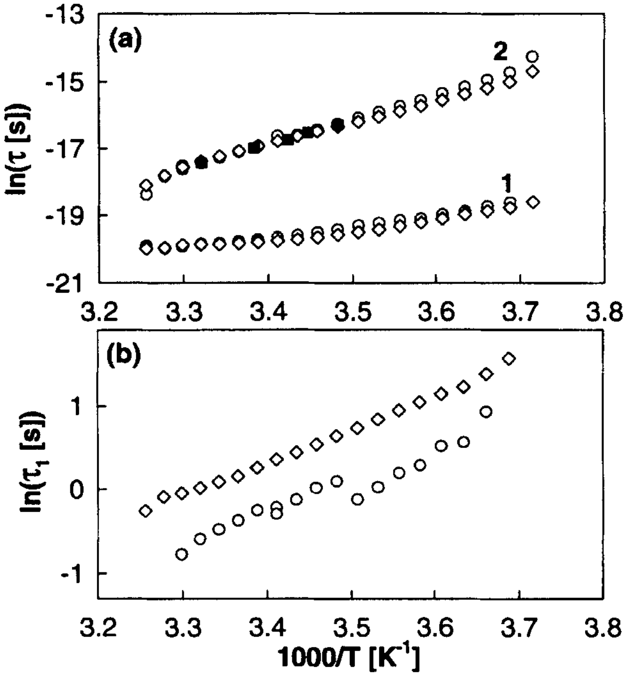

FIGURE 2: (a) - Temperature dependence of relaxation times for bulk-like and bulk processes. Open circles - hydrophobic; open diamonds - hydrophilic Aerosil, closed squares - bulk 5CB. 1 - tumbling mode; 2 - flip-flop reorientation around short axis. (b)- Temperature dependence of relaxation times of the low frequency relaxation process. Open diamonds - hydrophilic; open circles - hydrophobic.

cation of the surface of filling particles has weak influence on the dynamics of bulk-like modes. In the temperature range corresponding to bulk nematic phase the relaxation times of reorientation motion around the short axis in filled 5CB are very close to bulk values with the same temperature dependence. In the supercooled state the temperature dependence deviates from the bulk behavior. The relaxation times of both bulk-like modes have stronger temperature dependence in the supercooled state than in the nematic phase.

The modification of the surface of the particles has the strongest influence on the low frequency relaxation process. The characteristic frequencies of the slow process are lower for hydrophilic particles and in this sample the contribution of this process to the total polarization was greater than in the case of hydrophobic particles. These facts suggest that low frequency relaxation is Aerosil particle-liquid crystal interface related phenomena and the origin of this process maybe explained as relaxation of the surface induced polarization.

DYNAMICS OF DIRECTOR FLUCTUATIONS

In the dynamic light scattering experiment, one measures the intensity-intensity autocorrelation function

$$g_2(t) = \langle I(t)I(0)\rangle / \langle I(0)\rangle^2$$

which 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 and $q = 4\pi n \sin(\Theta/2)/\lambda$, ($n$ is the refractive index, Θ - the scattering angle and λ is the wavelength of laser radiation).

Dynamic light scattering in bulk nematic liquid crystals is very well understood [19], and the main contribution to the intensity of scattered light is due to the director fluctuations. In a uniformly oriented nematic sample, there are two modes determined by these fluctuations. The first mode is determined by a combination of splay and bend distortions and the second mode by a combination of twist and bend distortions. In the single elastic constant (K) approximation, if we assume that the six Leslie coefficients have the same order of magnitude and are $\sim \eta$ (η is an average viscosity), then the relaxation time of director fluctuations is [19]:

$$\tau = \eta / Kq^2$$

and is of the order of magnitude $\sim 10^{-4}$ s. The corresponding decay function is exponential:

$$f(q,t) = a \cdot \exp(-t/\tau).$$

Filling of 5CB with Aerosil particles has a strong influence on the relaxation properties of LC investigated in photon correlation experiments.

The difference between the dynamic behavior of bulk nematic multidomain 5CB and filled 5CB can be seen by comparing curves (1), (2) and (3) in Fig. 3 that represents normalized autocorrelation functions measured at 301.3 K in both filled 5CB samples as well as in bulk 5CB for comparison. In bulk 5CB (curve 1, Fig.3) there is only one relaxation process due to director fluctuations. This autocorrelation function deviates slightly from a single exponential, and the best fitting is provided by a single stretched exponential decay function $f(q,t) = a \cdot \exp(-(t/\tau)^{\beta})$ with $\beta = 0.94$ and $\tau = 1.4 \cdot 10^{-4}$ s. The small deviation of β from unity, in our case, is due to the

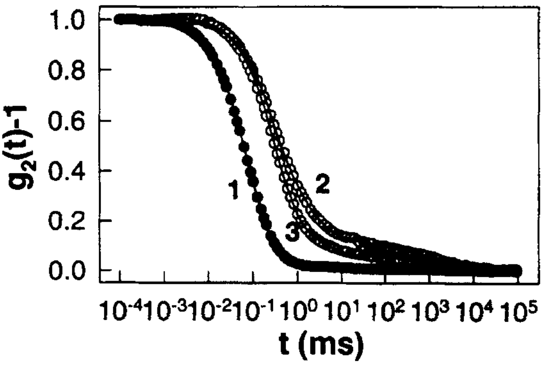

FIGURE 3: The normalized intensity/intensity autocorrelation functions measured at 301.3 K. 1 - bulk 5CB, 2 - 5CB filled with hydrophilic, and (3) - filled with hydrophobic Aerosil particles. Symbols - experiment, solid lines - fitting.

fact that we used a multidomain sample and the contribution from both modes is present. The autocorrelation functions of filled nematic samples are strongly modified by the network (see Fig.3). The bulk-like director fluctuation process in filled 5CB is considerably slower than in the bulk and the autocorrelation functions of filled 5CB show two slow decays. These low frequency decays are more pronounced in 5CB filled with hydrophilic particles than in the hydrophobic sample. The intensity-intensity autocorrelation functions of filled 5CB measured in the dynamic light scattering experiment, have been fitted by the superposition of three stretched exponential decays:

$$f(q,t) = \left[\sum_{i=1}^{n} a_i \cdot \exp(-(t/\tau_i)^{\beta_i})\right]^2 ,$$

where a_i, τ_i and β_i are the amplitude, relaxation time, and stretching exponent of i^{th} relaxation process, and n is the number of processes.

We assign the first decay to the bulk-like director fluctuations. This relaxation process is broader and slower ($\beta = 0.84$, $\tau = 0.51$ ms) than in bulk 5CB at the same temperature ($\beta = 0.94$, $\tau = 0.14$ ms). The second (middle frequency) relaxation process is most probably due to the director fluctuations in a thin LC layer in the vicinity of Aerosil particles. The relative contribution of this process to autocorrelation function in hydrophilic sample is considerably ($a_2/a_1 \simeq 0.9$) higher than in the hydrophobic one ($a_2/a_1 \simeq 0.4$) because of higher number of hydrophilic OH groups, which has resulted in stronger influence on the surface LC layer. This relaxation process is notably slower than the bulk-like director fluctuations due to higher viscosity in the vicinity of Aerosil particle-liquid crystal interface (so-called surface viscosity) and coupling of molecules to the surface. Additionally the surface relaxation process is broader than the bulk-like relaxation process and the value of the stretching exponent describing this process ($\beta_2 \approx 0.7$) is appropriate to glass-like relaxation processes. The relative contribution of the second and third relaxation processes in the hydrophilic sample are higher than in the hydrophobic sample.

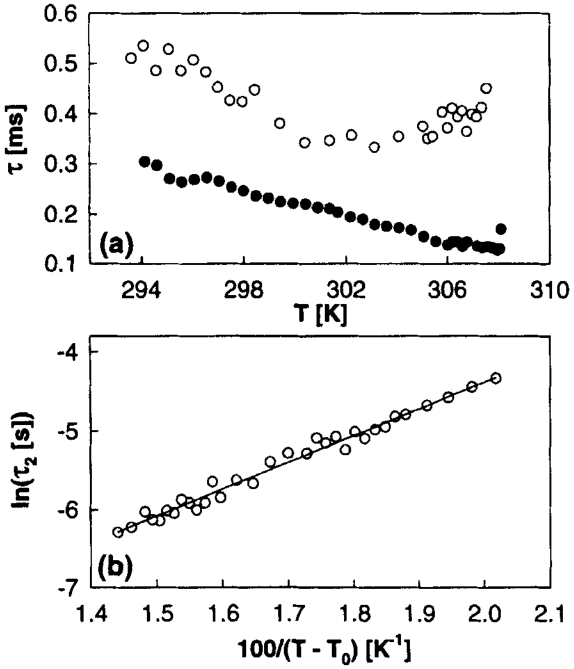

FIGURE 4: The temperature dependence of the relaxation time of the director fluctuations process - (a). (o) - 5CB filled with hydrophilic particles, (•) - bulk 5CB. The temperature dependence of the relaxation time of the middle frequency relaxation process - (b). Symbols - experiment, solid line - fitting.

The third (slowest) process could be due to a rotation of LC domains as a whole. However this third process is masked by the first two processes with much greater aptitude and the quantitative analysis of this process is very difficult. All three processes are obligatory to describe the dynamics of filled 5CB in the temperature range under investigation. It should be mentioned that all relaxation processes in filled 5CB are not frozen even 25 K below the crystallization point of bulk 5CB as it was observed in dielectric spectroscopy experiment. Figure 4a shows the temperature dependence of the relaxation times of the process due to the relaxation of director fluctuations in bulk 5CB and in hydrophilic samples (the first process) in the temperature range corresponding to the bulk nematic phase. In Figure 4b the temperature dependence of the relaxation times of the middle frequency relaxation process (τ_2) in hydrophilic FN are represented. The temperature dependencies of the relaxation time of the first process in FN and in bulk are different from each other. Primarily, the relaxation process in filled 5CB is slower than in bulk 5CB. Secondly, in bulk 5CB the increase of relaxation time is observed in a very narrow temperature range close to N-I phase transition, while in filled 5CB the relaxation time smoothly increases upon approaching the N-I phase transition. Smooth changes are due to the broadening of N-I phase transition. The increase of the director fluctuations relaxation time at the temperatures close to N-I phase transition is mostly related to the destabilization of the network, and therefore a reduction of the elastic constants.

The data analysis shows that the temperature dependence of the relaxation time τ_2 time of the middle frequency relaxation process in the temperature range from 280 to 300 K obeys the Vogel-Fulcher law:

$$\tau = \tau_0 \cdot \exp\left(B/(T - T_0)\right)$$

as illustrated in Fig.4 (b). The parameters describing this dependence are: $\tau_0 = 14$ ms, $B = 340$ K, $T_0 = 231$ K. If we determine the glass transition temperature (T_g) as the temperature at which $\tau = 100$ s [20] then we obtain $T_g = 253$ K.

The second process due to the relaxation of director fluctuations in surface layers formed in the vicinity of solid surface - LC interface is characterized by the two main features typical for conventional glass-forming fluids [20]: the stretched exponential relaxation is accompanied by the Vogel-Fulcher temperature dependence of the relaxation times. Non-Debye relaxation [17] process and the Vogel-Fulcher glass-like temperature dependence of relaxation times were observed previously [21] in liquid crystals confined to random porous media with narrow pores. Such a glass-like dynamical behavior seems to be the general property of thin confined fluid films [22].

CONCLUSION

The dielectric and photon correlation experiments show that the filling of LC with Aerosil particles significantly changes the physical properties of nematic liquid crystals. Filling of nematic LC has resulted in the appearance of a low frequency relaxation process dependent on the surface condition of the filling particles. The low frequency relaxation is Aerosil particle-liquid crystal interface related phenomena. It is more pronounced in hydrophilic samples since the modification of the surface LC layer in these samples is stronger than in hydrophobic one. The two bulk-like modes due to the rotation of molecules around the short axes and the tumbling motion are less affected by filling or modification of the surface of the filling particles.

The effect of the Aerosil network on the dynamical properties of the LC is similar to the effect of confinement in porous matrices and has resulted in the appearance of a slow relaxation with glass-like behavior. All relaxation processes in filled 5CB are not frozen even 25 K below the crystallization temperature of bulk 5CB.

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References

[1] P.S. Drzaic, *Liquid Crystal Dispersions,* (World Scientific, Singapore, 1996).

[2] *Liquid Crystals in Complex Geometries Formed by Polymer and Porous Networks,* edited by G.P. Crawford and S. Zumer (Taylor & Francis, London, 1996).

[3] M. Kreuzer, T. Tschudi, W.H. de Jeu, and R. Eidenschink, *Appl. Phys. Lett.*, **62**, 1712 (1993).

[4] M. Kreuzer and R. Eidenschink in: *Liquid Crystals in Complex Geometries Formed by Polymer and Porous Networks,* edited by G.P. Crawford and S. Zumer (Taylor & Francis, London, 1996), pp. 307–324..

[5] B. Zhou, G.S. Iannacchione, C.W. Garland, and T. Bellini, *Phys. Rev. E* **55,** 2962 (1997).

[6] T. Bellini, N.A. Clark, V. Degiorgio, F. Mantegazza, and G. Natale, *Phys. Rev. E.* **57,** 2996 (1998).

[7] G.S. Iannacchione, C.W. Garland, J.T. Mang, and T.P. Rieker, *Phys. Rev. E* **58,** 5966 (1998).

[8] F. Aliev, M. Kreuzer, N. Tabiryan, and B. Zel'dovich, *Mol. Cryst. Liq. Cryst.* **320,** 173 (1998).

[9] S. Tschierske, O.V. Yaroshchuk, and H. Kresse, *Cryst. Res. Technol.* **30,** 571 (1995).

[10] S.L. Abd-El-Messiah, J. Werner, H. Schmalfuss, W. Weissflog and H. Kresse, *Liq. Cryst.* **26,** 535 (1999).

[11] P.G. Cummins, D.A. Danmur, and D.A. Laidler, *Mol. Cryst. Liq. Cryst.* **30**, 109 (1975).

[12] D. Lippens, J.P. Parneix, and A. Chapoton, *J. de Phys.* **38,** 1465 (1977).

[13] J.M. Wacrenier, C. Druon, and D. Lippens, *Mol. Phys.* **43,** 97 (1981).

[14] T.K. Bose, R. Chahine, M. Merabet, and J. Thoen, *J. de Phys.* **45,** 11329 (1984).

[15] T.K. Bose, B. Campbell, S. Yagihara, and J. Thoen, *Phys. Rev. A* **36,** 5767 (1987).

[16] S.R. Rozanski, R. Stanarius, H. Groothues, and F. Kremer, *Liq. Cryst.* **20,** 59 (1996).

[17] G.P. Sinha and F.M. Aliev, *Phys. Rev. E* **58,** 2001 (1998).

[18] S. Havriliak and S. Negami, *Polymer* **8,** 101 (1967).

[19] P.G. de Gennes and J. Prost, *The Physics of Liquid Crystals,* second ed., (Clarendon Press, Oxford 1993).

[20] *Disorder Effects on Relaxational Processes,* edited by R. Richert and A. Blumen (Springler Verlag, Berlin 1994).

[21] X-l. Wu, W.I. Goldburg, M.X. Liu, and J.Z. Xue, *Phys. Rev. Lett.* **69,** 470 (1992).

[22] A.L. Demirel and S. Granik, *Phys. Rev. Lett.* **77,** 2261 (1996).