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Abstract
The complex dielectric permittivity of 4-(2-hexyloxyethoxy) 4'-cyanobiphenyl (6O2OCB) enclosed in porous samples of ZrO_2 has been studied in the frequency range 10^{-1}–10^6 Hz and over a wide temperature range. For the substance in the nearly spherical pores of ZrO_2 no phase transition has been found, while for the substance in the bulk a monotropic system of phases, with smectic and crystalline phases, was determined. The relaxation spectra observed for the liquid phase of 6O2OCB in porous material are rather complex and they have been separated into three parts using sums of Havriliak–Negami equations. Two lower-frequency relaxations have been ascribed to collective and ionic motions. Our interest is in the high-frequency relaxation connected with the reorientations of molecules around the short axes. That process was the only one found in the pure 6O2OCB substance. In both cases the temperature changes of that relaxation were found to conform with the Vogel–Fulcher–Tammann formula for the average relaxation time. The relaxation times of molecules in pores are smaller than in the bulk. In pores the substance survives in the isotropic liquid phase to lower temperatures before the glass transition occurs. For the substance enclosed in pores the thermal hystereses of the dielectric permittivity and the relaxation times were found and discussed.

1. Introduction

Investigations of various physical properties of liquids in porous materials were performed recently using different experimental techniques [1–6]. The results obtained by dielectric relaxation spectroscopy [7–9] help us to understand the influence of the surface interactions on the dynamics of the enclosed molecules. Formation of thermodynamic phases and the values

of the transition temperatures depend on the size and geometry of the pores. One can also expect to obtain information about a nucleation process and the effects of supercooling.

Liquid crystals seem to be promising subjects for such studies due to their particular properties. The liquid phase polymorphism observed in liquid crystals on cooling and on heating the sample is unique and the nematic and smectic phases have well defined order parameters. Moreover, interactions between elongated liquid crystal molecules and the surfaces of the pores are much stronger than those between the molecules themselves. That leads to ordering of the molecules by the pore surface over distances longer than for the isotropic molecules. It is also important that the size of the liquid crystalline molecule is of the same order of magnitude as the pore itself.

In the present paper we report the dielectric relaxation behaviour of 4-(2-hexyloxyethoxy) 4′-cyanobiphenyl (6O2OCB) in the ZrO_2 porous matrix. The aim of our studies is to determine the dynamics of entrapped molecules and to compare the results with those obtained for the pure 6O2OCB substance [10]. This substance was chosen for investigations of behaviour in a porous matrix due to the interesting phase diagram and the scheme of temperature changes of the relaxation time as detected previously by dielectric relaxation spectroscopy [10]: on slow cooling, the isotropic liquid phase crystallizes at room temperature: Cr $\xleftarrow{292\,K}$ I. A liquid crystalline phase has been detected only upon heating a glass obtained by fast cooling. Then above 210 K softening of the glass (G) into a supercooled isotropic liquid phase (I_{sc}) has been detected—which at about 228 K transforms into a smectic phase (S). On further heating, the crystallization has occurred at about 260 K. At room temperature the crystal (Cr) melts into the stable isotropic liquid phase (I):

$$G \xrightarrow{\sim 210\,K} I_{sc} \xrightarrow{228\,K} S \xrightarrow{260\,K} Cr \xrightarrow{292\,K} I.$$
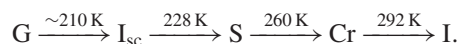
In phases which exhibit molecular rotational freedom, relaxations connected with the reorientations of 6O2OCB molecules around the short axes have been observed. It has been found that in the smectic phase, $\tau(T)$ exhibits Arrhenius behaviour with an energy barrier of 72 kJ mol^{-1}. Meanwhile, over the whole temperature range of the isotropic liquid phase a successful description can be given with the help of the Vogel–Fulcher–Tammann (VFT) formula [11]:

$$\tau(T) = \tau_0 \exp\left[\frac{DT_0}{(T - T_0)}\right]. \tag{1}$$

For $\tau_0 = 10^{-13.5}$ s (the high-temperature limit of the relaxation time), the limit value of the glass transition $T_0 = 167$ K and $D = 3.6$ [10]. It seems worth finding out how the confined geometry affects the various features of the substance.

2. Experimental details

The pure 6O2OCB substance was synthesized in the Chemical Department at the Military University of Technology, Warsaw. The porous matrix was prepared at the Ceramic Department of the Mining and Metallurgy Academy, Kraków, by pressing small grains of ZrO_2 compound. The distribution of the pore sizes has been checked. Most of the pores have diameters of about 10 nm. The volume of the pores in the sample has been estimated to be about 50% of the total volume of the sample. Liquid 6O2OCB has been introduced into the pores at 10 K above the clearing point. Previously, the disc-shaped porous matrix (10 mm diameter and 0.2 mm thickness) had been cleaned by acetone and treated with ultrasound. Then it was kept for two days at 600 K in the vacuum chamber (8.2 mbar) in order to remove water [6] and other volatile impurities [12].

For a porous sample with the 6O2OCB molecules inside, dielectric measurements of the complex dielectric permittivity $\varepsilon^*(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu)$ have been performed using the Solartron-Schlumberger frequency response analyser FRA 1260 with the Novocontrol active sample cell BDC-S. ε' means the real dielectric permittivity and ε'' means the dielectric loss. The resolution of ε'' was 10^{-3}. Measurements covered the frequency range from 0.03 Hz to 3 MHz and the temperature region down to 210 K. The disc-shaped sample was kept between two brass electrodes. The temperature of the sample was controlled using a Novocontrol Quatro system with a liquid nitrogen cryostat and measured with 0.1 K accuracy. Measurements were performed at 2.5 K intervals on heating and cooling the sample. The rate of temperature change was about 0.2 K min^{-1}.

3. Results and discussion

Figure 1 presents the dielectric loss versus frequency for 6O2OCB in the porous matrix of ZrO_2 as it evolves with lowering temperature. Due to very the high values of the absorption, the data are presented in a double-logarithmic plot. One can see that the experimental results for $\varepsilon''(\nu)$ indicate a complex relaxation phenomenon. On lowering the temperature, a continuous shift of the relaxation towards low frequencies can be seen and no clear evidence of any phase transition can be traced. On heating the sample, the data are the similar. The crystallization detected in the pure substance has not been found in the porous sample. In figure 2 the above data measured for two temperatures ($\times$ and $\triangle$) are compared with the results obtained for the isotropic ($\circ$: 227 K) and smectic (+: 237 K) phases of the pure substance. One can see that in the smectic phase (despite the higher temperature) the molecular motions are slower than in the isotropic phase. Moreover, for the molecular arrangement of smectic type the relaxation is connected with much smaller effective dipolar moments (smaller absorption) than in the isotropic phase. It seems clear that in a porous matrix containing only 50% of the pure substance, the data obtained should be compared with the results obtained for the isotropic phase of the pure substance, as those for the smectic phase are too small.

The complex $\varepsilon''(\nu)$ curves shown in figure 1 reveal three maxima down to 260 K. So the absorptions observed have been separated into three parts by means of a sum of Havriliak–Negami formulae [13]:

$$\varepsilon''(\nu) = \frac{\sigma_0}{\varepsilon_0} \frac{1}{2\pi\nu} + \sum \Delta\varepsilon_j [(1 + (2\pi\nu\tau_j)^{\alpha_j})^{-\beta_j}], \qquad j = 1, 2, 3 \qquad (2)$$

where σ_0 and ε_0 are the electric conductivity of the sample and the dielectric constant of the vacuum, $\Delta\varepsilon$ is the dielectric increment, τ is the relaxation time and α and β describe the magnitude and the shape of the distribution of the relaxation times[4]. The earlier observations of the dielectric relaxation of dipole substances in porous materials [7–9] help one to ascribe each relaxation to the appropriate mechanism. Thus, the absorption appearing at the highest frequencies seems to correspond to the process connected with the molecular reorientations of the molecules around the short axes which was observed previously for pure substances. Two other absorption regions can be related to collective motions of molecules (the weaker absorption) and to the ionic polarization effect (the stronger one) [6]. The results of the fitting procedure are presented in figure 3 for 260 K. On lowering the temperature, the lower-frequency absorptions were gradually shifted to below the apparatus limit. The molecular absorption was observed over the whole temperature range. The accuracy of fitting the formula (2) to the results seems reasonably good. It is confirmed by the monotonic changes of the parameters with temperature.

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[4] The real part of the permittivity is not discussed because part of it is connected with the porous matrix.
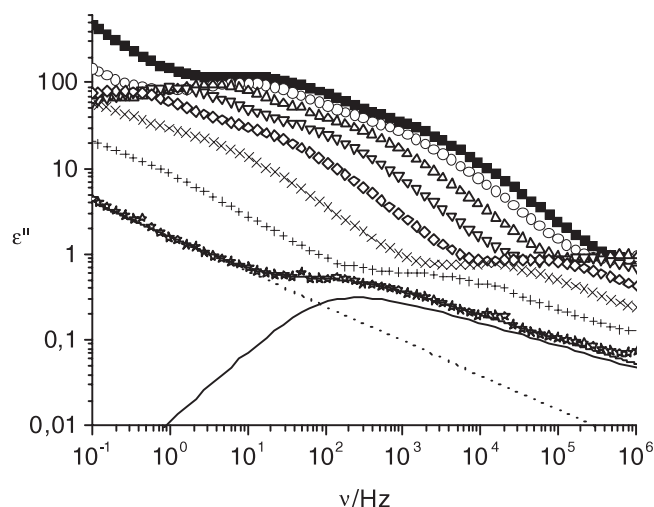
Figure 1. Dielectric loss versus frequency measured on cooling the sample of 6O2OCB in the porous matrix of ZrO_2 for various temperatures. Experimental data are presented in a double-logarithmic plot. Key to the symbols: ■: 298 K; O: 290.5 K; △: 280.5 K; ▽: 270.5 K; ◇: 260.5 K; ×: 250.5 K; +: 240.5 K; ★: 230.5 K. An example of the fit of the formula (2) to the results is presented for 230.5 K.
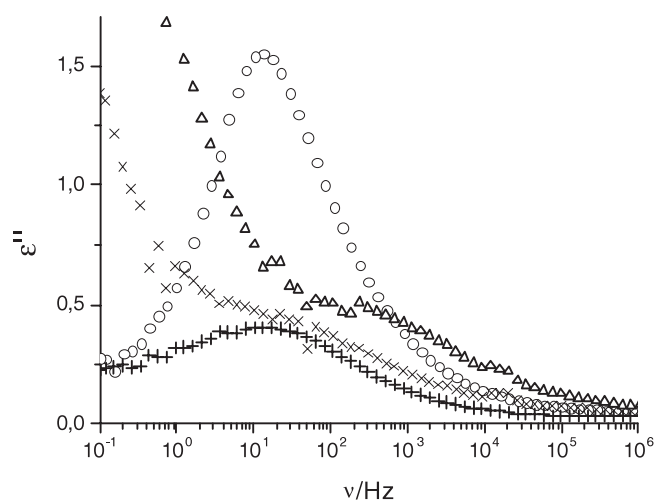

Figure 2. Dielectric loss versus frequency for 6O2OCB in the porous matrix for 225 K (×) and 235 K (△) and for 6O2OCB in the bulk (isotropic phase, 227 K (O), and smectic phase, 237 K (+)).

Our main interest is in the temperature dependence of the molecular process alone. It was found that near room temperature the α-parameter is close to 1. So the observed relaxation is of the Cole–Davidson type. Its deviation from the Debye type ($\beta \sim 0.2$) is much larger than for the pure substance ($\beta \sim 0.8$). On lowering the temperature, for description of the absorption both exponents were needed. This indicates a significant distribution of the relaxation times. It seems that the magnitude of the rate of reorientation depends on the distance of the molecule from the surface of the pores. For example, at 233 K, $\alpha = 0.7$ and $\beta = 0.4$. Over the whole
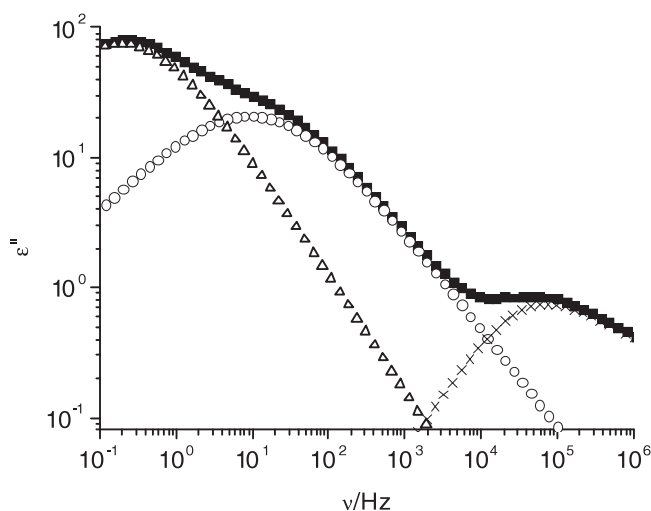
Figure 3. Dielectric loss versus frequency for 6O2OCB in the porous matrix of ZrO_2 at 260 K separated into three relaxation processes: molecular ($\times$), collective ($\bigcirc$) and ionic ($\triangle$). Experimental results are represented by ■. Data are presented in a double-logarithmic plot.
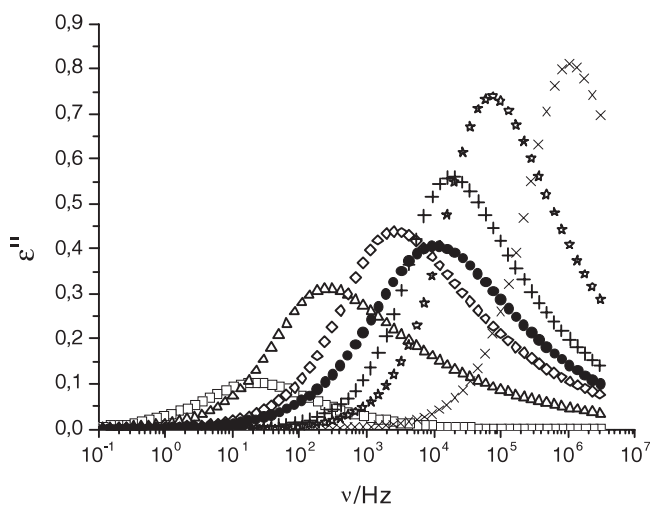

Figure 4. Dielectric loss of the molecular relaxation versus frequency for 6O2OCB in the porous matrix of ZrO_2 for several temperatures, observed on cooling the sample. Key to the symbols: □: 220 K; △: 230 K; ◇: 240 K; +: 250 K; ★: 260 K; ×: 280 K. For comparison, some data collected on heating are given for 250 K (●).

temperature range the half-width of the absorption curves is about 2.5 ± 0.5, which differs considerably from that, 1.45 ± 0.15, for the isotropic liquid phase in the bulk. The $\varepsilon''(\nu)$ curves presented in figure 4 reveal a strong and continuous decrease of $\varepsilon''(\nu)$ on cooling. For the data obtained on heating, the $\varepsilon''(\nu)$ are systematically slightly smaller than those presented in figure 4 but their temperature dependence is similar. It seems that these observations, when compared with the results for pure substance, can help in understanding the influence of the surface on the 6O2OCB molecules. In what follows, we try to demonstrate that the decrease of
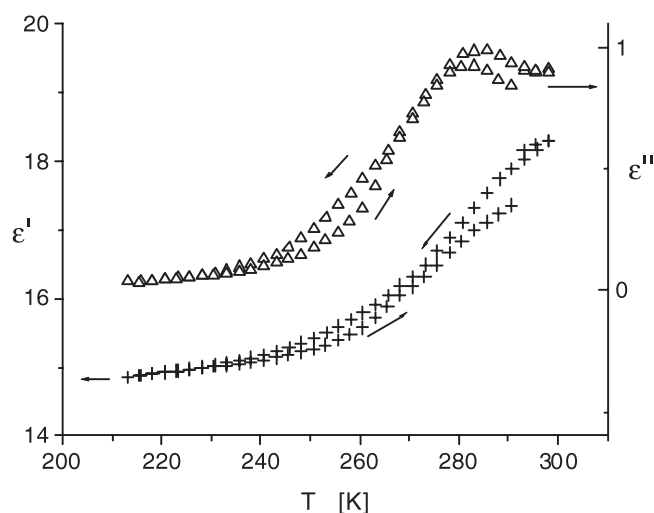
Figure 5. The thermal hysteresis effect for 6O2OCB in the porous matrix shown by the temperature dependence of the real (+) and imaginary (△) parts of the dielectric permittivity measured at the frequency 3.5×10^4 Hz, typical for molecular reorientations.

$\varepsilon''_{max}(T)$ in the cooling experiment is caused by surface interactions decreasing the number N of molecules which reorient in the pores. For liquid crystalline molecules of 3 nm length and 0.7 nm width (so of molecular volume equal approximately to 1.5 nm^3) in spherical pores of 10 nm diameter, N can be about 300. At temperature 280 K, in the pure substance, $\varepsilon''_{max} = 1.7$. Thus, for porous samples one can expect $\varepsilon''_{max} = 0.85$, as there is only 50% pure substance in the same volume of the sample. The experimental value is nearly the same, i.e. $\varepsilon''_{max} = 0.8$, which means that at high temperature nearly all molecules enclosed in the pores reorient as in the pure substance and their dielectric response is the same. The calculations have been done using the fact that $\varepsilon''_{max}(T) \sim N(T)[g(T)\mu^2/kT]$, where μ is the dipolar moment of the molecule whose reorientation is responsible for the relaxation observed [14]. $g(T)$ is the Kirkwood correlation parameter and it is assumed to be the same in the two situations. In the pure sample, N is constant, as in the isotropic phase all molecules reorient. The same reasoning for lower temperatures shows a different result. For example, at 230 K, $\varepsilon''_{max} = 2$ for pure substance and only 0.3 for the porous sample. One can deduce that, due to the anchoring phenomenon [15], the molecules close to the porous surface are aligned along it and they do not have enough freedom to reorient. One can calculate that the thickness of the layer of frozen molecules grows gradually with lowering temperature, reaching a value of about 1.7 nm at 230 K. This means that only about a third of the molecules in the central sphere of the pore give rise to the dielectric relaxation observed. Such reasoning seems appropriate also for understanding the fact that on cooling the $\varepsilon''(\nu)$ curves have higher values than those on heating (see figure 4). A small thermal hysteresis has been found also for other features of the substance in the porous matrix (see figure 5). Expressed simply: on cooling, the number of immobile molecules grows, while on heating, it decreases. $N(T)$ for mobile molecules is larger if the temperature of the measurement is reached from above than if it is reached from below, as the kinetics of the two processes are different.

In figure 6 the frequencies of maxima of the absorption curves observed in the temperature range from 220 to 370 K for pure substance (+) and for porous samples (△) are presented in an Arrhenius diagram. One can see that in both cases, the temperature dependence of the
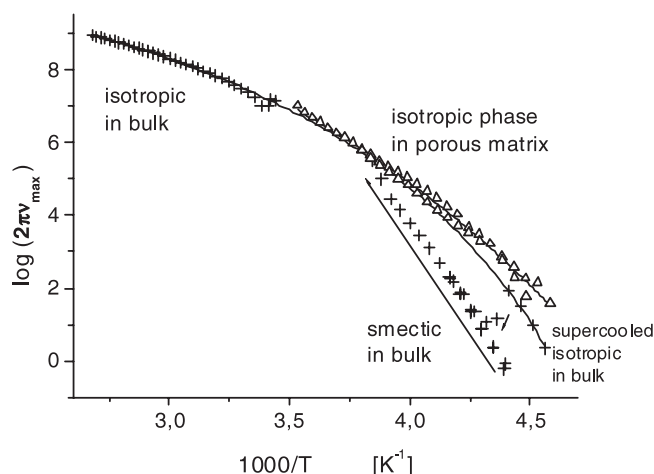
Figure 6. A plot of $\log(2\pi \nu_{max})$ versus $1000/T$ for 6O2OCB in the bulk (+) and in the porous matrix ($\triangle$). Solid curves show the results of fitting VFT formulae.

process observed in the isotropic phase should be described by the VFT equation (1). This shows that the pore size is large enough that N molecules behave like a liquid phase and not like an ensemble of single molecules, as was observed for glycerol in silicalite and silica sodalite pores where the Arrhenius type of relation, $\log \nu_{max}(1/T)$, was found [9]. The best fit of the VFT equation to the data for 6O2OCB in porous media gives $\tau_0 = 10^{-13.5}$ s and $T_0 = 133$ K, $D = 7.9$ (on cooling); $T_0 = 131$ K, $D = 8.8$ (on heating). Thus, the deviation of $\log \nu_{max}(1/T)$ from the Arrhenius type of behaviour is smaller for the liquid in a porous matrix than in the bulk, where $T_0 = 167$ K and $D = 3.6$. That means that for 6O2OCB in a porous matrix, the fragility parameter m [16] corresponding to D is smaller than in the isotropic liquid in the bulk. For the activational process described by the straight line in the Arrhenius diagram, D reaches a value of more than 50, corresponding to the lowest value of the fragility, i.e. $m = 16$. The lower value of T_0 estimated for the porous sample means that the 6O2OCB substance survives there in the liquid phase to lower temperature before it transforms into a glass. In pores, the molecules reorient faster than when surrounded by other molecules in the pure substance. This means that the molecules have more free volume in which to reorient in pores than in the bulk. One can see that the temperature changes of the relaxation rates in figure 6 confirm the earlier finding that there is no phase transition when the substance is enclosed in the porous matrix. The surface of the nearly spherical pores of 5 nm radius presents difficulties in the transition of the isotropic liquid into the state of free energy typical for smectic order of molecules. The pores are too small for the crystallization of all molecules. The small hysteresis effect observed for relaxation times shows that, on average, the molecular motions are slightly slower on heating than on cooling. This supports the earlier description of the ordering effect of the surface on 6O2OCB molecules.

The temperature dependences of the rate of relaxation for three processes observed in 6O2OCB—namely, molecular ($\bigcirc$), collective ($\triangle$) and ionic (+)—are presented in figure 7. The experimental points were obtained on cooling and on heating the porous sample. It seems clear that the data estimated for the collective phenomenon can also be described by the VFT formula. The best fit gives the high-temperature limit of the relaxation time for the collective motions, $\tau_0 = 10^{-5}$ s, the temperature at which those motions are frozen, $T_0 = 220$ K, and $DT_0 = 123$ K (the D-parameter itself has no physical meaning in this case). The ionic process
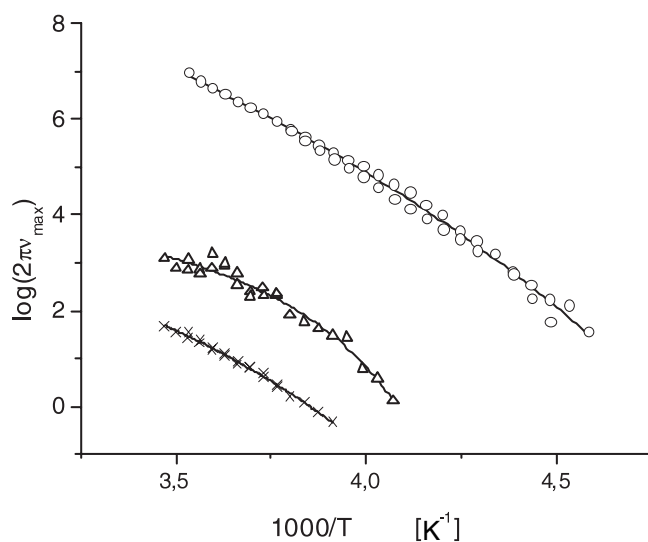
Figure 7. A plot of $\log(2\pi \nu_{max})$ versus $1000/T$ for 6O2OCB in the porous matrix for three relaxation processes: molecular ($\bigcirc$), collective ($\triangle$) and ionic ($\times$). Solid curves show the results of fitting the VFT formulae.

can be explained by the activational behaviour with an enthalpy barrier of $\Delta H = 45 \text{ kJ mol}^{-1}$. Both processes, however, need more detailed study.

4. Conclusions

The dielectric spectroscopy results obtained for the dipolar substance 4-(2-hexyloxyethoxy)4′-cyanobiphenyl (6O2OCB) in the porous material ZrO_2 with pores of 5 nm radius can be summarized as follows:

(1) The relaxation observed consists of three processes, the molecular one observed also in the pure substance and two new ones: the collective and the ionic. The shape of $\varepsilon''(\nu)$ has been described with the help of a sum of Havriliak–Negami formulae.

(2) None of the phase transitions observed previously for the pure substance have been confirmed. On cooling, the isotropic phase is supercooled and it transforms into glass at lower temperature than in the bulk. The creation of the smectic phase can be hindered by the shape of pores and by the existence of collective and ionic motions as well.

(3) The temperature dependences of the molecular and collective processes obey the VFT formula with high-temperature limits of the relaxation time τ_0 of $10^{-13.5}$ s and 10^{-5} s, respectively. The reorientations of the molecules turned out to be faster in pores than in the pure material.

(4) On cooling, the layers of aligned and immobile molecules grow along the pore surfaces. This fact helps us to understand the thermal hysteresis observed over a large temperature range for all physical parameters.

Acknowledgments

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