

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/26295986>

Nonlinear Dielectric Relaxation in the Isotropic Phase and Mesophases of Cholesteryl Oleyl Carbonate

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · JULY 2009

Impact Factor: 3.3 · DOI: 10.1021/jp902101u · Source: PubMed

CITATIONS

3

READS

21

2 AUTHORS:



Przemysław Kędziora

Institute of Molecular Physics, Polish Acad...

49 PUBLICATIONS 289 CITATIONS

SEE PROFILE



K. W. Wojciechowski

Polish Academy of Sciences

130 PUBLICATIONS 1,736 CITATIONS

SEE PROFILE

Nonlinear Dielectric Relaxation in the Isotropic Phase and Mesophases of Cholesteryl Oleyl Carbonate

Przemysław Kędziora* and Krzysztof W. Wojciechowski*

Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, 60-179 Poznań, Poland

Received: March 9, 2009; Revised Manuscript Received: May 12, 2009

The nonlinear dielectric spectra of chiral crystal cholesteryl oleyl carbonate (COC) were recorded in frequency range of 1–100 MHz in the presence of the strong static electric field $E_0 = 1 \times 10^7$ V/m. The measurements were performed within the temperature range of about 23 K in the isotropic, the blue phase, and the chiral nematic phase known also as the cholesteric phase. In the nonlinear dielectric relaxation spectra two absorption bands, related to molecular rotations (orientational band) and intermolecular interactions (chemical band), have been observed. The nonlinear dielectric results were interpreted by combination of a Debye-type and Coffey's equations, extended to the case of two simultaneous relaxation processes. The results revealed three regions in the temperature dependence of the chemical relaxation time behavior, corresponding to isotropic phase, blue phase and chiral nematic phase, respectively. Dynamic phenomena, observed in very narrow range of temperature (2 K) in the vicinity of the phase transition between the blue phase and the chiral nematic phase, were interpreted in frames of the Landau–de Gennes theory.

Introduction

Liquid crystals are frequently used for studies of phase transitions where one can observe different types of transitions in one system: first order (with discontinuous first derivatives of some thermodynamic potential, like the latent heat), second order (continuous transitions with critical effects) and weakly first order transitions (showing discontinuous first derivatives and critical-like behavior of some physical properties). The transition between the isotropic liquid and the simplest liquid crystalline phase, known as nematic and characterized by liquid-like order of molecular mass centers and long-range orientational order of molecular axes (which remain parallel), belongs to the last category. The pretransitional phenomena in this case, due to the fluctuations of order parameter, lead to the formation of domains with local nematic order in the isotropic phase. The size of the domains increases as the temperature of liquid comes down to the IN phase transitions.^{1–6} The domains can be characterized by the correlation length ξ .⁷ The Landau theory of the second order phase transition applied by de Gennes to the isotropic to nematic phase transition leads to the following dependence of the correlation length:⁷

$$\xi(T) = \xi_0 \left[\frac{T^*}{T - T^*} \right]^{1/2} \quad (1)$$

where ξ_0 is the molecular length scale and T^* is the temperature obtained within a mean-field approximation by assuming second-order phase transition. T^* is slightly below the true temperature of the IN phase transition, T_{IN} , due to the weakly first-order character of the transition. According to eq 1, the correlation length becomes infinite at T^* . The influence of the pseudonematic domains on the long time scale dynamics continues up to ~ 50 K above the IN phase transition temperature.^{1,2}

The Landau–de Gennes theory (LdG) has been successful in explaining the dynamics of the pretransitional fluctuations in the isotropic phase of liquid crystals in the dynamic studies as molecular spin–lattice relaxation,^{8,9} dynamic light scattering,¹⁰ optical Kerr effect^{12,11–13} and X-ray scattering.^{14,15} It should be emphasized that the dynamics of the pretransitional phenomena is observed nearly exclusively in the nonlinear studies, i.e. when an external impulse is sufficiently strong. Only when a strong electric field is applied to the mesogenic liquid does a new dielectric absorption band appears in the frequency region about 1 order of magnitude lower than that recorded in the linear spectroscopy as a band corresponding to the rotation of individual mesogenic molecules around their short axis. Hence, nonlinear dielectric spectroscopy can be used for a study of the dynamics of the pretransitional fluctuations.^{6,16–20} The case of rodlike nonpolar dimers of carboxylic acid (4-*n*-butylcyclohexanecarboxylic acid) shows that the nonlinear dielectric spectroscopy, despite extremely low strength of the nonpolar system response to an application of the strong electric field, is able to detect the pretransitional dynamic effects even in the nonpolar mesogenic materials.¹⁸ With linear dielectric spectroscopy these fluctuations can be seen indirectly only for polar compound having a strong dipole moment along the long molecular axis.²¹

Chiral nematics (known also as cholesterics) show more complex molecular ordering than the nematics: parallel ordered molecules form layers, and orientations of the consecutive layers show helical ordering. Recently, there is a considerable interest in the pretransitional fluctuations near the cholesteric phase in chiral liquid crystals.^{21–26} It is worth stressing that, in many cholesteric liquid crystals, the transition between helical and isotropic phases occurs through some transitions to intermediate structures known as “blue phases” (BPI, BPII, BPIII). The BPI and BPII have a three-dimensional periodic structure with cubic symmetry. The BPIII is a separate phase, thermodynamically distinct from cubic and isotropic phases. Although various theoretical models such as the cubic domain model,²⁷ the double-twist model²⁸ or the icosahedral model²⁹ have been proposed

* Corresponding authors. E-mail: kędziora@ifmpan.poznan.pl; kww@man.poznan.pl.

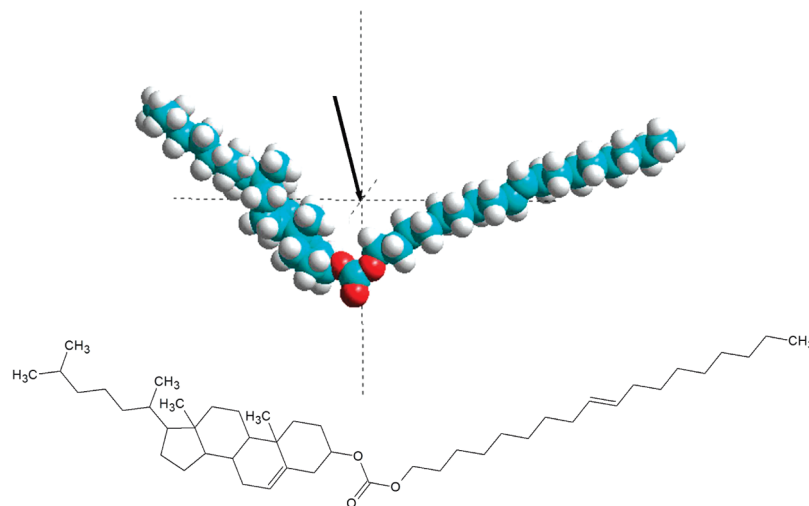


Figure 1. Molecular structure of cholesteryl oleyl carbonate (COC). The arrowhead indicates the direction of the molecular dipole.

for BPIII, most observations suggest that it is amorphous,³⁰ and the theoretical description of the short-range structure of BPIII is still an ongoing problem. By contrast, for BPI and BPII the lattice periods are of the order of the wavelength of visible light and they exhibit selective Bragg reflections. Therefore, blue phases may be considered as examples of self-organized tunable photonic crystals with many potential applications.^{31,32} Chirality can have an important influence on inducing the blue phases and also producing strong fluctuations effects. The blue phases, BPI and BPII, are induced only at moderate chiralities, and at higher chiralities these structures “melt” into the BPIII.^{23,33} One can add that the phase transitions between blue phase III and isotropic liquid is one of the most complex phenomena to account for theoretically. The main reason for this complexity lies in the need of including correlation effects even at the level of mean-field-like description.^{34,35} In this work our attention is paid to the dynamics of fluctuations of order parameter in the vicinity of the I–BP–N* phase transitions.

The pretransitional behavior of nonlinear dielectric relaxation measured for mesogens in isotropic phase in the vicinity of the isotropic to nematic or smectic A phase transitions was a subject of some recent papers.^{6,17–20} It was observed that approaching of the nematic phase transitions manifests itself by a critical-like behavior of the nonlinear relaxation time. The pretransitional fluctuations of the electric moment in the vicinity of the isotropic to nematic or smectic A phase transitions lead to the formation of the short-range domains in the isotropic phase. To the best of the authors’ knowledge there have been no attempts to measure the relaxation of the nonlinear dielectric effects in mesophases.

The aim of the present paper is to extend the study of the relaxation of the nonlinear dielectric effect (NDE) to mesophases (the BP and the chiral nematic N*) and to check if fluctuations exist in pretransitional regions in all these phases. For the study the liquid crystal cholesteryl oleyl carbonate (COC) has been chosen. This is because of two reasons: (i) it has the required sequence of the phases, i.e. isotropic–BP–chiral nematic, and (ii) the orientation of dipole moment is nearly transverse to the long axis of COC molecule, as shown in Figure 1. In the latter case, it is interesting to verify if there are any dielectric pretransitional fluctuations, which are not seen in experiments performed by linear dielectric relaxation methods.²¹

Experimental Section

Cholesteryl oleyl carbonate COC from Aldrich Chemicals was used in the experiment. As the material is very sensitive to

light, heat, and air oxidation and, hence, difficult to purify,³⁶ it was used without any additional purification. From heat capacity measurements by Van Dael²² the transitions in well purified material occur at temperatures I–309.78 K–BPIII–309.63–BPII–309.36–BPI–308.85–N*. The measurements of the nonlinear dielectric effect in the frequency domain were performed with equipment designed at the University of Leuven, Belgium.³⁷ In the method the electric field of high strength $E_0 = 1 \times 10^7$ V/m was used and low frequency (85 Hz) was perturbing periodically the system. The permittivity change, $\Delta\epsilon = \epsilon_{E_0} - \epsilon$, was measured with a weak field $E(\omega)$ of high frequency. The nonlinear dielectric data we obtained by monitoring the modulation of the parameters of a resonant circuit induced by the application of a high field to the capacitor of the circuit, filled with the liquid studied. An LC resonance circuit with exchangeable coils covered the frequency range from 1 to 100 MHz. The details of the method and the setup used were described elsewhere.^{6,37} The viscosity was measured with a Haake RV20 rotational viscometer. The details were also described earlier.³⁸

Results and Discussion

Figure 2 presents the nonlinear dielectric spectra recorded for the COC within the temperature range of about 23 K in the isotropic, BP and the chiral nematic phase. Two main features of the spectra shown seem to be important. First, the field-induced dielectric increments ($\Delta\epsilon$) consist of, at least, two components: negative and positive. Second, the character of the frequency dependences of real ($\Delta\epsilon'$) and imaginary ($\Delta\epsilon''$) parts of the nonlinear dielectric increment sharply changes in the temperature just below the BP–N* phase transition.

The dielectric nonlinearity can be caused, in general, by two molecular mechanisms occurring in isotropic liquids. The first of them is the Langevin saturation of the dipoles’ orientation in strong electric fields. This effect leads to a *decrease* of the permittivity of liquids. Thus the nonlinear dielectric increment ($\Delta\epsilon$) is negative and is proportional to the square of the field strength E_0 . The relaxation of the negative effect occurs in same frequency region as the linear dielectric relaxation.³⁹ This negative effect was observed for diluted solution of 4-(*trans*-4'-*n*-hexylcyclohexyl)isothiocyanatobenzene (6CHBT) in benzene.^{39,40} The second mechanism occurs for systems in which the intermolecular interactions (e.g., dipole–dipole or hydrogen bonds) lead to formation of aggregates with a compensated dipole moment, or when intramolecular processes (e.g., con-

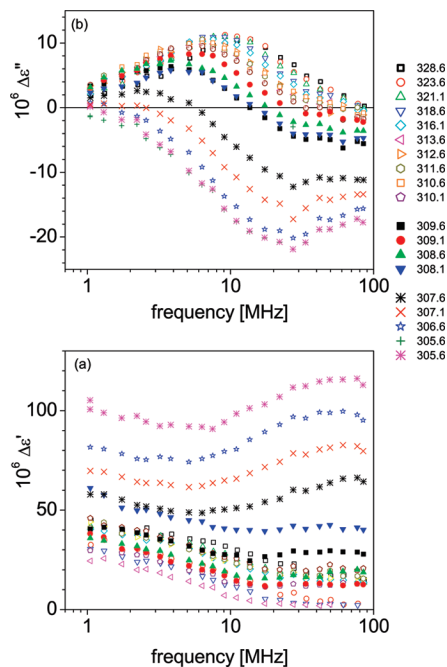


Figure 2. Frequency dependence of the real (a) and imaginary (b) parts of the nonlinear dielectric increment for various temperatures in the isotropic phase (open), BP (solid) and the cholesteric phase (stars) of COC.

formational change) involve a change of molecular polarity. The strong electric field shifts the equilibrium between the aggregates and the monomers (or other aggregates), or between the conformers, in favor of more polar species. This effect causes an *increase* of the permittivity of the liquid; i.e. the increment $\Delta\epsilon$ is positive and shows the relaxation in the frequency range corresponding to the kinetics of the aggregation process.⁴¹ In an earlier paper⁶ the results of the nonlinear dielectric relaxation studies performed for the mesogenic polar compound 6CHBT in the vicinity of the isotropic to nematic phase transition were presented. For that liquid crystal the nonlinear dielectric increment $\Delta\epsilon$ is positive and the nonlinear absorption bands $\Delta\epsilon(\omega)$ are of the Debye-type form with a single relaxation time (τ):

$$\Delta\epsilon^* = \Delta\epsilon' - i\Delta\epsilon'' = \frac{\Delta\epsilon^0}{1 + i\omega\tau} \quad (2)$$

where $\Delta\epsilon^0$ is the strength of the nonlinear dielectric effect and ω is the angular frequency of the measuring electric field of low intensity $E(\omega)$.

In the case of mesogenic molecules the positive nonlinear increment of permittivity can be related to the pretransitional phenomena which are due to existence of a short-range orientational order of the mesogenic molecules leading to the formation of the pseudonematic domains in the isotropic liquid. The negative components of the nonlinear dielectric spectra presented in Figure 2 concern the Langevin dipolar saturation relaxation. A theoretical description of the frequency dependence of the nonlinear dielectric phenomenon caused by the saturation of the dipoles orientation in strong electric fields has been proposed by Coffey and Paranjape,⁴² Kielich and co-workers,^{43,44} and Kimura and Hayakawa.⁴⁵ Here we will use the following Coffey equation⁴² extended to the case of the two simultaneous nonlinear relaxation processes, which fit well to our experimental conditions:

$$\Delta\epsilon'_L = \sum_{i=1}^2 L_i \frac{1}{1 + \omega^2\tau_i^2} \cdot F_{1i}(\omega) \quad (3)$$

$$\Delta\epsilon''_L = \sum_{i=1}^2 L_i \frac{\omega\tau_i}{1 + \omega^2\tau_i^2} \cdot F_{2i}(\omega) \quad (4)$$

where

$$L_i = -\frac{N\mu_i^4}{45\epsilon_0 k^3 T^3} \cdot E_0^2 \frac{\epsilon_s^4(\epsilon_\infty + 2)^4}{(2\epsilon_s + \epsilon_\infty)^2(2\epsilon_s + \epsilon_\infty^2)} \quad (5)$$

$$F_{1i}(\omega) = \frac{27 + \omega^2\tau_i^2 - 2\omega^4\tau_i^4}{3(1 + \omega^2\tau_i^2)(9 + \omega^2\tau_i^2)} \quad (6)$$

$$F_{2i}(\omega) = \frac{42 + 19\omega^2\tau_i^2 + \omega^4\tau_i^4}{3(1 + \omega^2\tau_i^2)(9 + \omega^2\tau_i^2)} \quad (7)$$

L_i denotes the dielectric strength, τ_i the relaxation time and i the number of the relaxation process taken into account during the fitting procedure. Finally, the following sum of the Debye and Coffey functions was used for fitting to the experimental data:

$$\Delta\epsilon'(\omega) = \epsilon_\infty + \frac{\Delta\epsilon^0}{1 + \omega^2\tau_D^2} + \Delta\epsilon'_L$$

$$\Delta\epsilon''(\omega) = \Delta\epsilon^0 \frac{\omega\tau_D}{1 + \omega^2\tau_D^2} + \Delta\epsilon''_L \quad (8)$$

where $\Delta\epsilon^0$ is the strength of the nonlinear dielectric effect, ϵ_∞ is the high-frequency limit of the permittivity and τ_D is the Debye dipolar relaxation time. For clarity only typical nonlinear dielectric spectra obtained at the temperatures, characteristic for three phases occurring in the COC, have been shown in Figure 3. The solid lines in Figure 3 correspond to the best fit of the functions eq 8, and dashed (lines 1–4) and dotted (lines 5–7) lines are the component bands resulting from fitting for the chemical (positive) and the orientational (negative) effects, respectively. For the first time one can observe both of the nonlinear dielectric relaxation processes in one mesogenic system. Usually when the frequency region corresponding to the “chemical” band occurs not too far from the absorption band due to rotation of the individual molecules, an interference of the two dielectric absorptions can lead to considerable reduction of the spectrometer sensitivity. In the case of the COC the frequency distance between these two bands is large enough for recording them in NDE spectrum.

As Figure 2 and Figure 3 show, the sudden change of the character of the frequency dependences of the dielectric increment is clearly visible in the temperature below the BP–N* phase transition which reveals as decreasing of the strength of positive (“chemical”) nonlinear dielectric absorption and increasing the strength of negative band (orientational). In the temperature region from 307.6 to 305.6 K there appears another orientational process with negative nonlinear effect. The relaxation of the positive “chemical” effect is observed in systems in which the intermolecular aggregates, susceptible to the strong

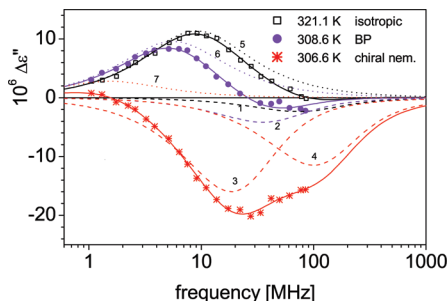


Figure 3. Examples of nonlinear dielectric relaxation spectra for COC in isotropic phase (open squares), blue phase (stars) and chiral nematic phase (full triangles). Solid lines represent the best fitting of the Debye–Coffey equations (eqs 8) to the experimental results (points). Dashed lines represent the nonlinear dielectric absorption components corresponding to the molecular rotation (1, in isotropic; 2, in BP; 3, 4, in chiral nematic phases). Dotted lines represent components relevant to the “chemical” effect (5, in isotropic; 6, in BP; 7, in chiral nematic phases).

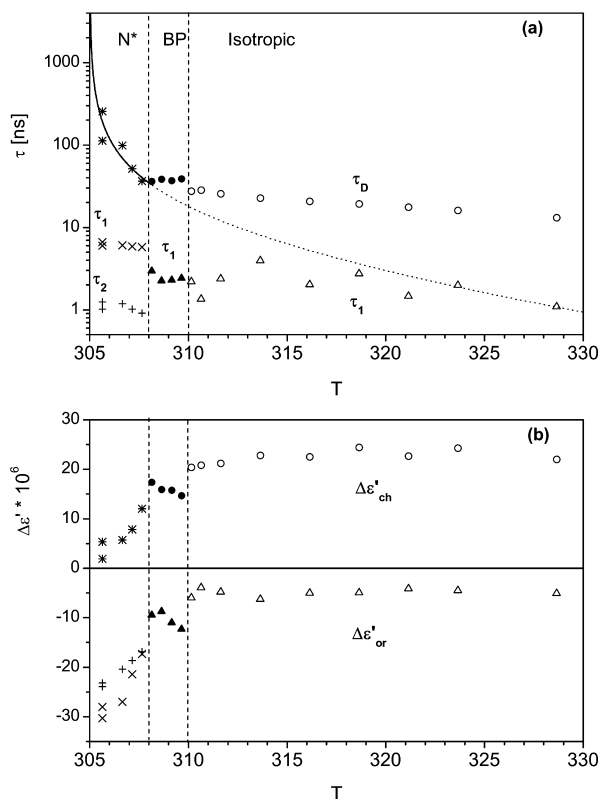


Figure 4. Temperature dependences of the chemical (τ_D) and orientational (τ_1, τ_2) relaxation times (a) and the strength of nonlinear dielectric increments $\Delta\epsilon$ (b), corresponding to the best fitting of eq 8 to the experimental nonlinear spectra. The line through the points of the temperature dependent chemical relaxation times, τ_D , is the LdG theoretical curve.

electric field, exist.^{37,41,46,47} The negative effect are the Langevin saturation of the orientation of the dipoles forced by the strong electric field.

The values of the relaxation times resulting from the best fitting of eq 8 to experimental nonlinear dielectric spectra are depicted in Figure 4 as a function of temperature. Figure 4 shows the monotonic increase of τ_D when the temperature of the isotropic phase is decreased. At a temperature 310, just below the phase transition to BP a sudden jump of the value of τ_D is observed which is the indication of the first order character of the transition. In the helical nematic phase (N^*), below 307.6 down to 305.6 K, close to the BP phase transition rapid growth

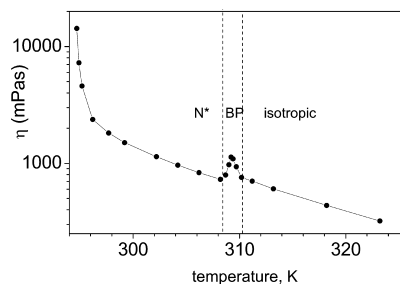


Figure 5. Shear viscosity of COC as a function of temperature.

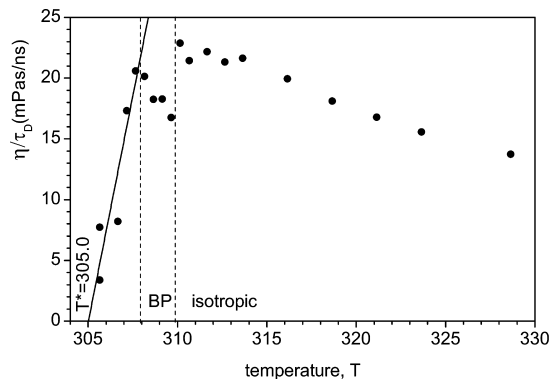


Figure 6. The linear relation of η/τ_D as a function of temperature, predicted by LdG theory.

of $\tau_D(T)$ is visible. This behavior is similar to that observed for 6CHBT in the vicinity of the isotropic to nematic phase transition.⁶ This similarity suggests a fluctuational origin of $\tau_D(T)$ behavior in the N^* phase. The observation of fluctuational behavior in helical nematic phase of COC in the vicinity of the N^* –BP phase transition was earlier reported by Rzoska et al.²⁶ from dielectric permittivity measurements. Landau–de Gennes (LdG) theory predicts that the pretransitional phenomena are described by an exponential decay function with the relaxation time $\tau_D(T)$ which diverges at the virtual phase transition temperature T^* as⁷

$$\tau_D(T) = \frac{V_{\text{eff}}^* \eta(T)}{k(T - T^*)^\gamma} \quad (9)$$

where V_{eff}^* is the mesogen’s effective volume,^{48,49} $\eta(T)$ is the viscosity and k is the Boltzmann constant. For liquid crystals γ has been shown to be ~ 1 , indicating the validity of the application of mean field theory.⁷ Deviations from LdG theory have been seen at temperatures sufficiently (up to ~ 50 K) above the nematic–isotropic transition.^{1,2,13}

The values of the viscosity used in calculation of the LdG theoretical curve are presented in Figure 5. A sharp increase of the viscosity is observed at the isotropic to blue phase transition. The line through the relaxation time τ_D data in Figure 4 was calculated using eq 9. The agreement with the predictions of LdG theory is quite good only in a very narrow range of temperature in the chiral nematic phase, from 307.6 to 305.6 K. A plot of η/τ_D as a function of temperature should be linear for γ equal to 1 and with an intercept with the temperature axis, for $T = T^*$ (Figure 6). We obtain second order phase transition temperature, $T^* = 305.0$ K. This range of temperature is much smaller than one finds in nonchiral nematic materials, where the pretransitional fluctuations occur even 50 K above the NI phase transition.^{2,13}

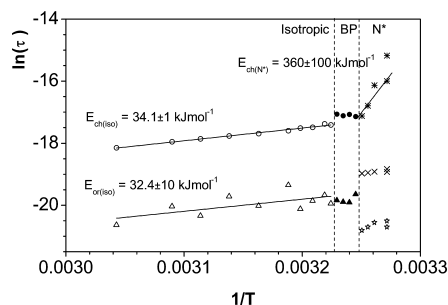


Figure 7. Arrhenius plots for the nonlinear dielectric relaxation times determined in isotropic phase and fluctuation region of the cholesteric phase of the COC.

The fluctuations in the chiral nematic phase, just below the BP–N* phase transition, lead to the formation of domains different in their structure from the helical nematic phase N*. According to eq 1, the size of domains was calculated using the value of the molecular correlation length ξ_0 of 1.5 nm for the COC, given by Koistinen and Keyes.²³ The correlation length ξ in transient temperature, from 307.6 to 305.6 K, increases from 16 nm up to 33 nm, the values convergent with that resulting from the light-scattering study of the COC.²³ The dynamics of these entities in the vicinity of phase transition is different from that of the pseudonematic domains existing in the isotropic phase of nonchiral thermotropic materials. First, their size is much larger than one finds $\xi \approx 15$ nm for the typical nematogen in the vicinity of the isotropic to nematic phase transition.^{2,13,17} Receding from the second order phase transition temperature T^* , the correlation length ξ does not decrease much, only to 16 nm, in contrast to that one in the isotropic phase of nematogen which diminishes to 2 nm. However, it is important to note that their average size is too small for a helix developing. The correlation length (ξ) is still significantly smaller than the helical pitch (from $\sim 1 \mu\text{m}$ to several hundred μm). Second, the strength of the positive band of the nonlinear dielectric absorption ($\Delta\epsilon'_{\text{ch}}$) decreases with decreasing of the temperature in the cholesteric phase as distinct from the rapid increasing of $\Delta\epsilon'_{\text{ch}}$ in the vicinity of the IN phase transition. At the temperature 305.0 K, the positive chemical band of nonlinear dielectric spectra disappears. It means that the system with fluctuations in the form of domains, probably with a supercooled blue phase, evolves slowly to the homogeneous cholesteric phase. Similar slow evolution to the cholesteric phase was observed by Zink and Van Dael²² in the light scattering studies of the COC.

The relaxation time dependences in the isotropic phase of the COC, above the BP's phase transition (328.6–310.1 K), do not show any remarkable features. As mentioned above (Figure 6), the temperature dependence of relaxation times cannot be interpreted in the frame of LdG theory, which means that the fluctuations of order parameter are absent in the isotropic phase of the COC. The absence of fluctuations is due to the fact that isotropic phase is not adjacent, in temperature scale, to the nematic or the helical nematic phase. The fluctuations do appear below the temperature of the BP–helical nematic phase transition.

Figure 7 allows one to make a comparison of the temperature dependencies of the relaxation times of both processes: chemical and orientational, in the isotropic phase of the COC. The activation energies calculated from $\ln(\tau)$ dependencies on $1/T$ (the Arrhenius plot) are nearly the same for these processes ($E_{\text{ch(iso)}} = 34 \text{ kJ mol}^{-1}$ and $E_{\text{or(iso)}} = 32 \text{ kJ mol}^{-1}$). Otherwise, it should be a large difference between the energy corresponding

to the formation of the pseudonematic domains and that of the diffusional rotation of single molecules. Indeed, for pre-nematic behavior in 6CHBT the values of these energies are, respectively, 95 kJ mol^{-1} and 32 kJ mol^{-1} .⁵⁰ In the case of COC this difference is even larger, 360 kJ mol^{-1} and 34 kJ mol^{-1} (Figure 7), due to larger size of domains in helical material than in typical nematogens. The large errors in calculation of the activation energy in the transient region of temperature are due to very small strength of the positive nonlinear dielectric absorption.

The interactions between the individual molecules of the COC are probably responsible for the positive nonlinear dielectric effect, which do not lead to short-range fluctuations in the isotropic phase. Due to a bent shape of the COC molecule and its relative large dipole moment (3.6 D), with its perpendicular location to the long molecule axis, there exists a possibility of formation of small entities, e.g. dimers of partially compensated dipole moment. The positive change of nonlinear dielectric increment is due to shifting the equilibrium toward more polar entities by the strong electric field. Unfortunately, the details of these interactions cannot be concluded from the present studies.

The transitions from the isotropic phase to the blue phase (310 K) and then to the cholesteric phase (308 K) are visible as sudden changes of chemical relaxation time (τ_D) (Figure 4 and Figure 6). The presence of the blue phase is noticeable also in the dependence of the shear viscosity (Figure 5). On the other hand, the blue phase is not visible in the temperature dependence of the orientational relaxation (Figure 4), whereas the transition to the fluctuation region of chiral nematic phase manifests by appearance of the second orientational band (component 4 in Figure 3). In the isotropic phase, this second orientational band occurs at higher frequencies of the NDE spectrum ($>100 \text{ MHz}$), which are out of the measurement range of the NDE equipment used in this study. In the cholesteric phase, the both of orientational bands are shifted to the lower frequencies and could be recorded by the NDE spectrometer. We suppose that these bands are connected with a diffusional rotation of single molecules around their axes, but an accurate analysis could be done only after more precise measurements of nonlinear dielectric effects in the cholesteric phase, below the fluctuation region of temperature. No significant differences in the temperature dependence of the relaxation time τ_{or} were observed in the blue phase in comparison to the isotropic phase, which could lead to the conclusion that the blue phase observed here is the BPIII, which is similar to the isotropic phase as suggest some authors.^{51,52}

Conclusions

For the first time the NDE measurements of the relaxation effect were performed not only in the isotropic but also in the blue phase and the chiral nematic phase of the liquid crystalline material. In contrast to nonchiral nematic liquid crystals, both the Langevin saturation of the orientation of the dipoles (negative effect) and relaxation of “the chemical” nonlinear dielectric effect concerning the intermolecular interactions (positive effect) were observed simultaneously in one mesogenic material.

Three regions in the temperature dependence of the chemical relaxation time behavior have been identified, respectively corresponding to (i) the isotropic phase, (ii) the blue phase and (iii) a region of the molecular fluctuations in the cholesteric phase near the phase transition to the blue phase. Dielectric pretransitional effects, which lead to the short-range order, are

absent in the isotropic phase and blue phase. An anomaly of the temperature dependence of the relaxation of the chemical NDE ($\tau_D(T)$), revealed just below the BP–N* phase transition, was interpreted in the frame of the Landau–de Gennes theory for weakly first-order phase transitions. The molecular fluctuations in the chiral nematic phase are limited to a very narrow interval of the temperature (2 K) in the vicinity of the N*–BP transition. These fluctuations manifest themselves as domains with supercooled blue phase structure. The fluctuations diminish as the temperature comes down and the system evolves slowly to homogeneous cholesteric phase. An appearance of the blue phase seems to exclude the existence of pretransitional fluctuations in the isotropic phase. The size of the domains in the COC (up to 30 nm) in the vicinity of the cholesteric–BP phase transition is significantly larger than their size in nonchiral nematic materials (up to 10 nm). The large size of the domains results in a large enhancement in the activation energy, ~ 10 times higher than that of the diffusional rotations of single molecules.

The described study indicates that the nonlinear dielectric spectroscopy can play a role of an effective research tool for the detection of the molecular fluctuations in the vicinity of the phase transitions from chiral nematic phase to the blue phase. In contrast to the linear dielectric relaxation, the application of an electric field, as high as 100 kV/cm, in the NDE spectroscopy increases its sensibility to changes of the dipole moment, which enables detection of pretransitional effects in materials with a centrally located dipole moment.

Acknowledgment. This work was supported by the Fonds voor Wetenschappelijk Onderzoek - Vlaanderen, Belgium, in the framework of the agreement for scientific cooperation with the Polish Academy of Sciences.

References and Notes

- (1) Stankus, J. J.; Torre, R.; Marshall, C. D.; Greenfield, S. R.; Sengupta, A.; Tokmakoff, A.; Fayer, M. D. *Chem. Phys. Lett.* **1992**, *194*, 213.
- (2) Stankus, J. J.; Torre, R.; Fayer, M. D. *J. Phys. Chem.* **1993**, *97*, 9478.
- (3) Gottke, S. D.; Brace, D. D.; Cang, H.; Bagchi, B.; Fayer, M. D. *J. Chem. Phys.* **2002**, *116*, 360.
- (4) Gottke, S. D.; Cang, H.; Bagchi, B.; Fayer, M. D. *J. Chem. Phys.* **2002**, *116*, 6339.
- (5) Cang, H.; Li, J.; Fayer, M. D. *Chem. Phys. Lett.* **2002**, *366*, 82.
- (6) Kędziora, P.; Jadżyn, J.; Hellemans, L. *Phys. Rev. E* **2002**, *66*, 021709.
- (7) de Gennes, P. G. *Physics of Liquid Crystals*; Oxford University Press: Oxford, 1974.
- (8) Cabane, B.; Clarke, G. *Phys. Rev. Lett.* **1970**, *25*, 91.
- (9) Gosh, S.; Tettamanti, E.; Indovina, E. *Phys. Rev. Lett.* **1973**, *29*, 638.
- (10) Stinson, T. W.; Litster, J. D. *Phys. Rev. Lett.* **1970**, *25*, 503.
- (11) Wong, G. K. L.; Shen, Y. R. *Phys. Rev. Lett.* **1973**, *30*, 895.

- (12) Deeg, F. W.; Fayer, M. D. *J. Chem. Phys.* **1989**, *91*, 2269.
- (13) Deeg, F. W.; Greenfield, S. R.; Stankus, J. J.; Newell, V. J.; Fayer, M. D. *J. Chem. Phys.* **1990**, *93*, 3503.
- (14) Bellini, T.; Rappaport, A. G.; Clark, N. A.; Thomas, B. N. *Phys. Rev. Lett.* **1996**, *77*, 2507.
- (15) Bellini, T.; Clark, N. A.; Link, D. R. *J. Phys.: Condens. Matter* **2003**, *15*, S175.
- (16) Drozd-Rzoska, A.; Rzoska, S. J.; Ziolo, J. *Phys. Rev. E* **1996**, *54*, 6452.
- (17) Kędziora, P.; Jadżyn, J.; Hellemans, L. *Phys. Rev. E* **2002**, *66*, 031702.
- (18) Kędziora, P.; Jadżyn, J.; Hellemans, L. *J. Phys. Chem. A* **2003**, *107*, 5650.
- (19) Kędziora, P. *Acta Phys. Pol., A* **2003**, *104*, 45.
- (20) Kędziora, P. *Acta Phys. Pol., A* **2005**, *107*, 907.
- (21) Leys, J.; Glorieux, C.; Wubbenhorst, M.; Thoen, J. *Liq. Cryst.* **2007**, *34*, 749.
- (22) Zink, H.; Van Dael, W. *Liq. Cryst.* **1989**, *5*, 899.
- (23) Koistinen, E. P.; Keyes, P. H. *Phys. Rev. Lett.* **1995**, *74*, 4460.
- (24) Pantea, M. A.; Keyes, P. H. *Phys. Rev. E* **2005**, *51*, 031707.
- (25) Kang, J. S.; Dunmur, D. A. *Phys. Rev. E* **1995**, *71*, 21219.
- (26) Pawlus, S.; Zasada, M.; Rzoska, S. J. *Z. Naturforsch.* **2002**, *57a*, 126.
- (27) Hornreich, R. M. *Phys. Rev. Lett.* **1991**, *67*, 2155.
- (28) Hornreich, R. M.; Kugler, M.; Shtrikman, S. *Phys. Rev. Lett.* **1982**, *48*, 1404.
- (29) Hornreich, R. M.; Shtrikman, S. *Phys. Rev. Lett.* **1986**, *56*, 1723.
- (30) Crooker, P. P. In *Chirality In Liquid Crystals*; Kitzrow, H.-S., Bahr, C., Eds.; Springer: 2001; pp 186–222.
- (31) Etchegoin, P. *Phys. Rev. E* **2000**, *62*, 1435.
- (32) Yokoyama, S.; Mashiko, S.; Kikuchi, H.; Uchida, K.; Nagamura, T. *Adv. Mater.* **2006**, *18*, 48.
- (33) Keyes, P. H. *Phys. Rev. Lett.* **1990**, *65*, 436.
- (34) Longa, L.; Cieřla, M.; Trebin, H.-R. *Phys. Rev. E* **2003**, *67*, 061705.
- (35) Cieřla, M.; Longa, L. *Phys. Rev. E* **2004**, *70*, 012701.
- (36) Lushington, K. J.; Kasting, G. B.; Garland, C. W. *Phys. Lett.* **1979**, *74A*, 143.
- (37) Hellemans, L.; De Maeyer, L. *J. Chem. Phys.* **1975**, *63*, 3490.
- (38) Jadżyn, J.; Czechowski, G. *Phys. Rev. E* **2001**, *64*, 052702.
- (39) Jadżyn, J.; Kędziora, P.; Hellemans, L.; De Smet, K. *Chem. Phys. Lett.* **1999**, *302*, 337.
- (40) Kędziora, P.; Jadżyn, J.; De Smet, K.; Hellemans, L. *Chem. Phys. Lett.* **1998**, *289*, 541.
- (41) De Smet, K.; Kędziora, P.; Jadżyn, J.; Hellemans, L. *J. Phys. Chem.* **1996**, *100*, 7662.
- (42) Coffey, W. T.; Paranjape, B. V. *Proc. R. Ir. Acad.* **1978**, *78*, 17.
- (43) Kasprowicz-Kielich, B.; Kielich, S. *Adv. Mol. Relax. Processes* **1975**, *7*, 275.
- (44) Alexiewicz, W.; Kasprowicz-Kielich, B. In *Modern Nonlinear Optics*; Evans, M.; Kielich, S., Eds.; Wiley: New York, 1993; Part 1, p 1.
- (45) Kimura, Y.; Hayakawa, R. *Jpn. J. Appl. Phys.* **1992**, *31*, 3387.
- (46) Jadżyn, J.; Hellemans, L. *Acta Phys. Pol., A* **1995**, *67*, 1093.
- (47) Jadżyn, J.; Hellemans, L. *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 205.
- (48) Perrin, F. *J. Phys. Radium* **1934**, *5*, 497.
- (49) Hu, C.; Zwanzig, R. *J. Chem. Phys.* **1974**, *60*, 4354.
- (50) Jadżyn, J.; Czechowski, G.; Dejardin, J.-L. *J. Phys. Chem. B* **2008**, *112*, 4948.
- (51) Anisimov, M. A.; Agayan, A.; Collings, P. J. *Phys. Rev. E* **1998**, *57*, 582.
- (52) Englert, J.; Stark, H.; Longa, L.; Trebin, H.-R. *Phys. Rev. E* **2000**, *61*, 2759.

JP902101U