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Dielectric Spectroscopy Studies of 4-Cyano-3-fluorophenyl 4-Butylbenzoate Liquid Crystal at High Pressure

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For 4-cyano-3-fluorophenyl 4-butylbenzoate, nematic glassformer at ambient pressure, dielectric relaxation studies were performed under elevated pressure. In the isobaric experiment, on cooling the nematic phase two superarrhenius α -relaxations, ascribed to the reorientations of molecules around short axes and precession of long molecular axes were found and the Arrhenius β -relaxation related to intramolecular motions. Complexity of dynamics at elevated and ambient pressure is similar. Shift towards lower frequencies was found for both α -relaxations.

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1. Introduction

Dielectric relaxation spectroscopy (DRS) is a useful method for studying dipolar molecules dynamics in orientationally disordered phases of condensed matter, e.g., in liquid crystalline phases. For some of them vitrification is easier than crystallization [1]. Then a dramatic slowing down of molecular motions can be traced on approaching glass transition temperature [2–4]. It is detected as a structural α -relaxation spanning many decades of frequency. The most characteristic feature of this process is the non-Arrhenius behavior of the structural relaxation times. On further cooling a new weak relaxation appears at much higher frequencies. It is the so-called secondary β -relaxation [5] ascribed to small-amplitude local motions of molecules, and in some cases, to rotation of intra molecular groups. The temperature dependence of the secondary relaxation time satisfies the Arrhenius law. Application of elevated pressure influences dynamics of molecules by reducing a free volume necessary for molecular motions [6]. Interest in dielectric measurements of liquid crystalline glassformers under elevated pressure still grows [7]. In the paper the dynamics of the 4-cyano-3-fluorophenyl 4-butylbenzoate is described at 220 MPa. The substance [8, 9] occurs to be a glassformer at ambient pressure; two phase transitions were detected by the DRS on cooling, i.e., from isotropic to nematic at 280 K and from nematic to its glass at 220 K. On heating the phase sequence was different: after softening of glassy nematic, in the metastable nematic phase a spontaneous

crystallization occurred at 233 K and next a solid–solid transition took place at 260 K. Transition from a stable crystal to isotropic phase was observed at 288 K. That phase sequence corroborates with the results obtained by the adiabatic calorimetry [9]. Dielectric measurements brought the following information about molecular motions: the α -relaxation identified below 288 K consisted of two processes described well by the Cole–Davidson formulae [10]. The main process was ascribed to the reorientations of molecules around short axes while the weaker one to a faster precession of the molecules. Both processes are of the super-Arrhenius type. In addition, a very weak secondary β -relaxation of the Arrhenius type was detected below glass transition and described by the Havriliak–Negami formula [11]. Results of dielectric measurements presented in this paper show how pressure influences molecular dynamics and phase situation of 4-cyano-3-fluorophenyl 4-butylbenzoate.

2. Experimental

The 4-cyano-3-fluorophenyl 4-butylbenzoate substance was synthesized at the Military University of Technology, Warsaw. Molecular structure of 4-cyano-3-fluorophenyl 4-butylbenzoate calculated by semi-empirical quantum chemistry parameterized model number 3 (PM3) method is shown in Fig. 1.

The DRS measurements of 4-cyano-3-fluorophenyl 4-butylbenzoate were carried out using high pressure setup consisting of the Novocontrol-Alpha spectrometer, high pressure chamber and thermostating system providing stability of sample temperature better than 0.1 K. Isobaric experiment started at the room temperature. Pressure was increased up to 220 MPa which was accompanied by growth of the temperature of the substance up

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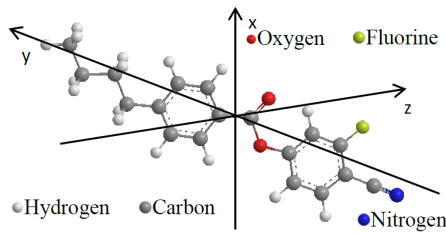


Fig. 1. Molecular structure of 4-cyano-3-fluorophenyl 4-butylbenzoate. Calculated components of the dipolar moment are the following: $\mu_x = 2.02$ D, $\mu_y = 0.26$ D, $\mu_z = 2.14$ D, $\mu = 2.95$ D.

to 323 K. The temperature dependence of the real ε' and imaginary ε'' parts of the complex dielectric permittivity $\varepsilon^* = (\nu, T, p) = \varepsilon'(\nu, T, p) - i\varepsilon''(\nu, T, p)$ was measured on cooling in the wide frequency range from 10^{-1} Hz to 3×10^6 Hz with accuracy better than 3%.

3. Results and discussion

Imaginary part of dielectric permittivity measured for 4-cyano-3-fluorophenyl 4-butylbenzoate sample at 220 MPa is presented in Fig. 2 for several temperatures from 323 K down to 261 K with temperature intervals of about 10 K. On lowering temperature shift of maxima of dielectric absorption towards lower frequencies seems to be similar as observed in glassforming phases [1]. No change connected with phase transition was detected. Due to increase of pressure nematic ordering in the sample appears at much higher temperature than at normal pressure. Effect of molecular ordering induced by a pressure was reported for liquid crystalline molecules, e.g. for butylthiocyanobiphenyl [12].

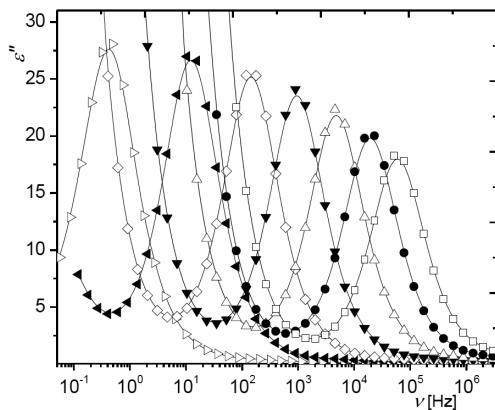


Fig. 2. Dielectric absorption as a function of frequency at constant pressure of 220 MPa for several temperatures from 323 K (□) to 261 K (▷) with about 10 K intervals.

In Fig. 3 the results of absorption measured at the same temperature but at normal and elevated pressure are compared. Increase of pressure essentially slows down

the relaxation rate. At 220 MPa one can clearly see similar complexity of dynamics as the observed in the nematic phase at ambient pressure. The observed dielectric absorption was described by a sum of three Havriliak–Negami formulae including additional term (A/ω) representing the dc conductivity contribution [11]:

$$\varepsilon''(\omega) = \frac{1}{2}(\varepsilon_0 - \varepsilon_\infty) \frac{\sin \beta \varphi}{[1 + 2(\omega\tau)^{1-\alpha} \sin(\frac{1}{2}\pi\alpha) + (\omega\tau)^{2(1-\alpha)}]^{\beta/2}} + \frac{A}{\omega}, \quad (1)$$

where $\varphi = \arctan \frac{(\omega\tau)^{1-\alpha} \cos(\frac{1}{2}\pi\alpha)}{1 + (\omega\tau)^{1-\alpha} \sin(\frac{1}{2}\pi\alpha)}$, α and β are the spectroscopic shape (symmetric and asymmetric) parameters. The case of $1-\alpha = \beta = 1$ corresponds to the Debye relaxation process. ε_∞ is the high frequency limit of dielectric permittivity. τ is the dielectric relaxation time describing the molecular motions. Parameter A is a measure of the electric conductivity.

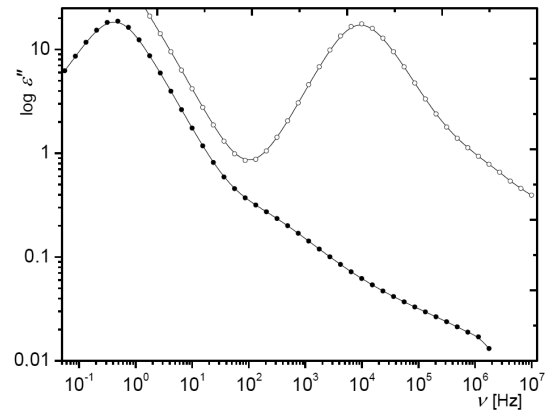


Fig. 3. Dielectric absorption as a function of frequency in double logarithmic scale measured at 261 K for 220 MPa (●) and for ambient (○) pressure.

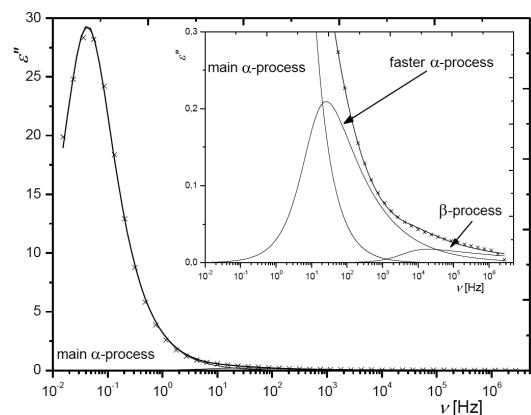


Fig. 4. Separation of the observed absorption into two α - and one β -relaxation processes in nematic phase for temperature of 256 K and pressure of 220 MPa. Inset shows contribution of the weaker α -process and the high frequency β -process.

The result of separation of the absorption into three processes is presented in Fig. 4 for 256 K. In Table the fitting parameters describing three processes of relaxation are collected for various temperatures of the nematic phase. The main relaxation is nearly the Debye process ($\alpha_1 = 0$, $\beta_1 \approx 1$). For faster α -process the values of α_2 parameter are close to 0, but in the whole temperature range the values of β_2 parameter are far from 1. The third relaxation is of the Cole–Davidson type and strongly deviates from the Debye process ($\alpha_3 = 0$, $\beta_3 \neq 1$). Temperature dependence of the relaxation times of the separated relaxation processes are shown in Fig. 5, together with the data obtained at ambient pressure [7]. Comparing the temperature dependence of relaxation times for ambient and elevated pressures one can see that α -relaxations, connected with rotation around short axis and precession, are sensitive to pressure. As change of a pressure seems not to influence the smallest β -relaxation process one can regard it as connected with intramolecular motions. Activation energy for them equals 51.7 kJ/mol as for ambient pressure. At ambient pressure contribution of the β -process to the dielectric absorption was detected much below glass transition while at 220 MPa it was observed up to 281 K.

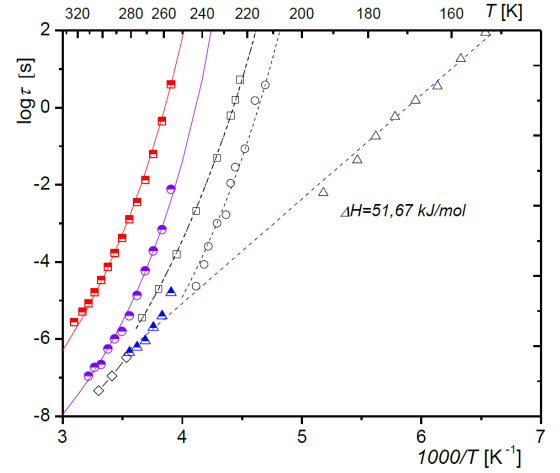


Fig. 5. Relaxation times vs. temperature for ambient pressure (open symbols): Δ in glass of nematic, \square and \circ in the nematic phase, \diamond in the isotropic phase and for elevated pressure in the nematic phase (half-filled symbols).

TABLE

Best fit values of fitting parameters for three relaxation processes in nematic phase of 4-cyano-3-fluorophenyl 4-butylbenzoate under pressure of 220 MPa.

T [K]	A	τ_1 [s]	$\varepsilon_0 - \varepsilon_\infty$	β_1	τ_2 [s]	$\varepsilon_0 - \varepsilon_\infty$	α_2	β_2	τ_3 [s]	$\varepsilon_0 - \varepsilon_\infty$	β_1
256		4.01	61.18	0.91	1.29×10^{-2}	0.71	0.08	0.44	3.51×10^{-5}	0.10	0.17
261		0.44	59.82	0.91	6.87×10^{-4}	0.69	0.01	0.45	3.98×10^{-6}	0.09	0.31
266	0.23	6.36×10^{-2}	56.54	0.97	1.93×10^{-4}	0.85	0.07	0.50	2.00×10^{-6}	0.09	0.43
271	1.11	1.32×10^{-2}	55.24	0.97	5.89×10^{-5}	0.97	0.01	0.37	9.00×10^{-7}	0.04	0.21
276	3.34	3.50×10^{-3}	54.11	0.96	1.34×10^{-5}	0.96	0.01	0.38	6.16×10^{-7}	0.05	0.21
281	12.79	1.26×10^{-3}	53.96	0.91	4.00×10^{-6}	0.89	0.01	0.39	4.52×10^{-7}	0.02	0.29
286	29.85	4.17×10^{-4}	50.43	0.97	1.59×10^{-6}	1.00	0.10	0.40			
291	60.44	1.71×10^{-4}	48.56	0.98	1.01×10^{-6}	1.16	0.13	0.41			
296	119.11	7.53×10^{-5}	47.21	0.97	5.54×10^{-7}	1.37	0.04	0.28			
301	246.56	3.43×10^{-5}	45.20	0.97	2.20×10^{-7}	1.38	0.16	0.40			
306	457.77	1.63×10^{-5}	43.05	0.98	1.86×10^{-7}	1.36	0.12	0.43			
311	760.66	8.40×10^{-6}	40.42	0.98	1.10×10^{-7}	1.00	0.10	0.80			
316	1150.20	5.04×10^{-6}	39.60	0.96							
323	1727.23	2.77×10^{-6}	37.36	0.97							

For description of both structural relaxations, showing super-Arrhenius temperature dependence of relaxation times, the Vogel–Fulcher–Tammann equation was applied [2, 3]:

$$\tau(T) = \tau_0 \exp\left(\frac{DT_0}{T - T_0}\right), \quad (2)$$

where the Kauzmann temperature T_0 , equal in general 20–50 K below T_g , is the temperature of divergence of $\tau(T)$, τ_0 is the relaxation time at the high temperature limit. The value of $1/D$ can be regarded as a measure of the deviation of the relaxation process observed from the Arrhenius one. Fitted values of D parameters for two α -processes show that pressure has weaker influence

on the molecular motions around short axis than on the precession of molecules: for main process the value of D parameter is 12.28 ($\tau_0 = 10^{-13}$ s), for weaker process it is 9.25 ($\tau_0 = 1.6 \times 10^{-13}$ s), while at the ambient pressure $D \approx 14$ ($\tau_0 = 10^{-13.5}$ s) for both processes. In case of substance under 220 MPa the Kauzmann temperatures T_0 are equal to 186 K and 183 K, respectively, while for ambient pressure T_0 equals 143 K. Value of T_g , assumed to be a temperature at which relaxation time of the main process is equal to 100 s, occurred to be much higher for sample at higher pressure: temperature of glass transition for pressure of 220 MPa is 249 K, while for ambient pressure it is 217 K. One can see that for β -process the

Arrhenius dependence of relaxation is valid only for relaxation times obtained for three highest temperatures. For lower temperatures small deviation of relaxation times towards higher values is evident (see Fig. 5). One can suppose that it is due to the fact that the maximum of this relaxation does not fit with frequency range and/or the β -relaxation is overlapped by the extra not observed process connected with reorientations around long axes.

4. Conclusions

For 4-cyano-3-fluorophenyl 4-butylbenzoate at the elevated pressure on cooling only nematic phase was evidenced. As at ambient pressure, two super-Arrhenius α -relaxations, ascribed to the reorientations of molecules around short axes and precession of long axes, and one Arrhenius β -relaxation were identified. At 220 MPa α -processes were shifted of more than four decades towards lower frequencies in respect of ambient pressure. The β -relaxation, not influenced by pressure, was ascribed to intramolecular motions. They were hindered by energy barrier of about 52 kJ/mol as in case of ambient pressure. Glass transition temperature was shifted by pressure to 249 K.

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