# Complex dielectric relaxation in supercooling and superpressing liquid-crystalline chiral isopentylcyanobiphenyl

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Results of broadband dielectric studies in glass-forming liquid crystalline chiral isopentylcyanobiphenyl (5\*CB) are presented. Tests conducted as a function of temperature and pressure revealed the coexistence of glassy and critical properties. The latter are associated with the isotropic-cholesteric phase transition at $T_{I\text{-Ch}}$ $\approx 250$ K under atmospheric pressure. Dielectric loss curves in the isotropic liquid and in the cholesteric phase are clearly broadened on cooling and pressuring towards the glass transition. Although in the isotropic phase there is a single stretched loss curve, in the mesophase an additional relaxation process can be distinguished. The evolution of relaxation times is non-Arrhenius and can be portrayed by the Vogel-Fulcher-Tamman relation or its pressure counterpart. The glassy dynamics coexists with the critical-like behavior for the static dielectric permittivity and for the maxima of the dielectric loss curves. Their temperature and pressure dependences are associated with the critical exponent $\phi = 1 - \alpha \approx 1/2$, where $\alpha \approx 1/2$ is the specific heat critical exponent. This behavior is associated with the continuous phase transition placed at $\Delta T \approx 1.5$ K below the clearing temperature for $P = 0.1$ MPa. It has been found that 5\*CB shows a unique pressure-temperature phase diagram. Pressure and temperature changes which begin in the isotropic liquid below at ca. $T \approx 265$ K always result in the transition to the cholesteric phase which can be supercooled or superpressed. For $T > 265$ K the phase transition to another phase, presumably a solid one, always occurs. However, a cholesteric-solid phase border seems to exist only in isothermal pressure tests. It does not appear in the temperature studies.

## INTRODUCTION

Despite great progress in studies of supercooled, glass-forming liquids, their properties still remain puzzling [1–6]. Hence, novel experimental results, such as involving [7] hydrostatic pressure [8–16] or a class of materials hardly explored up to now [4,6], are of particular importance. Regarding the latter, studies of liquid crystalline (LC) glass formers may be potentially richer than corresponding studies of simple supercooled liquids. This can be related to the opportunity of testing the glassy dynamics for different supercooled liquid-crystalline mesophases. However, basically important low-molecular calamitic liquid crystalline compounds, for instance *n*-alkylcynabiphenyls (*n*CB), most often crystallize on cooling [17]. Moreover, the vast majority of experimental results point to an almost Debye distribution of dielectric relaxation times and their Arrhenius evolution as a function of temperature or pressure [17–19,22]. These features agree with the simple mean-field description of the isotropic-nematic (*I-N*) transition dominating in basic monographs for the physics of liquid crystals [17–22]. Nevertheless, recent high-resolution, broadband dielectric spectroscopy (BDS) of isotropic *n*CB in the broad range of temperatures gave a clear evidence for the glassy, complex dynamics: the non-Debye form of dielectric loss curves, its broadening on cooling, and the non-Arrhenius evolution of dielectric relaxation times [23,24]. These results coincide

with dielectric studies conducted in supercooled nematic- and smectic-*A* phases three decades ago [25–30]. To overcome crystallization, which, for instance, in 5CB occurs about 15 K below the isotropic-nematic (*I-N*) clearing temperature, those tests were carried out in samples after a rapid cooling or in a thin layer of a LC compound [25–30]. In the last decade, the evidence for the glassy of mesogens behavior was also obtained for nonglassyfying calamitic LC compounds, for instance in 5CB, confined to a random surrounding [31–37]. It is noteworthy that the glassy dynamics clearly manifests in LC compounds with more complex molecular structures such as polymeric [38–44] or ferroelectric ones [17,45,46]. The glassy dynamics was also noted in dielectric studies of eutectic *E*7 and *E*8 liquid crystalline mixture of calamitic LC compounds. One of their components is the mentioned 5CB. Unfortunately, these studies were carried out only in a limited range of frequency [47]. Studies of the glassy state in LC compounds have become a challenging question also for the theoreticians in the last decade [48–53]. It seems that the results of Refs. [50,53] are worth recalling here which show the relationship between the glassy dynamics and the appearance of the ordered swarms in the orientational way (i.e., nematiclike) in the isotropic phase.

Unfortunately, there is only a limited number of experimental studies in simple calamitic LC compounds which can be supercooled in bulk without special experimental conditions mentioned above. Only recently such tests were conducted on chiral isopentylcyanobiphenyl (5\*CB) [54–58] and chiral isooctylcyanobiphenyl (8\*OCB) [59], which are isomers of 5CB and 4-*n*-octyloxy-4′-cyanobiphenyl

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(8OCB). In this paper, the tested 5*CB does not crystallize on cooling and after the isotropic-cholesteric transition at $T_{I\text{-}Ch} \approx 250$ K, it reaches the glassy state at $T_G \approx 220$ K. For 5CB the *I-N* transition occurs at $T_{I\text{-}N} \approx 303$ K and next it crystallizes at ca. $T_{N=S} \approx 295$ K [17]. BDS tests on 5*CB and 8*OCB showed the non-Arrhenius evolution of relaxation times and the broadening of loss curves on cooling [54,57,60,61]. Glass transition was also noted in differential scanning calorimetry (DSC) [55,56]. In 5*CB the inelastic scanning scattering showed the appearance of the boson peak [58]. Neither in studies on 5*CB [54–58] and 8*OCB [59–61] nor in other supercooling LC compounds mentioned above [25–53], there was experimental evidence of any pretransitional, critical-like behavior. Only recently, preliminary nonlinear dielectric studies have indicated the possible existence of the pretransitional, criticallike behavior in isotropic 5*CB [62]. This paper presents high-resolution BDS studies on 5*CB. Studies were conducted as a function of temperature and pressure. Studies aimed to test the possible existence of a critical-like behavior and the influence of the high hydrostatic pressure. Recent investigations in pressurized simple and polymeric glass-forming fluids showed that the simultaneous pressure and temperature tests may offer essentially new insight into the dynamics of glassy liquids [8–16]. The high-pressure studies are always associated with serious experimental difficulties. They are particularly pronounced in LC materials owing to the usually limited amount of samples available and the necessity of avoiding any contamination. The latter is associated with the fact that even a very small amount of any admixture may essentially influence the properties of a LC sample.

## EXPERIMENT

Dielectric measurements were conducted using the Novocontrol Concept 80 spectrometer with the Quatro temperature control system. Temperature was stabilized up to $\pm 0.02$ K. For pressure measurements the setup applied in our previous tests was used. It consists of a pressure chamber purchased from Unipress, Poland. As a pressure source, the Nova Swiss generator was used. Pressure was measured using Nova Swiss tensometric pressure meter with resolution $\pm 0.1$ MPa. To stabilize the temperature a jacket fed from Julabo HD 45 *S* thermostat with external circulation surrounded the chamber. The sample was placed in a measurement capacitor designed in our lab. It has unique features: only 0.3 cm$^3$ of the tested sample is needed, the sample is in contact only with Teflon, Invar, and quartz, and the pressure can be both decreased and increased without a risk of contamination from the pressurized liquid (silicone oil). The capacitor was placed within the pressure chamber and pressure was transmitted to the sample by the deformation of 50 $\mu$m Teflon film. It was already used in the earlier studies [62,65]. The parameters of the flat-parallel measurement capacitor were as follows: gap $d = 0.3$ mm and radius $r_o = 16$ mm. The tested compound (5*CB) was prepared in the Military University of Technology, Warsaw by Czuprynski and Dabrowski. Particular attention was paid to reduce the level of contamination, particularly of residual ionic ones to the low-
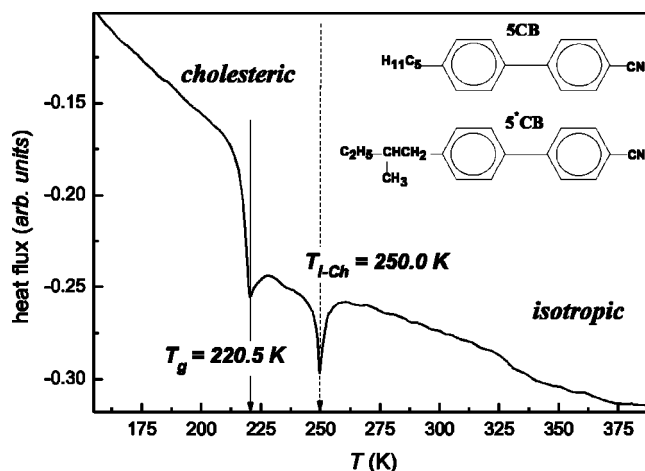


FIG. 1. The evidence of the isotropic-cholesteric and the glass transitions in the tested sample of 5*CB. The structure of 5*CB and ''classical'' 5CB nematogen is also shown.

est possible level. The DSC measurements showing the isotropic-cholesteric phase transition and the glass transition in the tested sample are shown in Fig. 1. The obtained temperatures are about 2 K higher than the ones reported earlier, which may be associated with the purification mentioned above. The figure also presents structures of 5*CB and 5CB, for comparison. Experimental data were analyzed using ORIGIN 7.1 software. Errors are given as three standard deviations.

## RESULTS AND DISCUSSION

The main part of Fig. 2 shows experimental loss curves obtained on cooling the 5*CB under atmospheric pressure from $T = 350$ K to 220 K. It can be seen that on passing the isotropic-cholesteric (*I*-Ch) phase transition, loss curves maxima drop by about 20% of their initial values in the
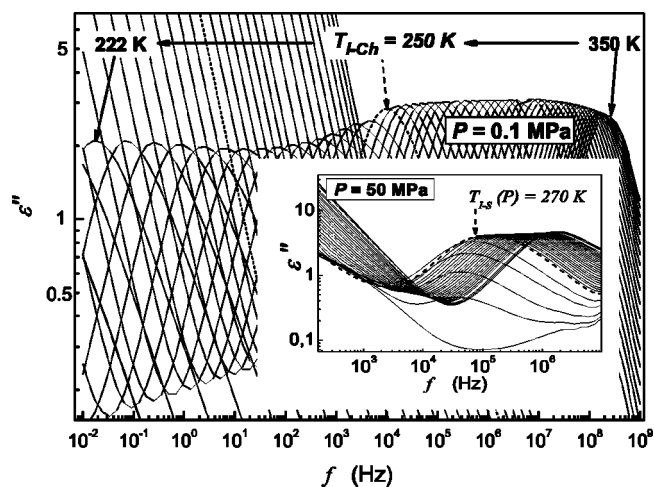


FIG. 2. Dielectric loss curves obtained for 5*CB on cooling in temperature tests under atmospheric pressure in isotropic and cholesteric phases. The arrow indicates the *I*-Ch clearing temperature. The inset shows the result of temperature studies under $P = 50$ MPa.
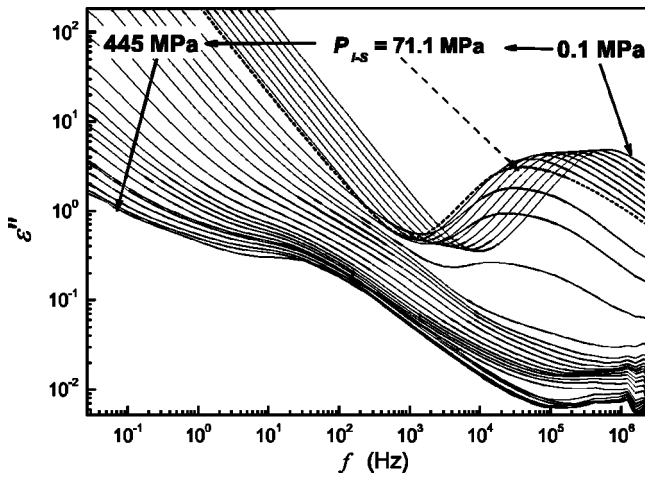
FIG. 3. Evolution of dielectric loss curves obtained in isothermal ($T = T^C + 20$ K), pressure studies. The arrow indicates the clearing pressure.

isotropic phase. However, temperature behavior under $P = 50$ MPa is dramatically different: on passing the phase transition at $T = 270$ K, the loss curves associated with the relaxation process dominating in the isotropic phase disappear. A similar behavior was noted in the isothermal pressure studies, presented in Fig. 3. Above the phase transition, the strong relaxation process observed in the isotropic phase disappears. However, on pressuring, a novel, weak relaxation process appears in the low-frequency region. It is probably associated with a solid phase as the comparison with results of studies in simpler, more classical, glass-forming liquids [4] may suggest. The behavior presented in the inset in Fig. 3 takes place in pressure and temperature studies if the phase transition temperature is higher than $T > 265$ K. In pressure and temperature tests which are associated with clearing temperatures $T < 265$ K, always the behavior similar to the pattern presented in the main part of Fig. 2 occurred. The latter was associated with the I-Ch transition. The obtained pressure versus temperature phase diagram is shown in Fig. 4. It is noteworthy that the cholesteric-solid phase (Ch-S) "border line" appears only in the isothermal, pressure studies (dashed line in Fig. 4). It does not appear in temperature investigations. If the cooling starts in the isotropic phase at $T > 265$ K, the I-S transition always occurs and the cholesteric phase does not appear when passing $T \approx 265$ K isotherm. If the cholesteric phase is reached by pressuring for isotherms $T < 265$ K and next the 5*CB sample is heated under high pressure, the solidification up to 10 K above 265 K occurs. This may suggest that the cholesteric phase exists in the stable and metastable forms as shown in Fig. 4. It is noteworthy that the linear dependence the pressures dependence, characterized by $dT^c/dP \simeq 0.37$ K MPa$^{-1}$, describes the pressure behavior of the clearing (I-Ch or I-S) temperature (Fig. 4). For comparison in 5CB for the I-N transition $dT^c/dP \approx 0.27$ K MPa$^{-1}$ up to at least 200 MPa. The inset in Fig. 4 shows the shift of the relaxation time, $\tau^c(T) = \tau(T^c)$ and $\tau^c(P) = \tau(P^c)$, along the phase transition line. Within the limit of experimental error, it can be approximated by a linear function with the slope $d\tau^c/dT \approx -0.053$ s K$^{-1}$. It is
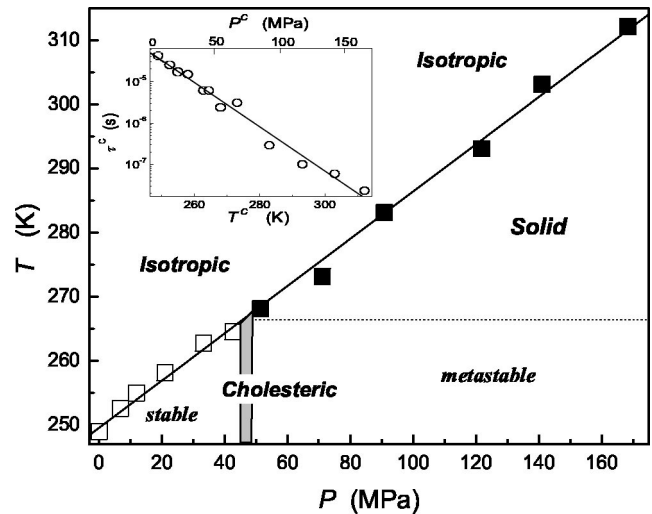


FIG. 4. The obtained temperature-pressure phase diagram for 5*CB. The dashed, thick line indicates $T = 265$ K isotherm. In isothermal, pressure studies, above this temperature always the I-S transition occurs. The inset presents the temperature and pressure evolution of dielectric relaxation time taken and the clearing (phase transition) point.

noteworthy that for $T = 303$ K, which is the I-N temperature in 5CB, the relaxation time $\tau^c$ is similar to the one noted in 5CB [23]. The shape of loss curves on cooling and pressuring 5*CB is presented in Fig. 5. It shows the normalized superposition of selected experimental loss curves for the isotropic phase of 5*CB for temperature and pressure paths of studies. Both on cooling and pressuring, loss curves broadens. Such a behavior occurs also for nonmesogenic supercooled [2–6] and superpressed [7–16] liquids. Solid curves in Fig. 5 present the parametrization by means of the Laplace transformation of the time-domain stretched exponential (SE) dependence to the frequency domain [4]:

$$\varepsilon''(\omega) = \int_0^\infty dt \left[ \frac{-d}{dt} \exp\left( -\left( \frac{t}{\tau_K} \right)^{\beta_{KWW}} \right) \right] \sin(\omega t), \qquad (1)$$
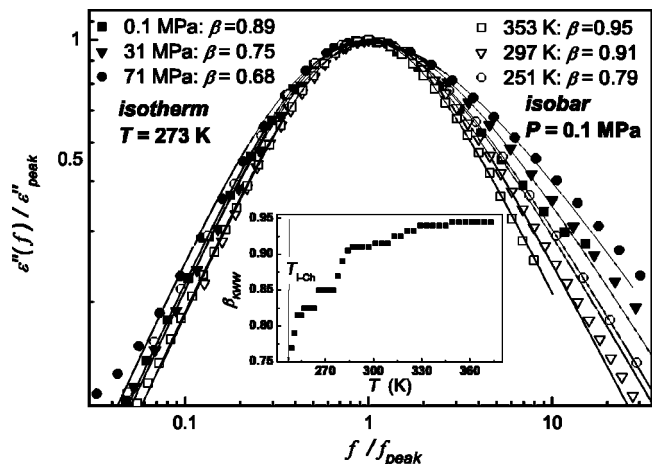


FIG. 5. The normalized superposition of chosen loss curves in the isotropic phase on cooling and pressuring. Solid lines are parametrized by relation (1).
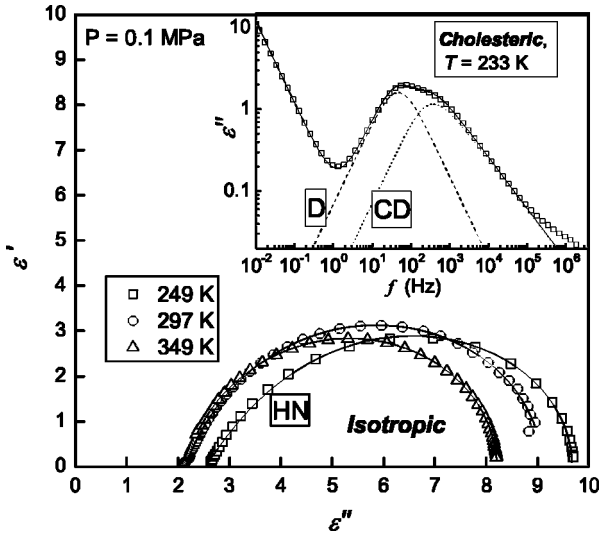
FIG. 6. The temperature dependence of dielectric relaxation times in the isotropic and cholesteric phases of 5*CB under atmospheric pressure. Solid lines are parametrized by the VFT dependence (3).



FIG. 7. The Cole-Cole plot of dielectric permittivity in isotropic 5*CB under atmospheric pressure. Data are portrayed using the Havriliak-Negami (HN) relation (2). The inset presents the applied way of analysis of experimental data in the cholesteric phase which is based on the Cole Davidson (CD) and Debye (D) distributions.

where $\omega = 2\pi f$, $\tau_K$ is the SE relaxation time, and $\beta_{KWW}$ denotes the SE exponent.

The inset shows the decrease of the SE exponent from 0.96 up to 0.75 in the immediate vicinity of the clearing temperature. Hence, it changes from the almost single relaxation time distribution to the clearly SE relaxation. The lowest value of the parameter $\beta_{KWW}$ is characteristic for a broad range of supercooled liquids [4]. The obtained values of $\beta_{KWW}$ agree well with earlier temperature studies in 5*CB [54]. To encompass the asymmetry of loss curve, further analysis was conducted in terms of the Havriliak-Negami (HN) dependence [4]:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{[1 + (i\omega\tau_{HN})^\alpha]^b}, \qquad (2)$$

where $\varepsilon_\infty$ represents the asymptotic value of permittivity at high frequencies and $\varepsilon_s$ is the value of the opposite limit. The power exponents $a$ and $b$ are responsible for the shape of the loss curve.

In the isotropic phase of 5*CB a single HN function was able to parametrize the experimental data. It is clearly shown in the main part of Fig. 6 where experimental data for both the real and imaginary parts of dielectric permittivity are given in the Cole-Cole plot. However, in the cholesteric phase an additional process, not found in earlier tests in 5*CB [54,57], appears in the high-frequency part of the spectrum. To portray such a loss curve, the split into two relaxation processes was assumed, as shown in Fig. 6. To minimize the number of fitted parameters and hence to reach a reasonable error of fitting, the Cole-Davidson [(CD): $a = 1$ in relation (2)] and the Debye [(D): $a = b = 1$ in relation (2) [4]] distributions were taken as components of the underlying relaxation processes in the cholesteric phase. The obtained evolution of parameters responsible for the distribution of relaxation is shown in Fig. 7. They are presented
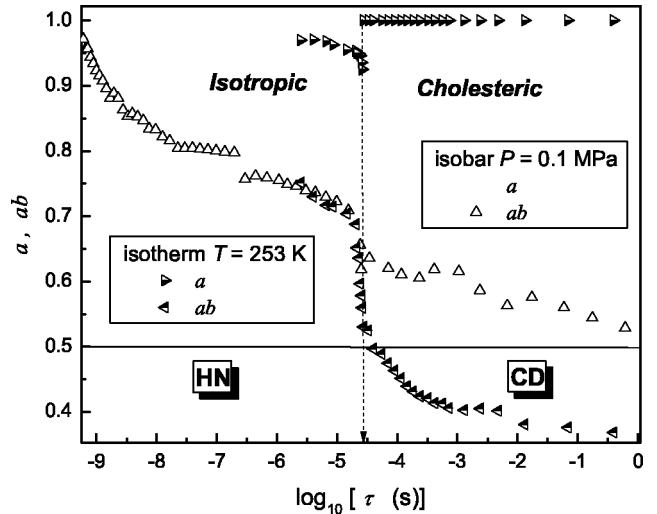
showing the form of loss curves above and below the loss curve peak [1,4]:

$$\varepsilon''(f) \propto \left(\frac{f}{f_{peak}}\right)^m, \quad m = a \quad \text{for } f < f_{peak}, \qquad (3)$$

$$\varepsilon''(f) \propto \left(\frac{f}{f_{peak}}\right)^{-n}, \quad n = ab \quad \text{for } f > f_{peak}, \qquad (4)$$

where parameters $m = 1$ and $n = 1$ are for the single relaxation time, Debye distribution. Both $m$ and $n$ shapes tend to 1 on heating or depressuring, i.e., remote from the clearing point in the isotropic phase. On approaching the clearing point, the parameter $m$ describing the low-frequency wing drops to 0.9. The parameter $n$, related to the high-frequency
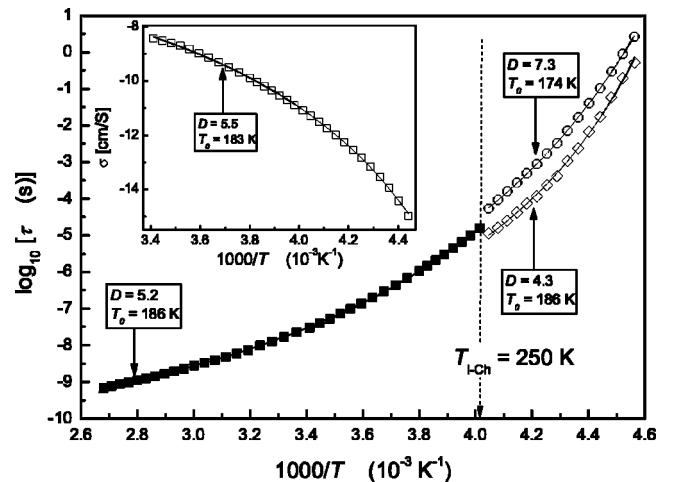


FIG. 8. The test of the breakdown of the validity of the simple DSE law. The obtained values of the fractional exponent from relation (5) are given in the figure.

wing of loss curves, drops up to about 0.6 near the clearing point. In the cholesteric phase only the high-frequency wing can be discussed as the result of the analysis applied: for the CD distribution $m = 1$. Regarding the parameter $n$, it decreases to almost 0.5 in temperature and to 0.4 in pressure studies. It is noteworthy that the value $n = 0.5$ is claimed to be a universal, system-independent value reached when approaching the glass transition temperature as shown in recent time-temperature superposition analysis [63]. Results obtained in this paper pose the question whether the more general pressure-temperature-time superposition universality is valid. It is noteworthy that although in 5CB the supercooled or superpressed state does not appear, the behavior distribution of relaxation times in the isotropic phase and in the surroundings of the clearing point is similar to the one discussed above for 5*CB.

In Fig. 8, the temperature evolution of dielectric relaxation is plotted as a function of temperature in the isotropic and cholesteric phases. The split in the mesophase, omitted in the previous tests in 5*CB [54,57], is also presented. It is visible that on cooling the distance between the two relaxation processes in the cholesteric phase remains constant. That points to the relationship between these relaxation processes and the structure of the cholesteric phase. The longer relaxation time may be associated with the relaxation of the rodlike molecule around its short axis. The cholesteric structure causes that the rodlike molecules are positioned at a certain angle around the nematic director vector. Hence, the faster process can be related to the relaxation of the projection of the rodlike molecule around the axis indicated by the director. The evolution of the obtained relaxation times, both in the isotropic phase and in the mesophases, is non-Arrhenius and can be portrayed by the VFT dependence [4]:

$$\tau(T) = \tau_0 \exp\left(\frac{DT}{T - T_0}\right), \qquad (5)$$

where $T_0$ is the extrapolated ideal glass temperature and the coefficient $D$ is the measure of fragility.

The validity of the above relation and fitted parameters is shown in Fig. 8. The same values of the ideal glass temperatures were obtained for each relaxation process, within the limit of the experimental error. The obtained values of coefficient $D$ are typical for fragile glass formers [4]. The non-Arrhenius evolution which can be described within the VFT dependence also exhibits dc conductivity, as shown in the inset in Fig. 8. The simultaneous availability of dc conductivity and $\alpha$ relaxation time from the broadband dielectric relaxation spectra enabled a test of the validity of the so-called fractional DSF law [4,11,13]:

$$\sigma \tau^s = \text{const}, \qquad (6)$$

where $\sigma$ denotes the magnitude of the dc conductivity and $\tau$ is the ($\alpha$) structural relaxation time.

The breakdown of a simple DSE law [$s = 1$ in relation (6)] is a well-known manifestation of the complex relaxation in glass-forming liquids [4]. The fitted values of the fractional exponent are given in Fig. 9. The non-Arrhenius evo-
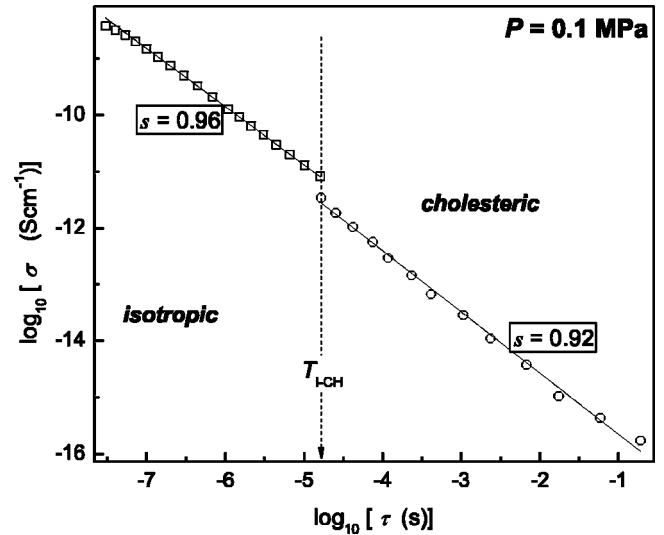


FIG. 9. Pressure dependence of dielectric relaxation times in isotropic and cholesteric 5*CB. For $T = 255$ K, 273 K, and 193 K data are portrayed by relation (6), the pressure counterpart of the VFT dependence. For $T = 313$ experimental data are parametrized by the simple Arrhenius dependence due to the limited range of pressure available for analysis. Fitted fragility coefficient $D_P$ and pressure $P_0$ are given in the figure.

lution of relaxation times was also noted in isothermal, pressure tests. Results presented in Fig. 10 show that both in the isotropic and in the cholesteric phases the pressure dependence of relaxation times can be well portrayed by the pressure counterpart of the VFT equation, proposed by some of the authors [7]:

$$\tau(P) = \tau_0^P \exp\left(\frac{D_P P}{P_0 - P}\right), \qquad (7)$$

where $P_0$ is the ideal glass pressure for the given temperature and $D_P$ is the equivalent of the fragility coefficient for pressure path of studies.

Noteworthy is the fact that the above mentioned split into two relaxation processes occurs also for pressurized cholesteric. Both processes are described by the same values of $P_0$ and $D_P$ within the limit of experimental errors. It is noteworthy that in the isotropic phase, the non-Arrhenius behavior cannot be observed for isotherms below 270 K, due to the limited range of pressure (see Fig. 4). Already for $T = 313$, only the Arrhenius dependence can be applied. In this case, the limited range of pressures is the result of the limited range of measurement frequencies available in pressure tests and the strong decrease of relaxation times on heating in isotropic 5*CB.

The influence of the vicinity of the phase transition point may be noted already in Fig. 7, for parameters describing the distribution of relaxation times. More pronounced influence of pretransitional fluctuations occurs for the temperature evolution of maxima of loss curves, as shown in Fig. 11. The obtained dependence can be well portrayed by the relation:
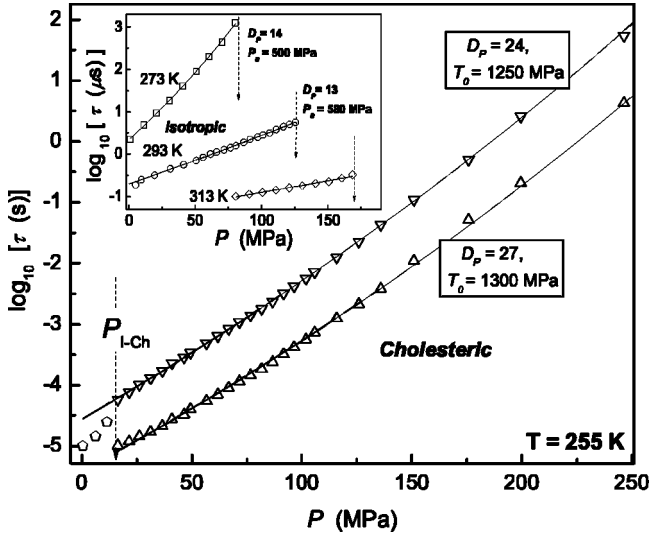
FIG. 10. The evolution of characterizing the distribution of relaxation time HN parameter. The parameter $n = ab$ is for the high-frequency wing and the parameter $m = a$ is for the low-frequency wing.

$$\varepsilon''_{peak}(T) = \varepsilon''^*_T + a''_T(T-T^*) + A''_T(T-T^*)^{1-\alpha}, \quad (8)$$

where $\varepsilon''^*_T$ and $T^*$ are coordinates of the extrapolated hypothetical continuous phase transition, $T^* = T^C - \Delta T$, $T_C$ is the clearing temperature, and $\Delta T$ is the measure of the phase transition discontinuity. The exponent $\alpha$ may be related to the critical exponent of the specific heat.

The following fitted parameters were obtained: $\varepsilon''^*_T = 4.0 \pm 0.03$, $a''_T = -0.013 \pm 0.002$ K$^{-1}$, $A^*_T = 0.41 + 0.02$ K$^{-\phi}$, $T^* = 248.5$ K, and $\phi = 1 - \alpha = 0.5 \pm 0.05$. A similar depen-

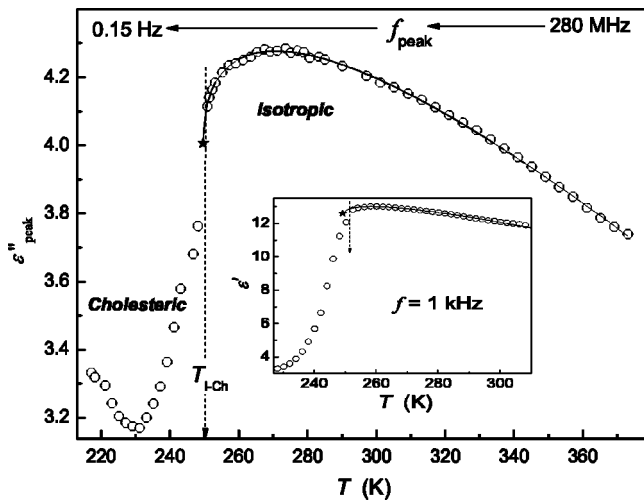

FIG. 11. The temperature evolution of maxima of loss curves in 5*CB. The inset shows similar dependence for the static dielectric permittivity. Solid curves are portrayed by relations (7) and (8). Arrows show the clearing temperatures. The stars indicate the position of the extrapolated temperature of the hypothetical continuous phase transitions.
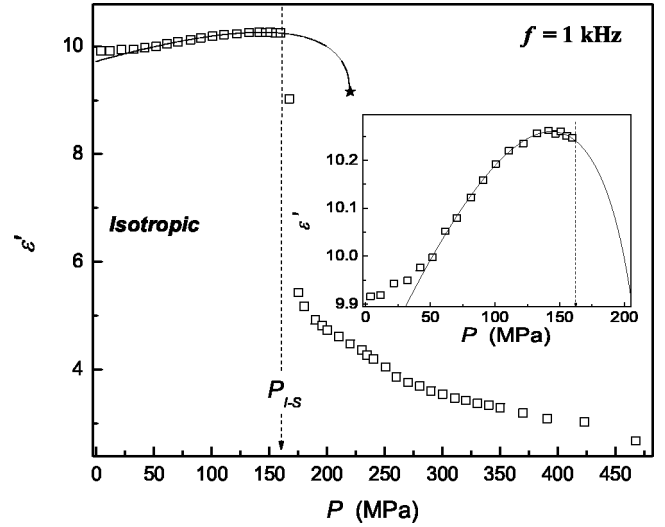


FIG. 12. Pressure dependence of static dielectric permittivity in isotropic 5*CB on approaching the solid phase. Solid curves are portrayed by relation (10). The arrows point the pressure of the phase transition. The stars indicate the position of the hypothetical continuous phase transition.

dence describes the evolution of the static dielectric permittivity for a given measurement frequency as shown by the inset in Fig. 11:

$$\varepsilon'(T) = \varepsilon'^*_T + a^*_T(T-T^*) + A'_T(T-T^*)^{1-\alpha}. \quad (9)$$

Fitted parameters are the following: $\varepsilon'^*_T = 12.51 \pm 0.1$, $a'_T = -0.016 \pm 0.003$ K$^{-1}$, $A'_T = 0.26 + 0.02$ K$^{-\phi}$, $T^* = 248.5$ K, and $\phi = 1 - \alpha = 0.5 \pm 0.1$. The obtained value of the critical exponent $\alpha \approx 0.5$ in relations (8) and (9) is the same as in 5CB on approaching the *I-N* transition.

In 5CB the validity of relations (8) and (9) was related to the so-called *fluidlike* model proposed recently for the *I-N* transition [23,64,65].

The evolution of maxima of loss curves and of the static dielectric permittivity for the isothermal pressure path of studies is presented in Figs. 12 and 13. They can be well portrayed by pressure counterparts of relations (8) and (9):

$$\varepsilon''_{peak}(P) = \varepsilon''^*_P + a''_P(P^*-T) + A''_T(P^*-P)^{1-\alpha}, \quad (10)$$

$$\varepsilon'(P) = \varepsilon'^*_P + a'_P(P^*-P) + A'_T(P^*-P)^{1-\alpha}, \quad (11)$$

where $P < P^C = P^* - \Delta P$, $P^C$ is the clearing pressure, $\Delta P$ is the measure of the phase transition discontinuity, $\varepsilon''^*_P$, $\varepsilon'^*_P$, and $P^*$ are coordinates of the extrapolated hypothetical continuous phase transition.

Relation (10) is parametrized by $\varepsilon''^*_P = 0.995 \pm 0.01$, $a''_P = -0.016 \pm 0.005$, $A''_P = 0.36 \pm 0.08$ MPa$^{-\phi}$, $\phi = 1 - \alpha = 0.52 \pm 0.1$, and $P^* = 220.5$ MPa. Relation (9) is associated with the following parameters: $\varepsilon'^*_P = 9.15 \pm 0.2$, $a'_P = -0.015 \pm 0.004$ MPa$^{-1}$, $A'_P = 0.25 \pm 0.02$ MPa$^{-\phi}$, $\phi = 1 - \alpha = 0.52 \pm 0.1$, and $P^* = 220$ MPa. It is noteworthy that for pressure tests the critical exponent also is equal to $\alpha \approx 0.5$. The isomorphism of relations (8),(10) and (9),(11) may be
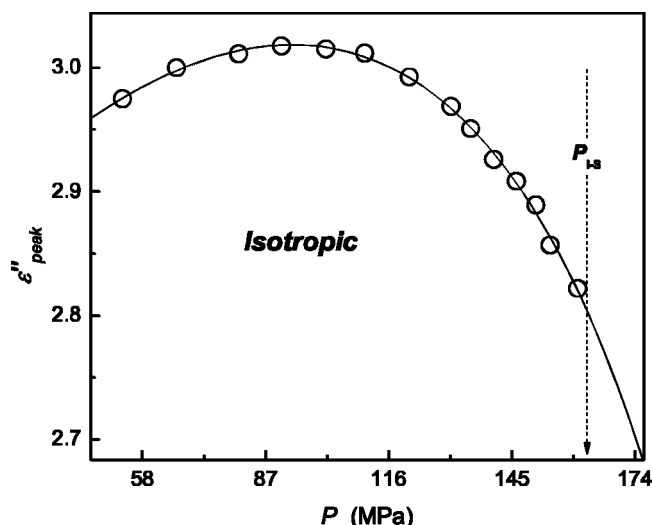
FIG. 13. Pressure dependence of the maxima of loss curves in isotropic 5*CB on approaching the solid (?) phase. Solid curves are portrayed by relation (9). Arrows show the pressure of the phase transition. Stars indicate the position of the hypothetical continuous phase transition.

considered as the consequence of the postulate of isomorphism of critical phenomena [66]. The isomorphism of relations (10),(11) and (8),(9) may be considered as the consequence of the validity of the Kramers-Kronig equations [67] for the discussed temperature and pressure pretransitional behavior of dielectric permittivity. It is particularly noteworthy that results presented in Fig. 11 are for the isotropic-cholesteric phase transition. The pretransitional bending down may be here associated with the antiparallel ordering of perpendicular permanent dipole moments ordered in an orientational way prenematic fluctuations. Such a behavior was already noted for the *I-N* transition, for instance in 5CB, as well as for the isotropic–smectic-*A* [68] and isotropic–smectic-*E* [69] phase transitions. However, pressure results in Figs. 12 and 13 are for the isotherm where the solidification probably occurs. The validity of relations (9) and (10) may suggest that between the hypothetical solid phase and the isotropic phase a mesophase exists. The next possibility is the orientational ordering of the solid (?) phase. It is noteworthy that the discontinuity of the *I*-Ch transition is equal to $\Delta T \approx 1.5$ K. Similar values were noted for weakly discontinuous phase transition in nematogenic $n$CB, where it increases up to about 70% on pressuring up to 200 MPa. For results presented in Figs. 12 and 13, the discontinuity $\Delta P = P^* - P^C \approx 57$ MPa. The approximate conversion of this value to temperature scale using the value of $dT^C/dP$ gives $\Delta T \approx 21$ K.

## CONCLUSIONS

The presented results showed that glass-forming mesogen 5*CB exhibits both glassy and critical properties. The tem-

perature behavior in the isotropic phase under atmospheric pressure is very similar to the one obtained for 5CB, the compound which does not form the glassy state in bulk during slow cooling or pressuring. However, presented results for 5*CB give the first evidence of the pretransitional behavior of dielectric permittivity for the *I*-Ch transition.

Noteworthy is the isomorphism of obtained dependences for temperature and pressure paths. It is interesting that pressure tests may suggest that the same critical-like behavior with the exponent $\alpha = 0.5$ occurs for the phase transitions both from the isotropic to the cholesteric and from the isotropic to the (presumably) solid phase. Unique features, not observed for 5CB and other simple calamitic compounds, exhibit the pressure-temperature phase diagram for 5*CB. Regarding the glassy behavior, in temperature studies, the analysis of dielectric relaxation showed the validity of the VFT description in the isotropic phase, in agreement with Refs. [54,57]. In the cholesteric phase, two relaxation processes, not reported in Refs. [54,57], were detected. Each VFT relation is associated with the same fragility $D$, "ideal glass temperature" $T_0$, and the glass temperature $T_g$, within experimental error. A similar evidence was obtained for the isothermal pressure paths of studies. It was strongly suggested in Ref. [63] that on cooling the high-frequency wing of loss curves of glass-forming liquids is universal on approaching $T_g$: its slope should approach $n = 1/2$. For 5*CB this seems to occur in temperature tests and probably not for pressure paths. Although in 5*CB loss curves systematically broaden on cooling, near the clearing point both high- and low-frequency wings show some anomalous changes, similar to those observed for 5CB. Regarding the possible relevance of results presented for theoretical analysis, apart from Refs. [50,53] mentioned in the Introduction, the recent model proposed by Tanaka [70] is worth recalling here. It was suggested that for glass-forming liquids apart from density fluctuations (1), cooperative medium range bond-ordering structures (2) may play a basic role. Depending on the domination of factors (1) or (2), Tanaka's model leads to the liquid-liquid phase transition with the critical pretransitional behavior or to the glass transition with the possible spinodal liquid-liquid transition below the glass temperature. For glass-forming liquids, the possible critical point might be expected in the negative pressure region. In 5*CB the existence of bond-ordering structures, i.e., pretransitional, premesomorphic fluctuations, is evident. The important disagreement with Tanaka's model is due to the fact that for 5*CB the glass temperature is ca. 60 K below the liquid-liquid (*I*-Ch) transition.

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