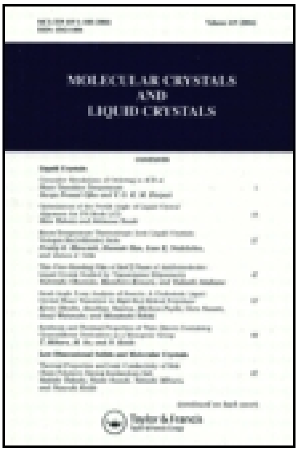

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The Glassy Dynamics in Liquid Crystalline 4-n-Pentyl-4′-Cyanobiphenyl as Studied by Thermally Stimulated Currents

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The Glassy Dynamics in Liquid Crystalline 4-*n*-Pentyl-4′-Cyanobiphenyl as Studied by Thermally Stimulated Currents

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*The slow molecular mobility in the model liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl has been investigated by thermally stimulated depolarization currents and differential scanning calorimetry in the amorphous nematic solid state. The phase transition temperatures were determined, as well as the respective enthalpy changes. The glass transition relaxation was analyzed, and the fragility index of this glass-forming liquid crystal was determined.*

Keywords α-relaxation; 5CB; fragility; mesophase; thermally stimulated current; TSDC

Introduction

Liquid crystals and plastic crystals are interesting systems because of their mesophase character; the knowledge of the features of the molecular mobility in those systems is important to understand their macroscopic behavior. The experimental technique most widely used to study the slow molecular motions in those systems is broadband dielectric relaxation spectroscopy (DRS). In the present work, we use the dielectric-related technique of thermally stimulated depolarization currents (TSDCs), which has been successfully used in recent years to study the slow relaxation dynamics in a variety of materials [1]. A drawback of TSDC is its narrow frequency range, compared with the 16 decades of frequency of DRS. However, TSDC is a high-sensitivity technique, with an enhanced resolution power of the different relaxation processes. The most important advantage of TSDC is however the possibility of using the experimental procedure of thermal sampling, or partial polarization, in order to resolve a global distributed peak into its individual relaxation modes; this allows the calculation of the temperature-dependent relaxation time, $\tau(T)$, associated with single modes of motion. Note that DRS is not able to determine the temperature-dependent relaxation time of a single (or narrowly distributed) relaxation mode, but rather the mean relaxation time of the whole distribution. The two dielectric techniques thus appear as very complementary tools to study slow motional processes.

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Several TSDC studies on plastic crystals have been published in the literature [2–7], and the same occurs with liquid crystalline polymers [8–12]. However, to our knowledge, studies by TSDCs of the slow molecular dynamics in low molecular weight liquid crystals are very scarce. An interesting paper on nematics MBBA [N-(4-Methoxybenzylidene)-4-butylaniline] and EBBA [N-(4-Ethoxybenzylidene)-4-butylaniline] was published 30 years ago [13] and, more recently, in a conference proceedings, a work on a columnar liquid crystal was reported [14]. Besides, we do not know any published study deserving reference. The aim of the present study is to begin to explore the possibilities of TSDC in this area. We chose 4-*n*-pentyl-4′-cyanobiphenyl (5CB) as a model nematic liquid crystal, with a strong longitudinal dipole moment that facilitates dielectric measurements, and we report the results of a study of the slow molecular mobility in the amorphous nematic solid state using TSDCs and differential scanning calorimetry (DSC).

Experimental

Materials

5CB, $CH_3(CH_2)_4C_6H_4C_6H_4CN$ (CAS [40817-08-1], molar weight of $M_w = 249.36$ g·mol^{-1}), was purchased from Aldrich (purity 98%) and was used without further purification.

Techniques

TSDCs. TSDC experiments were carried out with a TSC/RMA spectrometer (TherMold, Stamford, CT, USA) covering the range from −170°C to +400°C. For TSDC measurements, the sample (thickness of ~0.5 mm) was placed between the disc-shaped electrodes (7 mm diameter) of a parallel plane capacitor. The sample is immersed in an atmosphere of high-purity helium (1.1 bar).

The TSDC technique is adequate to probe slow molecular motions (1–3000 s). The fact that the relaxation time of the motional processes is temperature-dependent, and becomes longer as temperature decreases, allows to make it exceedingly long (freezing process) compared with the timescale of the experiment. In order to analyze specific regions of the TSDC spectrum, the partial polarization (PP) procedure, also called thermal windowing, is often used. Two important parameters in a TSDC experiment are the polarization temperature, T_P, at which the polarizing electric field is turned on, and the temperature $T_P{}' < T_P$ at which the field is turned off [15]. The difference $T_P{}' - T_P$ is the width of the polarization window of the experiment. If it is wide, the retained polarization (and of course the current peak that is the result of a TSDC experiment) will correspond to a complex set of energy-distributed motional modes. Oppositely, the PP experiment, where the polarizing field is applied in a narrow temperature interval, allows probing more narrowly distributed relaxation modes. In the conceptual limit of a very narrow polarization window, the experimental depolarization current peak is supposed to correspond to a single mode of relaxation [16]. In the present work and in most of our previous ones, we use polarization windows two degrees wide, and we tacitly assume that this window isolates single relaxation processes. This assumption is based on the observation that similar PP experiments with polarization windows of 0.2°, 1°, or 2°C lead essentially to the same results.

The physical background of the TSDC technique is presented elsewhere [17–19]. The basic description of the TSDC experiment, and the discussion of the nature of the information it provides, is presented in detail in previous publications [20,15]. A review on TSDC applications is available [1].

The analysis of TSDC experimental data (of the partial polarization current peaks) is based on the Debye relaxation concept and is performed using the so-called Bucci method [21,22]. In this context, the assumption is that, at each temperature of the linear heating ramp, the decay of the polarization with time is a first-order rate process:

$$\frac{dP(T)}{dt} = -j(T) = -\frac{P(T)}{\tau(T)}, \tag{1}$$

where $P(T)$ is the remaining polarization at temperature T of the heating ramp (temperature is parameterized in time), $\tau(T)$ is a temperature-dependent relaxation time characteristic of the elementary mode of motion under consideration, and $j(T)$ is the depolarization current density (current intensity per unit area), i.e., the rate of decreasing of the polarization. The importance of Equation (1) is that it allows the calculation, from the experimental result, of the temperature-dependent relaxation time of a single relaxation process. Due to the nonexponentiality of the main relaxation in molecular glasses and amorphous polymers, this usual methodology based on the Debye relaxation concept has been criticized, and the alternative use of the Kohlrausch function (stretched exponential) was suggested [23,24]. However, it was claimed that the original form of the Kohlrausch function is not adequate to the analysis of TSDC data, and it was shown that the temperature-dependent relaxation time, $\tau(T)$, of a nonexponential motional process can be correctly obtained from TSDC data by using a modified Kohlrausch decay law, which leads to the same results as the Bucci method based on the Debye relaxation law [25–27].

DSC

The calorimetric measurements were performed with a 2920 MDSC system from TA Instruments, Inc. The samples of ~10–12 mg were introduced in aluminium pans. The measuring cell was continuously purged with high purity helium gas at 30 $\text{mL}\cdot\text{min}^{-1}$. An empty aluminium pan, identical to that used for the sample, was used as the reference. The heating rate used in our experiments was 10°C min^{-1}. Details of the calibration procedures are given elsewhere [28].

Results and Discussion

DSC

The transition from nematic to isotropic is at $T_{\text{NI}} = (35.4 \pm 0.1)°\text{C} = (308.5 \pm 0.1)$ K, with a transition enthalpy of $\Delta_{\text{NI}}H = (2.44 \pm 0.12)\ \text{J}\cdot\text{g}^{-1} = (0.61 \pm 0.03)\ \text{kJ}\cdot\text{mol}^{-1}$ (see Table 1). The uncertainty of our results corresponds (as will be the case in the following results) to the standard deviation of the mean.

Two crystalline polymorphs were detected (see Fig. 1). One, Cr1, with $T_{\text{Cr1N}} = (23.8 \pm 0.1)°\text{C} = (297.0 \pm 0.1)$ K, with a transition enthalpy of $\Delta_{\text{Cr1N}}H = (54.17 \pm 0.53)\ \text{J}\cdot\text{g}^{-1} = (13.5 \pm 0.1)\ \text{kJ}\cdot\text{mol}^{-1}$. This polymorph 1 was obtained on heating a sample that was prepared by fast cooling from the isotropic phase (to prevent crystallization) down to $T < \sim$–40°C; cold crystallization occurred on heating, followed by melting at 23.8°C (see Fig. 1(a)). The other polymorph, Cr2, has $T_{\text{Cr2N}} = (17.7 \pm 0.1)°\text{C} = (290.9 \pm 0.1)$ K and $\Delta_{\text{Cr2N}}H = (62.1 \pm 0.5)\ \text{J}\cdot\text{g}^{-1} = (15.5 \pm 0.1)\ \text{kJ}\cdot\text{mol}^{-1}$, and was obtained on heating a sample that was prepared by fast cooling from the isotropic phase down to $T > \sim$–30°C; cold crystallization also took place in this case, but the melting peak is now located at 17.7°C (see Fig. 1(b)). An alternative way for preparing Cr2 is to cool down

Table 1. Temperatures and enthalpies of the phase transitions of 4-*n*-pentyl-4′-cyanobiphenyl, determined on heating by DSC. The heat capacity jump at the glass transition is$^{(1)}$ $\Delta C_p = 0.347 \pm 0.005$ J·g^{-1}·K^{-1}. The uncertainty of our values corresponds to the standard deviation of the mean. Literature values are shown for comparison

Transition	T_{tr} (°C, this work)	Literature	Δ_{tr}H (kJ·mol^{-1})	Literature
Glass transition	–65.1 (10 K·min^{-1}) [a]	–65.1 [39]	0	–
Cr2-N	17.7 ± 0.1[b]	17.2 [40]	15.5 ± 0.1[b]	14.7 [40]
Cr1-N	23.8 ± 0.1[c]	21.9 [39]; 22.9 [41]	13.5 ± 0.1[c]	16.7 [39]
N-I	35.4 ± 0.1[d]	34.9 [39]; 35.3 [42]; 34.2 [41]; 33.8 [40]	0.61 ± 0.03[d]	0.50 [39]; 0.39 [42]; 0.46 [40]

[a] Mean over 41 independent runs.
[b] Mean over nine independent runs.
[c] Mean over eight independent runs.
[d] Mean over 14 independent runs.

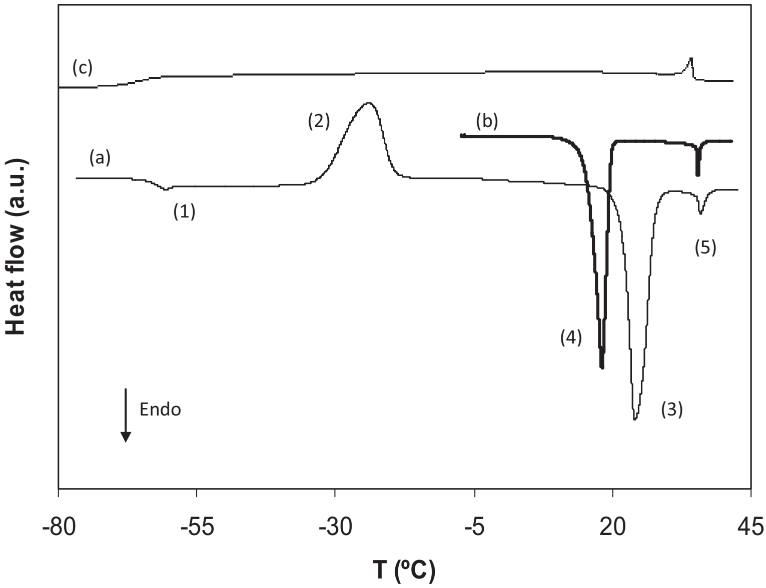

Figure 1. DSC thermograms showing the melting peak of two polimorphs of 5CB. (a) After cooling fast ($r > 2$–3 K·min^{-1}) from the isotropic liquid down to –90°C, amorphization takes place; on heating we see the glass transition signal (1), followed by cold crystallization (2), and melting of the polymorph 1 at 23.8°C (3). (b) Thicker line, after cooling fast ($r > 2$–3 K·min^{-1}) from the isotropic liquid down to $T > -30$°C, cold crystallization also occurs on heating (not shown), but now polymorph 2 is formed, melting at 17.71°C (4). The endothermic peaks (5) at 35.4°C correspond to the nematic isotropic transition. (c) The heat flow curve obtained on cooling at $r > 20$ K/min, showing that no crystallization occurs.

slowly (0.5–1 K·min^{-1}) from the isotropic or nematic liquids to induce crystallization; the crystal formed under these conditions is the polymorph 2.

The amorphous nematic solid was easily obtained by cooling from the isotropic phase at cooling rates higher than 2–3 K·min^{-1}. At lower cooling rates, crystallization often occurs from the metastable nematic, some tens of degrees below the melting temperature. On the other hand, we never obtained the sample in the metastable isotropic liquid state since $T_{\mathrm{NI}} = T_{\mathrm{IN}}$ for cooling rates from 1 to 17 K·min^{-1}. This means that the glass formed on cooling (at the available cooling rates) is indeed the amorphous nematic solid and not the amorphous isotropic solid. As will be seen latter, this is confirmed by our TSDC results. The onset of the glass transition signal appears at T_g = –65°C = 208 K (on heating at 10 K·min^{-1}), and the heat capacity jump at T_g is $\Delta C_p = 0.347 \pm 0.005$ J·g^{-1}·K^{-1}.

The technique of DSC was also used to estimate the activation energy of the structural relaxation and the fragility index of 5CB. One of the methods of thermal analysis allowing the determination of glass-former fragility is based on the scanning rate dependency of T_g [29,30]. This dependence reads as [31]

$$\frac{d \ln |r|}{d\left({}^{1}\!/_{Tg}\right)} = -\frac{E_a}{R}, \tag{2}$$

where r is the heating rate, E_a the activation energy for the relaxation times controlling the structural relaxation, and R is the ideal gas constant. From the linear fitting of the data

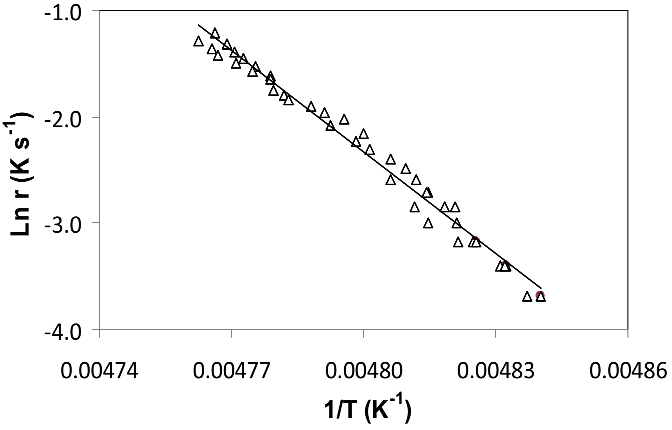

Figure 2. “Arrhenius plot” (logarithm of the heating rate, *r*, as a function of $1/T_{g,\mathrm{on}}$) for the glass transition of 4-*n*-pentyl-4′-cyanobiphenyl studied by DSC.

presented in Fig. 2 we determined the activation energy of the structural relaxation of this nematic glass, $E_a = 265.4$ kJ·mol^{-1}.

The fragility index was calculated from the definition

$$m = \left[\frac{d\log_{10}\tau(T)}{d(T_g/T)}\right]_{T=T_g} = \frac{1}{2.30_3}\left[\frac{E_a(T_g)}{RT_g}\right] \tag{3}$$

as $m = 66$. This value of the fragility index of 5CB will be discussed later, in comparison with the values obtained by TSDC and broadband DRS.

TSDCs

Four kinds of slow molecular motions can be considered in low molecular weight nematic liquid crystals: (i) translational or flow motion of entire molecules; (ii) reorientational cooperative motions of the whole molecules, involving a variable number of them; (iii) localized motions of one voluminous part of the molecule relative to the other; (iv) internal rotations of small groups. The first two kind of motions are practically frozen below T_g, and the second, corresponding to the α-relaxation, also called main relaxation, is associated with the glass transformation region. The third and fourth kinds of motion correspond to the so-called secondary relaxations (β-, γ-, δ-relaxations in the order of decreasing temperature). The glass transition phenomenon and the molecular mechanism of the β-relaxation are not yet fully understood. However, the α-relaxation process is generally attributed to cooperative motions of molecules. Furthermore, it is generally accepted that the secondary relaxations originate from librational motions, small-amplitude reorientational modes of entire molecules, and internal rotations about single covalent bonds (motions of one voluminous part of the molecule relative to the other, and/or simple internal rotations of molecular groups).

The TSDC signature of the α-relaxation is shown in Fig. 3. The thick and higher intensity curve was obtained with a wide polarization window, and thus corresponds to a large distribution of relaxation times. The other peaks displayed are a series of PP current peaks with polarization temperatures, T_P, in the glass transformation temperature range.

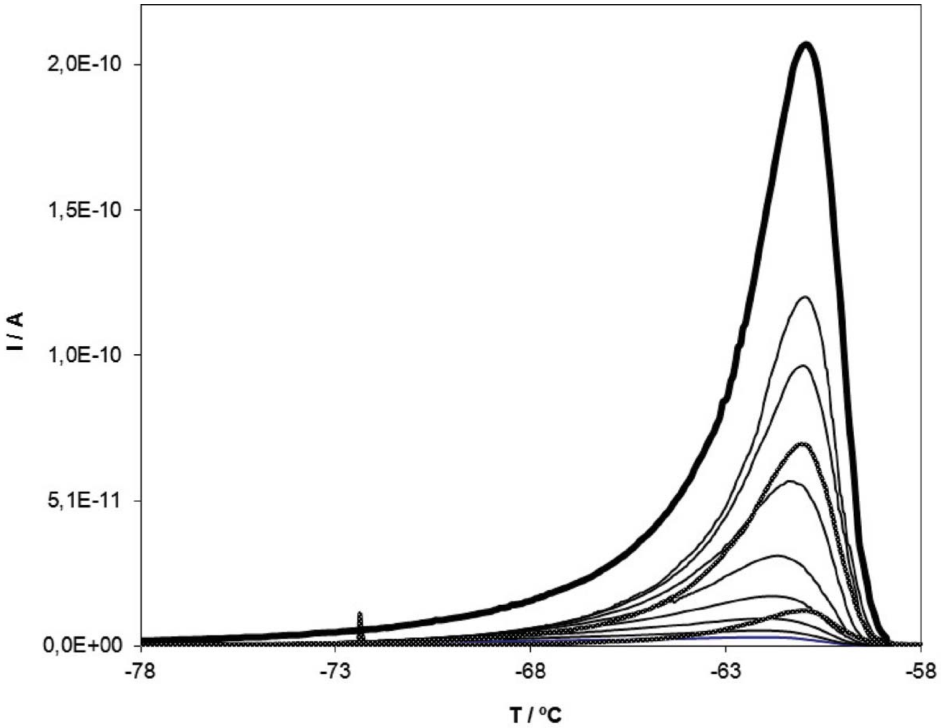

Figure 3. The thick and higher intensity curve was obtained with a wide polarization window experiment (with T_P = –64°C down to T_P' = –110°C), electric field, $E = 360$ V·mm^{-1}; polarization time, $t_P = 5$ min; heating rate, $r = 8$°C min^{-1}. The other curves are partial polarization (PP) components (obtained with narrow polarization windows – width $\Delta T = 2$°C), polarization temperatures from $T_P = -76$°C to -58°C with intervals of 2°C. The other experimental conditions were: strength of the polarizing electric field, $E = 380$ V·mm^{-1}; polarization time, $t_P = 5$ min.; heating rate, $r = 4$°C min^{-1}. The higher intensity curve of PP corresponds to $T_p = -62$°C and the two gray lines (where the peak intensity is decreasing with increasing T_P) refer to $T_P = -60$°C and -58°C.

They have been obtained with sharp polarization windows, and each of them is believed to correspond to a single motional mode (to a single relaxation time).

The DSC results told us, as reported before, that no metastability was observed in the isotropic liquid (for the available cooling rates), and that the amorphous solid obtained had a nematic structure. To verify this conclusion, and be sure about the glassy state we are dealing with, we performed wide polarization window experiments similar to that with T_P = –64°C and T_P' = –110°C depicted in Fig. 2, but using two different procedures to previously prepare the glass. In one of them, the sample was, prior to the experiment, quenched from 30°C (nematic state) down to –100°C, so that the obtained glass is the amorphous nematic solid. In the other one, the sample was quenched from 45°C (isotropic liquid state) down to –100°C, so that the obtained glass could be the amorphous isotropic solid (if the nematic phase was not formed, for kinetic reasons, during the fast cooling from the isotropic), or it could be the amorphous nematic solid (if the nematic phase was formed on cooling from the isotropic liquid despite the high cooling rate). We concluded that the TSDC results confirmed the DSC ones, i.e., the TSDC peaks obtained in both cases were similar, with the same temperature-dependent relaxation time, $\tau(T)$. This means that the glass formed on cooling is indeed the amorphous nematic solid and not the amorphous isotropic.

The α-relaxation corresponds to the large-scale molecular motions associated with the transition from the glass to the metastable nematic, and the PP peak with higher intensity in Fig. 3 (T_p = –62°C) is considered as the manifestation of a mobility mode that most strongly contributes to the glass transition. The temperature of maximum intensity of this PP peak, T_M, is the glass transition temperature provided by the TSDC technique (at the heating rate of the experiment) [9,32]: $T_M = T_g$ = –61°C (at 4°C min^{-1}). The analysis of this singular peak allows the determination of the activation energy for the structural relaxation, $E_a(T_M)$, and also of the fragility index of this glass former (see below).

Figure 4 displays the so-called Arrhenius plot (representation of ln $\tau(T)$ *versus* $1/T$) for the ten PP depolarization peaks shown in Fig. 3. Let us comment that the two lower temperature motional modes (polarization temperatures T_p = –76°C and –74°C, lines on the left hand side of the figure) have nearly linear lines (Arrhenius behavior), and display low slope, i.e., have small activation energies, indicating that they correspond to localized motions (they are modes of some secondary relation). As T_p increases, going through the glass transformation region, the curvature and the slope (at T_g) of the ln $\tau(T)$ versus $1/T$ lines increase, i.e., the complexity of the molecular motions increases.

As noted before, the temperature of maximum intensity of the PP peak with higher intensity, T_M, is often considered as the glass transition temperature provided by the TSDC technique: $T_M = T_g$ = –61°C. However, as pointed out by a referee, this temperature is probably not the onset temperature of the glass transformation region. In fact, at about

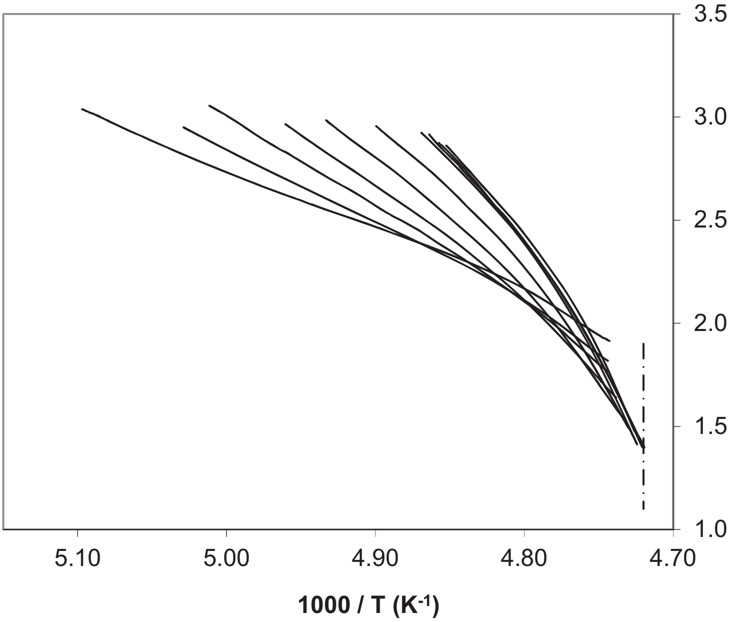

Figure 4. Arrhenius plot (ln $\tau(T)$ *versus* $1/T$) for the 10 partial polarization peaks shown in Fig. 3. The dash–dotted vertical line indicates the temperature of maximum intensity, T_M, of the partial polarization peak with higher intensity in Fig. 3($T_p = -62$°C). From left to right, the lines correspond to motional modes with increasing polarization temperatures (from $T_P = -76$°C to -58°C with intervals of 2°C).

$1000/T = 4.8$ (i.e., at $T = –65°\text{C}$), the lines of the lower temperature modes in Fig. 4 show an inflection that indicates the transition from the noncooperative to the cooperative behavior. The temperature of this inflection, which fully agrees with the calorimetric T_g (see Table 1), thus appears as a better temperature location of the onset of the glass transition.

In order to calculate the fragility index, the ln $\tau(T)$ *versus* $1/T$ line of this PP peak with higher intensity (obtained with $T_p = –62°\text{C}$) was fitted to the Vogel equation, and the activation energy was obtained from the slope at the temperature of the maximum, T_M. The fragility index measures the degree of deviation of the relaxation time from an Arrhenius-type temperature dependence; materials are called “fragile” if their $\tau(T)$ dependence deviates strongly from an Arrhenius type behavior and “strong” if $\tau(T)$ is close to the Arrhenius behavior. The obtained activation energy for the motional mode at $T_M = 212$ K $= –61°$C is $E_a\ (T_M) = 420\ \text{kJ·mol}^{-1}$, and the fragility index, calculated from Equation (3), is $m = 110$.

An interesting feature of the TSDC technique is that, at the temperature of maximum intensity of a PP peak, $T_{\max}$, there is a crossing between the timescale of the depolarization process (defined by the temperature derivative of the relaxation time) and the timescale of the PP experiment (defined by the reciprocal of the heating rate). Saying otherwise, at the temperature of maximum intensity of a PP current peak, the Deborah number should be equal to unity [33]

$$D(T_{\max}) = \frac{\left[\frac{d\tau(T)}{dT}\right]_{T=T_{\max}}}{\frac{dt}{dT}} = \frac{E_a(T_{\max}) r\tau(T_{\max})}{RT_{\max}^2} = 1.0, \tag{4}$$

where $E_a(T_{\max})$ and $\tau(T_{\max})$ are, respectively, the activation energy and the relaxation time at the temperature of the peak’s maximum, $T_{\max}$, r is the heating rate of the TSDC experiment, and $D(T)$ is the Deborah number. Considering the higher intensity peak (maximum intensity at T_M) and combining Equations (3) and (4), we have

$$m = \frac{1}{2.30_3}\left[\frac{T_M}{r\tau(T_M)}\right], \tag{5}$$

where $\tau(T_M)$ is the relaxation time at the temperature of the maximum intensity. Equation (5) provides an independent method to estimate the fragility index from TSDC data, and allows checking the consistency of the TSDC results. From our results it comes out that the relaxation time at $T_M = 212$ K is $\tau(T_M) = 11.5$ s, so that the fragility index calculated from Equation (5) is also $m = 110$. This value obtained by TSDC is however significantly different from the value $m = 66$ we reported before based on DSC data. On the other hand, other values of m are reported in the literature, obtained from DRS data, namely, $m = 60$ (using $T_g(\tau = 100\ \text{s}) = 208$ K) [34], and $m = 89$ [35] (using $T_g(\tau = 100\ \text{s}) = 214.2$ K), both calculated using the parameters of the Vogel equation obtained by fitting the dielectric relaxation data. Despite the dispersion of these values, all converge to suggest that 5CB is a very fragile glass former. The previous results highlight the often observed discrepancy between the fragility values obtained from different experimental techniques and also from different authors using the same experimental technique [36–38]. This dispersion of values, that seems to become more pronounced for high fragility liquids, may arise from the difference in the type of relaxation used (viscosity, dielectric, mechanical, enthalpy relaxation), i.e., from the different nature of the experimental probes, or from different procedures of obtaining data and of calculation.

Finally, we tried to polarize our samples in the sub-T_g region, but no TSDC peaks were obtained. This is an uncommon and unexpected result since the β-relaxation or Johari-Goldstein relaxation is believed to be present in all glass-forming systems. The explanation for this observation is probably related to the molecular features of our liquid crystal. The cyanobiphenyl core is rigid, and the pentyl tail, which is the only flexible part of the molecule, has very low bond or group dipole moments, so that it is dielectrically inactive. Moreover, small amplitude and noncooperative reorientations of the cyano dipoles are prevented by the structure of the nematic glass: it is disordered with respect to the center of gravity of the molecules, but exhibits a high degree of order with respect to the direction of the molecular axes.

Conclusions

In the present work, we used TSDCs and DSC in order to investigate the dynamics in the liquid crystal 5CB. We confirmed by TSDC and DSC the presence of a relaxation that corresponds to the transition between the nematic glass and the metastable nematic and exhibits the properties typical of simple isotropic liquids. The glass transition temperature was determined for this glass former, and the fragility index calculated from TSDC and DSC data. The obtained values were compared with others, published in the literature. No TSDC signal was detected that could be attributed to the β-relaxation or Johari-Goldstein relaxation of this glass-forming material.

Acknowledgments

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