Dielectric and mechanical relaxation in isooctylcyanobiphenyl (8*OCB)

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Abstract
The dynamics of isooctylcyanobiphenyl (8*OCB) was characterized using dielectric and mechanical spectroscopies. This isomer of the liquid crystalline octylcyanobiphenyl (8OCB) vitrifies during cooling or on application of pressure, exhibiting the typical features of glass-forming liquids: non-Debye relaxation function, non-Arrhenius temperature dependence of the relaxation times, τ_α, a dynamic crossover at $T \sim 1.6 T_{\mathrm{g}}$. This crossover is evidenced by changes in the behavior of both the peak shape and the temperature dependence of τ_α. The primary relaxation time at the crossover, 2 ns at ambient pressure, is the smallest value reported to date for any molecular liquid or polymer. Interestingly, at all temperatures below this crossover, τ_α and the dc conductivity remain coupled (i.e., conform to the Debye–Stokes–Einstein relation). Two secondary relaxations are observed in the glassy state, one of which is identified as the Johari–Goldstein process. Unlike the case for 8OCB, no liquid crystalline phase could be attained for 8*OCB, demonstrating that relatively small differences in chemical structure can effect substantial changes in the intermolecular potential.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Glass is omnipresent, with glassy materials employed for diverse purposes from window glass to engineering thermoplastics. Although glasses have solidlike properties, their microscopic structure is characteristic of the liquid state. Accordingly, much effort has been expended to understand the physics of vitrifying liquids; however, no first-principles theory of supercooled liquids exists. One of the most useful methods for studying the dynamics of supercooled liquids is dielectric spectroscopy (DS), primarily because of its wide frequency range, covering 14 or more decades [1]. Many studies have shown that the temperature dependence of the primary (structural) α-relaxation time, τ_α, is stronger than Arrhenius [2] and described by the empirical Vogel–Fulcher–Tamman (VFT) relation [3]

$$\tau_\alpha = \tau_0 \exp\left(\frac{D_T T_0}{T - T_0}\right) \qquad (1)$$

where τ_0, D_T, and T_0 are material constants. The degree of departure from Arrhenius behavior varies among liquids and a convenient measure of this departure is the T_{g}-normalized slope at T_{g}

$$m = \left.\frac{\mathrm{d}\log\tau_\alpha}{\mathrm{d}(T_{\mathrm{g}}/T)}\right|_{T_{\mathrm{g}}}, \qquad (2)$$

referred to as the fragility or steepness index [4].

Although commonly applied, the VFT equation is able to describe the τ_α only over a limited temperature range. Above a 'crossover temperature', T_B, the relaxation dynamics change, with new set of VFT parameters required to describe $\tau_\alpha(T)$. This 'dynamic crossover' is especially evident in derivative plots [5]. The characteristic value, $\tau_B = \tau_\alpha(T_B)$, varies by more than four orders of magnitude among different liquids; for example, $\tau_B = 4 \times 10^{-4}$ s for phenolphthalein–dimethylether (PDE) and $\tau_B = 4 \times 10^{-8}$ s for propylene carbonate [6]. However, for a given material τ_B is constant, independent of pressure and volume [7–9].

The dispersion of the α-relaxation of supercooled glass formers is invariably wider than for a Debye process [10]. The

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broadened shape of the loss spectrum reflects the interactions with molecules in the vicinity of a given relaxing species; such cooperativity of the dynamics is intrinsic to condensed matter. The one side Fourier transforms of the Kohlrausch–Williams–Watts (KWW) function [11, 12]:

$$\phi(t) = \exp[-(t/\tau)^{\beta_{KWW}}], \qquad 0 < \beta_{KWW} \leqslant 1 \quad (3)$$

is often used to describe this non-Debye behavior. Böhmer *et al* [13] found an empirical connection between the shape of the primary relaxation as described by the stretch exponent, β_{KWW}, and the fragility

$$m = (250 \pm 30) - 320\beta_{KWW}. \quad (4)$$

Another near universal feature of supercooled liquids is the presence of one or more secondary relaxations, preceding in time the α-process. The molecular mechanisms underlying secondary relaxations are different for different materials. Some have an intramolecular origin, such as rotation of pendant groups [14]. However, other secondary relaxations, present even in rigid molecules, involve all atoms in the molecule [15] and are known as a Johari–Goldstein (JG) process [16, 17]. Certain criteria can be applied to define a JG process and thereby distinguish it from intramolecular secondary relaxations [18]. One important main criterion is that the dynamic properties of the JG relaxation are correlated with those of the primary α-relaxation. Theoretical support for this correlation comes from the coupling model of Ngai [19]. According to the coupling model, there is a primitive relaxation process that has characteristics of the JG relaxation, in particular being unaffected by intermolecular coupling. The primitive relaxation time, τ_0, and the JG relaxation time, τ_{JG}, are expected to be comparable in magnitude

$$\tau_0 \approx \tau_{JG}. \quad (5)$$

According to this model,

$$\tau_0 = (t_c)^{1-\beta}(\tau_\alpha)^\beta \quad (6)$$

where the crossover time $t_c = 2 \times 10^{-12}$ s. Thus, equations (5) and (6) connect the values of the α- and the JG relaxation times. In the vicinity of T_B the JG process merges with the structural relaxation, so that secondary relaxations are usually measured below T_g, where $\tau_{JG}(T)$ follows an Arrhenius law [20].

In addition to structural and secondary relaxations, DS experiments detect at lower frequencies a dc conductivity, σ, originating from translation of mobile ions. τ_α and σ are often related according to the Debye–Stokes–Einstein (DSE) relation

$$\sigma \tau_\alpha = \text{const} \quad (7)$$

expressing a correlation between translational and rotational motions of different entities. However, in the supercooled regime there usually is a decoupling of σ and τ_α, described by a fractional DSE relation (FDSE):

$$\sigma \tau_\alpha^s = \text{const} \quad (8)$$

where s is less than unity [21]. The change from DSE behavior at higher temperatures to FDSE at lower temperatures occurs at the dynamic crossover [14].

While these general features are characteristics of glass-forming liquids, how specific changes in chemical structure influence the dynamic properties is poorly understood. The degree to which the molecular structure engenders intermolecularly cooperative motion correlates well with the magnitude of both β_{KWW} and m [22]. However, detailed aspects of the dynamics are not obviously connected to structure. For example, the class of phthalate derivatives have very similar properties [23], whereas PDE and the structurally similar crephthalein–dimethylether have distinctly different behaviors [24]. Liquid crystalline materials also show pronounced changes in relaxation dynamics for modest changes in molecular structure [25]. Systematic studies of the effect of chemical structure on relaxation properties are clearly of great value.

In this paper, dielectric relaxation measurements on isooctylcyanobiphenyl (8*OCB) are presented. This material is an isomer of the liquid crystalline octylcyanobiphenyl (8OCB) but does not exhibit any liquid crystal formation. 8*OCB shows most of the characteristic features of glass-forming liquids described above, with a few exceptions noted herein. This study was extended to include mechanical measurements, to gain a more complete picture of the dynamics.

2. Experimental details

The compound (8*OCB) was prepared in the Military University of Technology, Warsaw by Czuprynski and Dabrowski and used without further purification. DS measurements were performed using the Novocontrol Concept 80 equipped with Alpha and Agilent 4291B impedance analyzers. We measured the complex permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ over the frequency range from 1 mHz to 1 GHz. The sample was in parallel plate cell (diameter = 20 mm and thickness = 0.1 mm), sealed to isolate it from the silicon oil used as a pressurizing fluid. The sample chamber was enclosed with a jacket through which thermostated (Julabo HD 45S) fluid was circulated; in combination with a cryosystem, ±0.1 K temperature stability was achieved. Pressure measurements used a Unipress chamber with a Nova Swiss generator and Nova Swiss tensometric meter (resolution = ±0.1 MPa).

Dynamic mechanical measurements were performed using a Bohlin VOR rheometer with a parallel plate geometry. The sample diameter were varied in the range from 6 to 25 mm in accordance with material stiffness (thickness = 0.8 mm). Dynamic shear experiments were carried out over the range from 10^{-4} to 1 Hz at temperatures in the supercooled regime.

3. Results and discussion

3.1. α process and DC conductivity

Representative isothermal dielectric relaxation spectra measured at ambient pressure are shown in figure 1. In addition
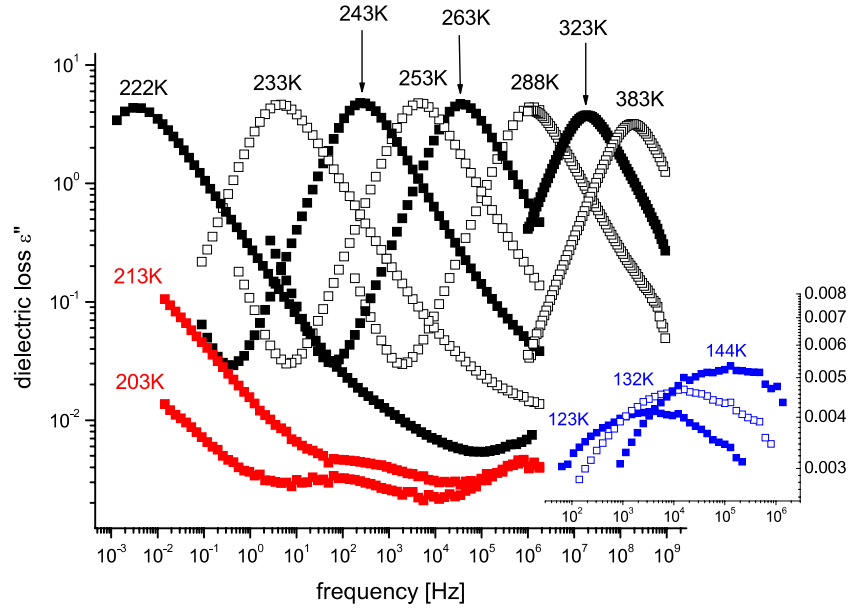
Figure 1. Temperature dependence of dielectric loss at ambient pressure above and below T_g. Inset: selected spectra of the γ process deep in the glass state.
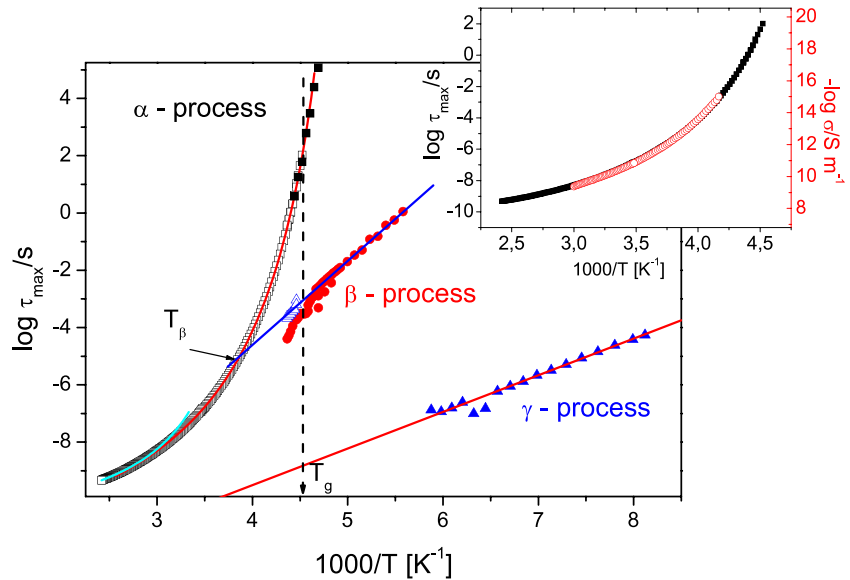

Figure 2. Arrhenius plot of primary and secondary relaxation times. Solid curves represent the VFT fit of τ_α and Arrhenius fit of the secondary relaxation times. Also included are the mechanical relaxations times (solid squares) shifted by a factor of 32 to overlap the dielectric τ_α. Empty triangles are τ_0, calculated from equation (6). In the inset are τ_α (solid squares) and the dc conductivity (open circles), notice that the scale span is the same for both (about 12 decades).

to the primary α-relaxation, a dc conductivity contribution is seen at lower frequencies. Also in the vicinity of and below T_g, higher frequency secondary relaxations are observed. The dielectric loss spectra were fit to a superposition of two Havriliak–Negami (HN) functions with added conductivity contribution:

$$\varepsilon''(\omega) = \frac{\sigma_{DC}}{\varepsilon_0 \omega} + \text{Im} \sum_{i=1}^{2} \left(\frac{\Delta \varepsilon}{[1 + (i\omega\tau_{HN})^{\alpha_{HN}}]^{\beta_{HN}}} \right). \quad (9)$$

In equation (9) α_{HN} and β_{HN} are the respective shape parameters, characterizing the symmetric and asymmetric

broadening of the peak, $\Delta\varepsilon$ is the process strength and σ_{DC} is the DC conductivity. Relaxation times were determined as the reciprocal of the frequency of the maximum in $\varepsilon''(\omega)$, the latter obtained from the HN fits. Figure 2 displays an Arrhenius plot of the relaxation times versus reciprocal temperatures. The curvature of the plots is significant, corresponding to a fragility (using $T_g = 221$ K for which $\tau_\alpha = 100$ s) equal to 86. Two sets of VFT parameters are required to fit τ_α over all measured temperatures: for 224 K $< T <$ 348 K, $\log(\tau_0/s) = -11.49 \pm 0.01$, $D_0 = 5.79 \pm 0.01$, and $T_0 = 186.3 \pm 0.1$ K; for $358 < T < 413$, $\log(\tau_0/s) = -10.62 \pm 0.02$,

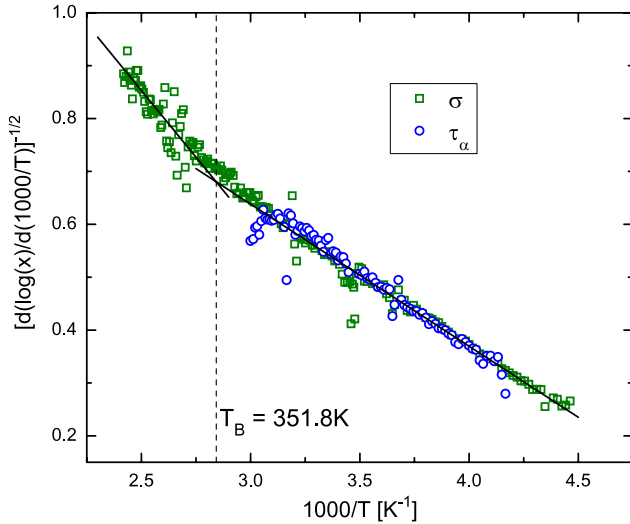**Figure 3.** Stickel derivative plot of the α-relaxation and dc conductivity data from figure 2.

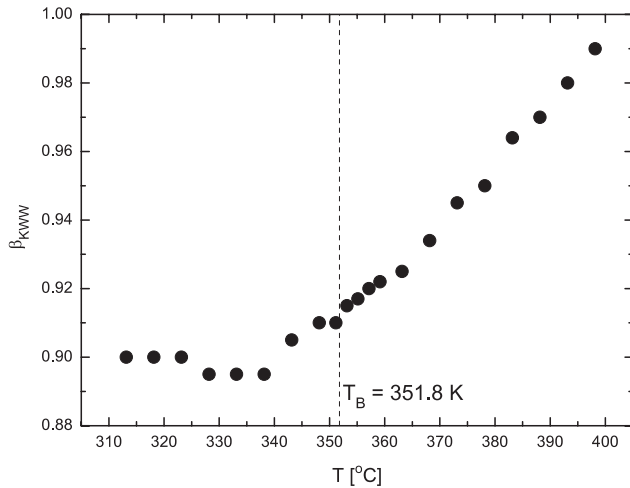**Figure 5.** Representative loss spectra measured at different pressures and $T = 268$ K.

Figure 4. Stretch exponent for the α-relaxation as a function of temperature. The dotted lines denote the temperature of the dynamic crossover determined from $\tau_\alpha(T)$.
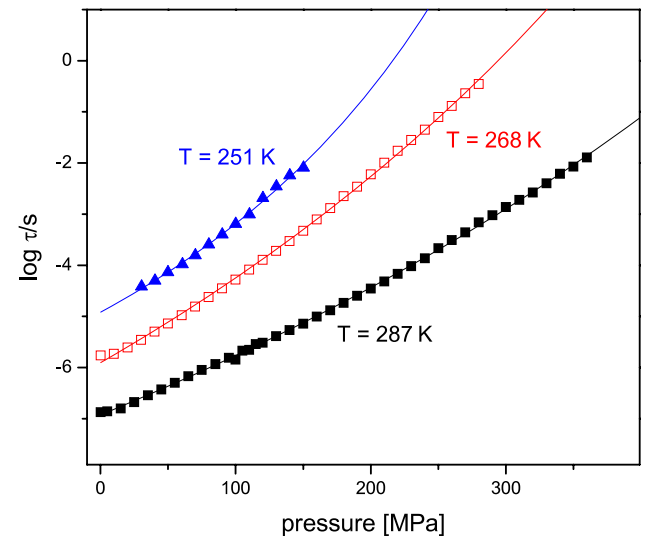
Figure 6. Pressure dependence of τ_α at different temperatures. Solid lines are the fits to the equation (10).

$D_0 = 2.18 \pm 0.09$, and $T_0 = 238.4 \pm 2.2$ K. From the Stickel derivative plot in figure 3, we determine $T_B = 351.8$ K and $\tau_B = 2.3 \times 10^{-9}$ s at ambient pressure. This is an unusually low value, smaller than reported to date for any molecular liquid or polymeric glass-forming material [6, 26].

In figure 4 the stretch exponent is plotted as a function of temperature. The deviation from Debye behavior is weak. In the vicinity of T_g there is a change in the temperature dependence of β_{KWW}. The continued broadening of the peak with decreasing temperature above T_B ceases, with a constant value of $\beta_{KWW} = 0.9$ assumed for lower temperatures. This is similar to the behavior observed for other vitrifying materials [27, 28].

While the temperature dependencies of τ_α and β_{KWW} both evidence the existence of a dynamic crossover, the usual decoupling between the dc conductivity and the α-relaxation is absent (inset to figure 2). The data conform to
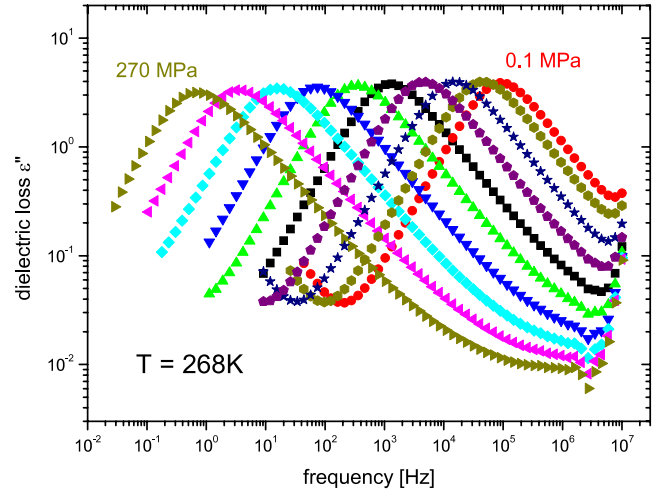
the DSE relation (equation (7)) throughout the temperature regime below the dynamic crossover (note that the crossover temperature, 351.8 K, is much higher temperature than the highest temperature at which the conductivity was measured).

In figure 5 representative dielectric loss spectra measured at various pressures and 268 K are displayed. Qualitatively, the effect of increasing hydrostatic pressure is similar to that of decreasing the temperature. The pressure dependence of τ_α for three isotherms at 251, 268 and 287 K are depicted in figure 6. These relaxation times can be fitted with an equation analogous to the VFT relation [29, 30]

$$\tau = \tau_a \exp\left(\frac{D_P P}{P_0 - P} \right), \qquad (10)$$

where τ_a denotes the corresponding relaxation time at ambient pressure, and P_0 and D_P are material constants. The resulting fits are shown as lines in the figure.
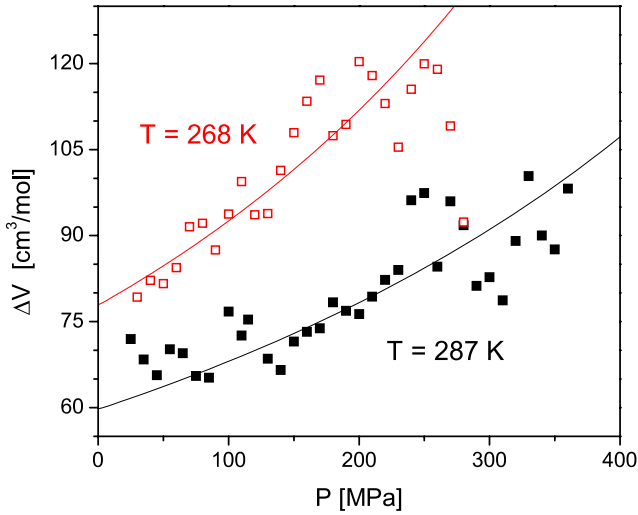
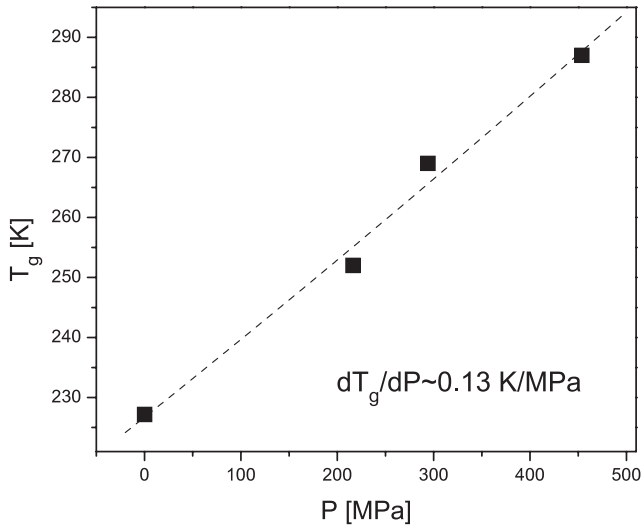**Figure 7.** Pressure dependence of the activation volume.

Figure 8. Pressure dependence of the glass transition temperature.

Figure 9. Comparison of dielectric loss measured at different conditions corresponding to constant τ_α. Solid curve is fit to KWW equation.

Figure 10. HN shape parameters for α-relaxation for various conditions of T and P, showing the invariance of the peak for constant τ_α.

A useful parameter to characterize the pressure dependence of τ_α is the activation volume, defined as

$$\Delta V^{\#} = \frac{RT}{\log(e)} \left(\frac{\mathrm{d}\log\tau}{\mathrm{d}P} \right) \bigg|_T. \qquad (11)$$

Having the units of volume, $\Delta V^{\#}$ is often interpreted as the volume requirement for a change in molecular orientation [31]. The variation with pressure of $\Delta V^{\#}$ for $T = 268$ and 287 K are shown in figure 7; the increase in activation volume with increasing pressure is normal behavior. Similarly $\Delta V^{\#}$ increases with decreasing temperature. Both effects reflect the increasing cooperative nature of the dynamics at higher P or lower T [32]. The glass transition temperature varied linearly with pressure, $\mathrm{d}T_g/\mathrm{d}P \sim 0.13$ K MPa^{-1} (figure 8), a low value for a non-associated liquid [33].

Relaxation measurements at different combinations of temperature and pressure enable a comparison of the shape of the loss spectra at constant τ_α. Figure 9 is an example of such
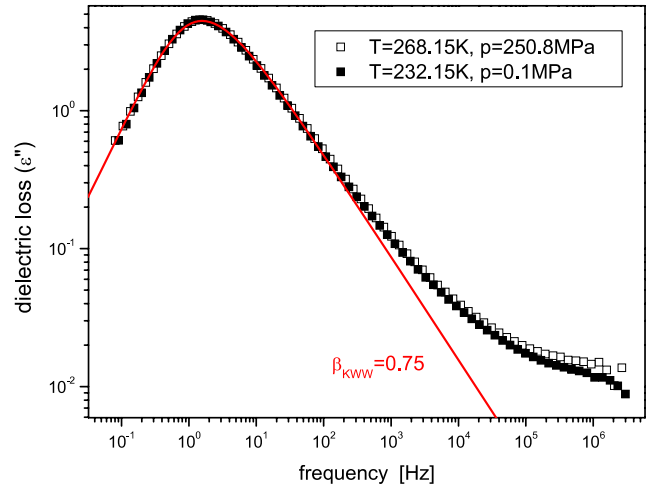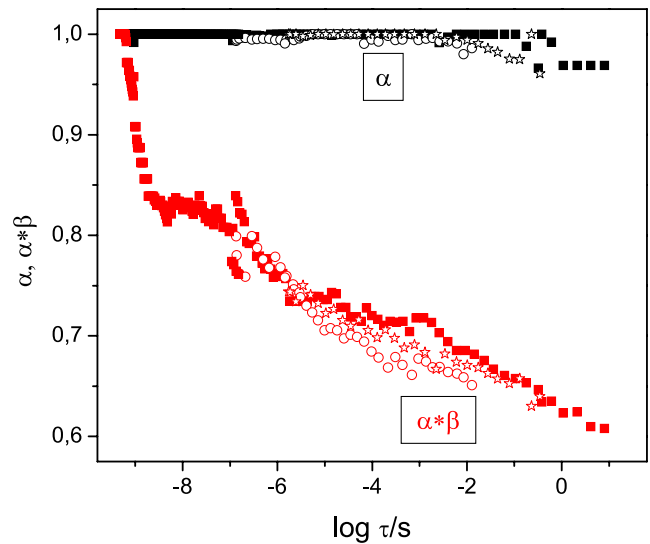
a comparison, wherein the two peaks are seen to superpose. Such behavior conforms to the general pattern that at constant τ_α, the shape of the α-relaxation function is constant; that is, β_{KWW} is determined solely by the magnitude of the structural relaxation time [34, 35]. This is true herein for all pressures and temperatures, as shown in figure 10 in the plot as function of τ_α of the HN shape parameters for the isobaric and isothermal data. Generally the α-relaxation peak becomes broader with increasing τ_α; however, this breadth is constant for any fixed value of τ_α.

As was mentioned above many materials conform at least approximately to the empirical correlation between *fragility* and β_{KWW} described by equation (4). However, 8*OCB clearly deviates from this pattern: m estimated from equation (4) is 32 ± 30, much smaller that the measured value of 86.
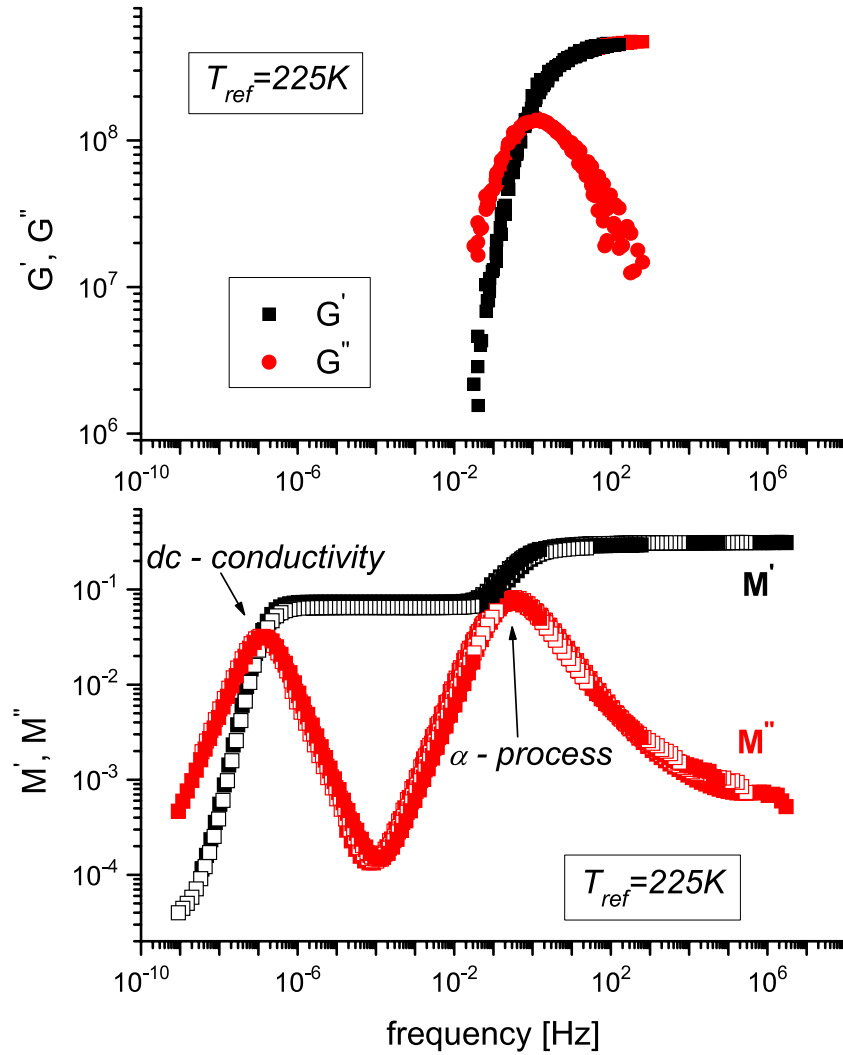
Figure 11. Top panel: master curves of the storage and loss mechanical moduli. Bottom panel: corresponding master curves of the dielectric in-phase and out-of-phase moduli.

3.2. Secondary relaxation

Like most supercooled liquids, 8*OCB undergoes secondary relaxations, as seen in figure 1. In the vicinity of T_g a slower β process emerges from the wing of the α-peak, whereas a faster γ process is only observed at temperatures well below T_g (see inset). The symmetric Cole–Cole function describes both secondary peaks, and as shown in figure 2 below T_g the relaxation times for both have an Arrhenius temperature dependence, with activation energies equal to 56.6 ± 1.1 kJ mol^{-1} for the slower γ process and 24.5 ± 0.2 kJ mol^{-1} for the higher frequency one. Above T_g the β relaxation exhibits a change in its temperature dependence, as is commonly observed [20, 36, 37].

To identify the molecular origin of the two secondary processes in 8*OCB we apply equations (5) and (6). The calculated secondary relaxation times are shown as open triangles in figure 2. The primitive relaxation times from the coupling model are in reasonable agreement with the values for the slower secondary process, whereby we identify it as the intermolecular Johari–Goldstein relaxation. The γ relaxation,

on the other hand, must involve only some atoms in the 8*OCB molecule. It is noteworthy that the temperature of the merging of the α- and β-relaxations, obtained by extrapolation of the Arrhenius regime, is 258.7 K, which is almost one hundred degrees lower than T_B. This reflects the error in extrapolated the Arrhenius temperature dependence of the glassy state to above T_g. Extrapolation of the γ process never superimposes with the α-relaxation, since the two are unrelated.

3.3. Mechanical relaxation

From the mechanical measurements at various temperatures, master curves of the storage (G') and loss (G'') shear moduli were constructed (figure 11). Notwithstanding the clear breakdown of time–temperature superpositioning (the mechanical loss peak changes shape with changes in T), the breadth of the peak is approximately equivalent to the dielectric loss α-peak. The relaxation strengths, however, are quite different.

The mechanical relaxation times determined from the inverse frequency of the peak in G'' are included in figure 1

6

after multiplying by a factor 32. The latter brings them into coincidence with the dielectric τ_α. Invariably mechanical relaxation times are shorter than the corresponding dielectric τ_α [38, 39]. Buchenau *et al* [40] have ascribed this difference to the possibility that dielectric relaxation involves not only molecular orientation but also the shorter range order and the density. This is an intriguing area for further study.

4. Conclusions

The relaxation dynamics of isooctylcyanobiphenyl was studied by dielectric and mechanical spectroscopies, using both temperature and pressure as experimental variables. In contrast to the related octylcyanobiphenyl, 8*OCB does not form a liquid crystalline phase, but does exhibit features typical of glass-forming liquids, such as non-Arrhenius and non-Debye behaviors, a dynamic crossover above T_g, and the existence of multiple secondary processes having intra- and intermolecular origins. However, the α-relaxation time at the dynamic crossover is shorter for 8*OCB than observed heretofore for other supercooled liquids. Also, 8*OCB strongly deviates from the empirical correlation between the shape of the primary α-peak and the fragility. It is intriguing that in the octylcyanobiphenyls, similarly to the properties of pentylcyanobiphenyls [25], small changes in chemical structure exert such a marked effect on the dynamics.

Acknowledgments

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