The effect of pressure on the structural and secondary relaxations in 1,1′-bis (p-methoxyphenyl) cyclohexane

S. Hensel-Bielowka and J. Ziolo
Institute of Physics, Silesian University, Uniwersytecka 4, 40-007 Katowice, Poland

M. Paluch and C. M. Roland
Naval Research Laboratory, Chemistry Division, Code 6120, Washington, DC 20375-5342

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The dielectric spectrum of the organic glass former 1,1′-bis (p-methoxyphenyl) cyclohexane was measured over a range of temperatures and pressures, corresponding to a variation of the structural relaxation time, $\tau_a$, by 8 decades. The temperature dependence of $\tau_a$ corresponded to a fragility equal to 72, which is consistent with the correlation of same with the shape (breadth) of the relaxation function. The dependence on pressure of $\tau_a$ could be described as a simple activated process, with a pressure-independent activation volume equal to $\sim$230 cm$^3$/mol, varying inversely with temperature. The pressure coefficient of the glass temperature, $T_g$, was 240 K/GPa. At frequencies beyond the structural relaxation peak, there is a second, thermally activated process, having an activation energy $\sim$ 74.2 kJ/mol. The relaxation times for this process were invariant to pressure. Extrapolation of these relaxation times (measured below the $T_B$) intersects the ambient pressure structural relaxation data at a temperature, $T_B$ = 268 K. This is about equal to the temperature, $T_B$, at which the structural relaxation times deviated from a single Vogel–Fulcher–Tammann curve. In this respect, the secondary process exhibits the properties of a Johari–Goldstein relaxation. However, since $T_B$ varies with pressure, it remains to be seen whether its equivalence to $T_B$ is maintained at elevated pressure. © 2002 American Institute of Physics.

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I. INTRODUCTION

Dielectric spectroscopy is an especially appealing method to study the relaxation phenomena in supercooled liquids. The enormous dynamic range of dielectric spectrometers enables the different phenomena occurring in supercooled liquids to be measured independently. At the lowest frequencies, ionic drift causes a dc conductivity to be observed. With increasing frequency, the primary structural relaxation ($\alpha$-process), arising from rotational motion of molecular dipoles, begins to contribute. The $\alpha$-relaxation is characterized by an asymmetrically shaped peak, which often broadens as the glass temperature, $T_g$, is approached. The $\alpha$-relaxation dispersion is commonly described using the Laplace transform of the Kohlrausch function,$^2$ with the dielectric loss given by

$$e^{-}(2\pi f) = \int_0^\infty dt \left[ -\frac{d}{dt} \exp[-(t/\tau_K)^\beta] \right] \sin(2\pi f t), \quad (1)$$

in which $f$ is frequency, $\tau_K$ the Kohlrausch relaxation time, and $\beta$ the stretch exponent.

Another feature of the $\alpha$-process is the non-Arrhenius temperature dependence of the relaxation times. An important characteristic by which glass formers can be classified is the degree to which this temperature dependence departs from Arrhenius behavior, as measured, for example, by the fragility$^3$

$$m = \left| \frac{\partial \log \tau_a}{\partial (T_g/T)} \right|_{T=T_g}^{T=T_0}. \quad (2)$$

This parameter spans the range from $m \approx 15$ for strong liquids, having near-Arrhenius dependence, to $m$ as large as 350 for fragile liquids with marked non-Arrhenius behavior.$^4$ In many cases, the $\tau(T)$ dependence can be described over significant temperature ranges using the Vogel–Fulcher–Tammann (VFT) expression$^5$

$$\tau_a(T) = \tau_0 \exp \left( \frac{D_F T_0}{T - T_0} \right), \quad (3)$$

in which $\tau_0$ and $D_F$ are constants, and $T_0$ is approximately the Kauzmann temperature.$^6$ However, over the entire range of temperatures for which $\tau_a$ can be measured, a second VFT, or an Arrhenius equation must be employed as well, to completely account for the temperature dependence of $\tau_a$.$^7$

The transition from one temperature dependence to another occurs at a temperature, $T_B$, approximately equal to the temperature, $T_B$, at which the $\alpha$- and $\beta$-processes merge. The $\beta$-process (or secondary relaxation) is faster than the $\alpha$-relaxation, but has an origin that remains open to debate. Referred to as the Johari–Goldstein (JG) relaxation, this secondary relaxation involves the same atoms as the structural relaxation, and merges with the latter at temperatures somewhat above $T_g$.$^8$ The JG relaxation can be distinguished from relaxation processes originating from intramolecular motions, involving for example methyl group rotation or mo-

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$^1$Electronic mail: mike.roland@nrl.navy.mil

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tion of a pendant moiety. The latter are well separated from the \( \alpha \)-process at all temperatures, and weakly coupled to it.\(^9,10\)

Johari and Goldstein\(^11\) carried out the first systematic studies of the \( \beta \)-relaxation in nonpolymeric liquids. From their work, some characteristic features of the \( \alpha \) relaxation can be drawn. The dielectric loss for this process is broad and symmetric, and usually orders of magnitude weaker than the \( \alpha \)-relaxation. Moreover, unlike structural relaxation which is arrested at \( T_g \), the \( \alpha \) relaxation can be observed in the glassy state. Distinct from the \( \alpha \)-relaxation, the temperature dependence of \( \alpha \)-relaxation times often follow an Arrhenius law. From the fact that the \( \alpha \) relaxation can be detected in rigid molecules, Johari and Goldstein\(^11\) concluded that this process has an intermolecular origin. Such a definition does not distinguish between processes involving the entire molecule or only part of it, the only requirement being that the motion is “governed” by intermolecular interactions. Notwithstanding their intermolecular aspects, \( \alpha \) processes are generally found to depend at most weakly on pressure.\(^12\),\(^13\)

The feature distinguishing it from structural relaxation was the origin of the \( \alpha \) relaxation in motion of molecules within “islands of mobility;” that is, regions of the liquid in which the local density is much less than the bulk value.\(^14\)

More recently, Vogel and Rössler,\(^15\) on the basis of nuclear magnetic resonance (NMR) studies on toluene, identified the \( \alpha \) relaxation as a local reorientation restricted to angles less than \( 10^\circ \). They also verified the assumption of Williams and Watts,\(^16\) that all molecules participate in the strongly hindered rotation.

An interesting aspect of the \( \alpha \) process is the fact that not all liquids exhibit it. For these materials, a different behavior is observed at frequencies beyond the \( \alpha \)-relaxation peak. There lies an “excess wing,” described by a second-power law, with a slope that is less than the \( \beta \) characterizing the high-frequency side of the \( \alpha \)-relaxation in the vicinity of the loss maximum [viz. Eq. (1)].\(^17\)–\(^22\) The molecular origin of the excess wing, and its relation to \( \alpha \) relaxation, remains to be satisfactorily established.

Recent developments involve the use of dielectric measurements on glass formers subjected to high pressure. The effect of pressure (density changes) and that of temperature (both thermal and volume changes) can be quite different for the \( \alpha \)- and \( \beta \)-processes.\(^23\),\(^24\) It is of interest to compare the influence of both variables on the relaxation properties. Examples both of differences and similarities between the relaxation behavior of supercooled liquids under high pressure as opposed to low temperature have been reported.\(^25\)–\(^32\)

In this article, we report isothermal and isobaric measurements on the molecular glass former 1,1’-bis (\( \rho \)-methoxyphenyl) cyclohexane (BMPC). The dynamics of this material at ambient pressure have been investigated previously. Meier \textit{et al.}\(^33\) found that the shape of the dielectric loss peak due to the \( \alpha \)-relaxation of BMPC was invariant to temperature. More interestingly, they reported that no \( \alpha \)-type process was evident in the dielectric spectra, although a high-frequency process was detected by deuterium NMR. From line shape analysis, the authors concluded that this process was due to flipping of the methoxyphenyl rings. Such local motion, dependent on chemical structure, would not constitute a \( \alpha \) process. However, the properties Meier \textit{et al.}\(^33\) reported for the putative phenyl ring flipping are consistent with a \( \alpha \)-type relaxation—an activation energy of 63 kJ/mol, and (extrapolated) merging with the structural relaxation at a temperature tens of degrees above \( T_g \).

Subsequently, Hansen and co-workers\(^8\) carried out more extensive ambient pressure, dielectric measurements on BMPC. They observed a secondary-dielectric relaxation, corresponding closely to the process seen in the \( ^{2}H \) NMR experiments of Meier \textit{et al.}\(^33\) The activation energy for the dielectric secondary relaxation was 50 kJ/mol, with a merging temperature \( T_\beta=T_g+30 \). From these results, the authors concluded that this was indeed a \( \alpha \) relaxation.\(^8\)

We have recently pursued an understanding of the microscopic origin of secondary relaxations in glass forming liquids.\(^23\)–\(^24\) Using pressure as a variable offers a route to gaining new insights into this problem.\(^35\),\(^36\) In this article, we describe measurements of the dielectric spectrum of BMPC at elevated pressures.

II. EXPERIMENT

The BMPC (obtained from Dr. T. Wagner of the Max Planck Institute for Polymer Research, Mainz, Germany) has the structure depicted in Fig. 1. It is also referred to as bisphenol-\( C \)-dimethyether.

For ambient pressure measurements, we used a Novo-Control GmbH dielectric spectrometer, equipped with a Solatron SI1260 frequency response analyzer and broadband dielectric converter. The dielectric permittivity, \( \varepsilon^*(\omega) = \varepsilon'(\omega) - i \varepsilon''(\omega) \), was measured in the frequency range \( 10^{-2} - 10^6 \) Hz. The sample was contained in a parallel-plate cell (diameter 10 mm and gap 0.1 mm). Temperature was controlled using a nitrogen-gas cryostat, with a temperature stability better than 0.1 K.

The high-pressure measurements employed the equipment described in Ref. 37. The capacitor, filled with the test material, was placed in the high-pressure chamber, and compressed using silicone fluid, via a piston in contact with a hydraulic press. The sample capacitor was sealed and mounted inside a Teflon ring to separate it from the silicon oil. Pressure was measured by a Nova Swiss tensometric meter (resolution=1 MPa). The temperature was controlled within 0.1 K by means of liquid flow from a thermostatic bath.

III. RESULTS AND DISCUSSION

A. Structural relaxation

Representative dielectric loss spectra of BMPC measured under both isothermal and isobaric conditions are displayed in Fig. 1. Two different relaxation processes are observed. The most prominent is the \( \alpha \)-dispersion, related to structural relaxation. As seen in Fig. 1, the position of the \( \alpha \)-peak depends strongly on both temperature and pressure. A secondary relaxation occurs at frequencies higher than associated with the \( \alpha \)-relaxation. As discussed in more detail...
below, this latter process has only a weak dependence on temperature and a virtual insensitivity to pressure.

As noted previously by Meier et al.,33 the shape of the structural relaxation peak does not change significantly with temperature. In Fig. 2, we show a representative dielectric loss spectrum. The best fit of the linear $\varepsilon''$ data to Eq. (1) gives a value of 0.60 for the stretch exponent. As is evident from Fig. 2, the data deviate from the Kohlrausch function at higher frequencies. In the inset to Fig. 2, we display a double-logarithmic plot of the data, whereby the power-law behavior for $0.04 \lesssim \log \nu \lesssim 1.5$ is evident. The slope yields $\beta = 0.44$. These values, 0.44 and 0.60, bracket the stretch exponent obtained by Meier et al.,33 from fitting the transform of the dielectric loss to the Kohlrausch function. These differences are due to the fact that the $\alpha$-relaxation for BMPC does not conform to the Kohlrausch function over the entire frequency range. Consequently, fitting linear dielectric loss (as in Fig. 2) emphasizes the peak of the dispersion, whereas fitting a power law (inset to Fig. 2) or Meier et al.’s33 fitting in the time domain gives greater weight to the wings of the spectrum.38

From the dielectric spectra, we determined the most probable relaxation time ($\tau_\alpha = 1/2\pi v_{max}$, where $v_{max}$ is the frequency of the maximum in the dielectric loss), for the structural relaxation. These are plotted in Fig. 3 as a function of temperature. The fit to Eq. (3) is shown by the solid line through the data points. Also included in Fig. 3 are the dielectric data of Meier et al.,33 and of Stickel39 for the same temperature range. Their results are in good agreement with the relaxation times measured herein.

Hansen et al.8 have shown that, beyond the characteristic temperature $T_B = 270$ K, the $\alpha$-relaxation times for BMPC depart from a single VFT equation. This deviation becomes evident when the data are plotted in the derivative form,7,8 for which Eq. (3) yields a straight line. Indeed, as seen in the inset to Fig. 3, such a departure can be observed in the present data for temperatures above $270$ K. However, over the range of our measurements, a single VFT is adequate to describe the temperature dependence of $\tau_\alpha$.

As seen in Fig. 1, increasing pressure has qualitatively the same effect as decreasing temperature; that is, the molecular motions responsible for structural relaxation can be arrested by either compression or cooling, the former enhancing molecular packing, while the latter reduces both the volume and thermal energy. Unlike the temperature dependence of $\tau_\alpha$, which is rarely Arrhenius, there are cases in which the pressure dependence of the logarithm of the relaxation times appears linear, including $\alpha$-terphenyl (OTP),40,41 cresolphaleindimethylether (KDE),42 phenolphaleindimethylether (PDE),42 and bis-methyloxymethylphenylcyclohexane (BMPC).43 More generally, the $\tau_\alpha(P)$ behavior can be fit to a pressure coun-

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**FIG. 1.** Representative dielectric loss spectra of BMPC obtained at ambient pressure (upper curves: 240 K $< T < 288$ K) and under isothermal conditions (lower curves: 0.5 MPa $< P < 160.4$ MPa) conditions. The molecular structure of BMPC is as shown.

**FIG. 2.** The dielectric loss for BMPC at ambient pressure and 248 K, along with the best fit to the Kohlrausch function; this yields a value equal to 0.6 for the stretch exponent. However, when plotted on a logarithmic ordinate scale (inset), the exponent for the high-frequency power-law regime is 0.44. At the highest frequencies (>100 Hz), the contribution from the secondary process becomes evident.
terpart of Eq. (3) \[ \tau_a \propto \exp \left( \frac{PV}{RT} \right) \] In Fig. 4, we show the dependence on pressure of \( \tau_a \) for BMPC measured at six different temperatures. At least over this range of pressures, any deviation from linearity is negligible. Thus, we can describe the response to pressure of BMPC as a simple volume activated process, whereby

\[ \tau_a = \tau_0 \exp \left( \frac{PV}{RT} \right). \] 

\( V \) is an activation volume and \( R \) is the gas constant. The origin of deviation from linearity in some glass formers, but not others, is unknown. This situation evokes the pattern seen for the temperature dependence of \( \tau_a \), in which the extent of deviation from Arrhenius behavior reflects the fragility, and hence strength of the intermolecular constraints, for the \( \alpha \)-relaxation. \(^{47-52}\)

In Fig. 5 we plot the activation volumes extracted from the data in Fig. 4. These \( V \) range from 207 to 251 cm\(^3\)/mol over temperatures from 284 to 254 K. This is the usual effect of temperature. The activation volume represents the difference between the volume occupied by a molecule initially and in its transition state. As temperature is reduced, the consequences of intermolecular cooperativity become magnified, and \( V \) increases.

A glass temperature can be defined in the customary fashion as the temperature at which the structural relaxation time equals 100 s. Figure 6 shows the variation in \( T_g \) with pressure. These data can be described using the empirical equation

\[ T_g = a \left( 1 + \frac{b}{P} \right)^{1/b}. \] 

yielding \( a = 241 \) K, \( b = 3.61 \), and \( c = 1.01 \) GPa. From this, we obtain in the limit of zero pressure, \( dT_g/dP = 240 \) K/GPa. At ambient pressure, \( T_g = 241.3 \) K, whereby from Eq. (2) we calculate for the fragility, \( m = 72 \). This intermediate degree of fragility is consistent with the shape of the peak breadth (Fig. 2), given the expected correlation of these quantities. \(^{3,4}\)

### B. Secondary relaxation

The aforementioned results pertain to the \( \alpha \)-relaxation. Evident in Fig. 1 at lower temperatures and in the inset to Fig. 2 is a second process, transpiring in the dielectric spectrum of BMPC at frequencies beyond about 100 Hz. Both lower temperature and higher pressure yield greater separation of the primary and secondary processes. Figure 7 shows representative spectra of BMPC obtained at 284 K for various pressures. For the higher pressures in Fig. 7 (>200 MPa), the \( \alpha \)-process has moved out of our experimental window, whereby a resolved secondary relaxation is seen within the accessible range of frequencies. Note that the relaxation time for this secondary process is virtually independent of pressure. Such behavior is distinctly different from that of
the \( \alpha \)-relaxation, as illustrated in Fig. 4, which includes the pressure dependence of the relaxation times measured for the secondary process at 284 K.

This pressure invariance is in accord with the findings of Vogel and Rössler,\(^{15}\) who interpreted their NMR experiments to indicate that the JG relaxation in low molecular glass forming liquids can be attributed to molecular axis jumps subtending only a small angle. Such molecular motion is strongly restricted in space, and therefore should be relatively impervious to pressure. The shape of the secondary relaxation process was also found to be relatively insensitive to pressure. Fitting the peak to the Cole–Cole function,\(^{54}\) we obtain an average value for the shape parameter \( \delta = 0.59 \), decreasing by less than 0.01 over the measured range of pressures. The dielectric strength of the secondary process likewise shows a weak decrease (\( \sim 20\% \)) up through the highest applied pressures; however, potential displacement of the electrodes with pressure makes this measurement uncertain.

Since the isobaric structural relaxation times vary strongly with pressure, while those for the secondary process do not, it is of interest to compare the effect of pressure on the temperature at which the two relaxation times become equivalent. At \( T_{\beta} \), the two processes bifurcate from a single peak as temperature is lowered. Figure 8 shows the \( \alpha \)-relaxation times for various pressures, along with fitted VFT curves. In Fig. 8, we also plot the secondary-relaxation times measured at \( T \leq T_g \) and ambient pressure. (Values for the latter obtained at elevated pressure would be scarcely different.) The temperature dependence of the secondary mode is Arrhenius, yielding a value of 74.2 kJ/mol for the activation energy. This is substantially larger than the value of Hansen et al.,\(^{8}\) who reported 50 kJ/mol. From NMR measurements on BMPC, Meier et al.\(^{33}\) obtained 63 kJ/mol for the same process.

Since the secondary-relaxation times are pressure independent, the intersection of the fitted Arrhenius line with the \( \tau_\alpha \) curves yields a measure of \( T_{\beta} \) for all pressures. For ambient pressure, we obtain \( T_{\beta} = 268 \) K, at which the relaxation time is about \( 10^{-4} \) s. This is much longer, by at least two decades, than for most simple liquids and polymers.\(^{55}\)

\( T_{\beta} \) decreases with increasing pressure, as shown in Fig. 6, although the respective pressure dependences of the merging temperature and the glass temperature are different. At zero pressure, we obtain \( dT_{\beta}/dP = 350 \) K/GPa, which is 50\% larger than \( dT_g/dP \).

The merging temperature has often been shown to relate to the cross-over temperature, \( T_B \), at which the structural relaxation time transitions from one VFT dependence to another VFT or Arrhenius regime. For BMPC, Hansen et al.\(^{8}\) reported \( T_B = 270 \) K, which is consistent with the data in the insert to Fig. 3. This value of \( T_B \) is quite close to the value of \( T_{\beta} \) determined herein.
IV. SUMMARY

The dielectric spectrum of BMPC exhibits two peaks, the lower frequency one associated with structural relaxation. In the vicinity of the peak maximum, this \( \alpha \)-dispersion can be described using Eq. 2 with \( \beta = 0.60 \). The shape deviates from the Kohlrausch function at higher frequencies, however, yielding \( \beta = 0.44 \) in the power-law regime. The breadth of the peak is consistent with an intermediate degree of fragility, \( m = 72 \).

The structural relaxation times vary by eight orders of magnitude in response to changes in temperature and the applied pressure. Although the temperature dependence of \( \tau_s \) conformed to a single-VFT equation, a derivative plot shows the expected break at \( T_B \approx 270 \) K. The pressure dependence of the structural relaxation time could be described as an activated process, with a constant (pressure-independent) activation volume. For temperatures in the range \( T_s + 43 > T_B \approx T_s + 13 \) (\( T_s = 241.3 \) K at ambient pressure), the activation volume varied from 204 to 264 cm\(^3\)/mol. The pressure coefficient of the glass temperature was determined to be 240 K/GPa, which is in the range of other nonhydrogen bonded, small molecule glass formers.\(^{56} \)

The secondary relaxation in BMPC is thermally activated, with an activation energy equal to 74.2 kJ/mol. Quite distinct from the structural relaxation, the secondary process was insensitive to pressure, implying an activation volume nearly equal to zero. As a result, the overlapping of the two peaks above \( T_g \) can be circumvented by the application of pressure. This ability to resolve close-lying dispersions is one of the advantages of using pressure as an experimental variable.

The properties of the secondary process in BMPC (pressure independent relaxation times, merging with the structural relaxation at a temperature \( T_B > T_g \)) are consistent with its identity as a JG relaxation, in accord with the conclusion of Hansen et al.\(^{8} \) However, this does not rule out the possibility suggested by the NMR experiments of Meier et al.,\(^{33} \) that this process reflects rotation of the methoxyphe- nol moiety. However, the latter must involve intermolecular interactions to be regarded as JG motion. A potential means to resolve this issue is by determining the pressure dependence of \( T_B \). Continued equivalence at elevated pressures between \( T_B \) and \( T_B \), as is seen for ambient pressure, would argue for a JG identification of the high-frequency process. However, such experiments require dielectric measurements at higher frequencies (>10\(^7\) Hz) than can be attained with the presently available high-pressure dielectric equipment.

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