Primary and secondary relaxations in bis-5-hydroxypentylphthalate

S. Maślanka
Institute of Chemistry, Szkolna 9, 40-006 Katowice, Poland

M. Paluch[a)]
Institute of Physics, Silesian University, Uniwersytecka 4, 40-007 Katowice, Poland

W. W. Sułkowski
Institute of Chemistry, Szkolna 9, 40-006 Katowice, Poland

C. M. Roland[b)]
Naval Research Laboratory, Chemistry Division, Code 6120, Washington, DC 20375-5342

Broadband dielectric spectroscopy was used to study the relaxation dynamics in bis-5-hydroxypentylphthalate (BHPP) under both isobaric and isothermal conditions. The relaxation dynamics exhibit complex behavior, arising from hydrogen bonding in the BHPP. At ambient pressure above the glass transition temperature T_g, the dielectric spectrum shows a broad structural relaxation peak with a prominent excess wing toward higher frequencies. As temperature is decreased below T_g, the excess wing transforms into two distinct peaks, both having Arrhenius behavior with activation energies equal to 58.8 and 32.6 kJ/mol for slower (β) and faster (γ) processes, respectively. Furthermore, the relaxation times for the β process increase with increasing pressure, whereas the faster γ relaxation is practically insensitive to pressure changes. Analysis of the properties of these secondary relaxations suggests that the β peak can be identified as an intermolecular Johari–Goldstein (JG) process. However, its separation in frequency from the α relaxation, and both its activation energy and activation volume, differ substantially from values calculated from the breadth of the structural relaxation peak. Thus, the dynamics of BHPP appear to be an exception to the usual correlation between the respective properties of the structural and the JG secondary relaxations. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1851980]

I. INTRODUCTION

A considerable number of research efforts continue to focus on the glass transition phenomenon, as many fundamental issues remain to be fully resolved. Dielectric spectroscopy is an especially useful probe, allowing the dynamics of supercooled liquids to be monitored over many decades of frequency. Recent progress has been made by carrying out measurements at elevated hydrostatic pressure. A salient advantage of such experiments is that advantage can be taken of the differing response to pressure of the primary α (or structural) relaxation and any other dielectric processes. Overlapping dielectric absorption peaks often become separated at high pressure, enabling the properties of the secondary β relaxations to be examined. Among the latter, the most important is the Johari-Goldstein (JG) secondary relaxation. This process involves all atoms of the molecules, and thus is observed even in rigid molecules, lacking pendant moieties.[1] The JG relaxation is believed to be universal to glass formers, although the peak is broad and often much weaker than the primary α dispersion, so that a JG peak may not be evident in the dielectric spectrum of all materials.

Recent work has shown that various properties of the JG relaxation are correlated with those of the α relaxation, and that the JG relaxation, occurring sooner in time, serves as the precursor of the primary α relaxation.[2] This means that fundamental insight into the glass transition dynamics necessarily requires accounting for the behavior of the JG relaxation.

One difficulty, leading to some confusion in the literature, concerns identification of secondary β relaxations which may not be JG processes. Illustrative examples include the β relaxation in 1,1′-bis (*p*-methoxyphenyl) cyclohexane (BMPC) and in tripropylene glycol (TPG). The dielectric spectrum of the former has a secondary relaxation that, by its behavior, ostensibly appears to be the JG relaxation; to wit, it is the slowest observed secondary relaxation, and extrapolation of its relaxation times intersects the α-relaxation times at a merging temperature $T_\beta = T_g + 30$.[3] However, NMR measurements[4] reveal that this β secondary, involving flipping of the methoxyphenol rings, is an internal mode and thus not a JG process. Further evidence that the β peak in BMPC is not a JG relaxation comes from the finding that the β-relaxation times are nearly invariant to pressure.[5]

TPG also has a distinct secondary β relaxation in its dielectric spectrum that has conventionally been regarded as a JG process.[6,7] However, under elevated pressure a new secondary peak emerges intermediate in frequency to this β peak and the main α peak.[8] The frequency of this new peak is more sensitive to pressure than the β peak, implying stronger intermolecular cooperativity. That, and the fact that it is

---
[a)]Author to whom correspondence should be addressed; Electronic mail: mpaluch@usctouxl.cto.us.edu.pl
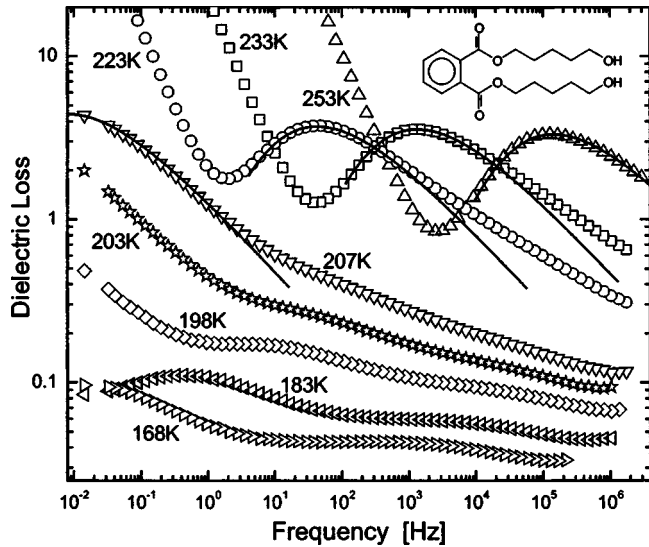[b)]Author to whom correspondence should be addressed; Electronic mail: mike.roland@nrl.navy.mil

FIG. 1. Dielectric loss spectra at ambient pressure and the indicated temperatures. The solid lines are the best fits of Eq. (3) to the α peak, yielding $\beta_K=0.55$. Also shown is the chemical structure of the di-5-hydroxypentylphthalate.

FIG. 2. The dc conductivity plotted as a function of the relaxation times for the α peak. The power-law exponent is 0.82.

the slower of the two, indicates that the new peak, unobserved in low pressure measurements, is the JG process.[8] Misidentification of secondary peaks hinders development of the understanding of JG secondary relaxations, and their relationship to the glass transition dynamics.

In this work we have carried out dielectric measurement on a newly synthesized glass former, bis(5-hydroxypentyl)phthalate (BHPP). The presence of two hydroxyl groups, along with the ester functionality, imparts a strong dipole moment. This facilitates measurement of the dielectric response at elevated pressures. However, in addition to its capacity for hydrogen-bond formation, BHPP has a complex molecular structure. The result is a complicated dielectric spectrum, with an excess wing at low pressures, and at sufficiently high pressures, two secondary peaks. An aim of this paper is to sort out the nature of these relaxations.

II. EXPERIMENT

The bis(5-hydroxypentyl)phthalate was prepared from phthalic anhydride and pentamethyl glycol. The synthesis was carried out in xylene at elevated temperature for 9 h, until the acid number of the product was less than 5 mg KOH/g. The product was purified and dried under vacuum, with the purity confirmed by elemental analysis and NMR. The chemical structure of the compound is illustrated in Fig. 1.

The temperature-dependent dielectric measurements were carried out with Novo-Control GmbH equipment. We measured the complex permittivity over ten decades of frequency using an Alfa analyzer ($10^{-2}-10^6$ Hz), in combination with an Agilent network analyzer (10^7-10^9 Hz). The temperature was controlled by the Quatro system, employing a nitrogen-gas cryostat; temperature stability at the sample was better than 0.1 K. For high-pressure measurements, we used a Unipress system, with the sample contained between two steel plates mounted in a Teflon bellows. Pressure was
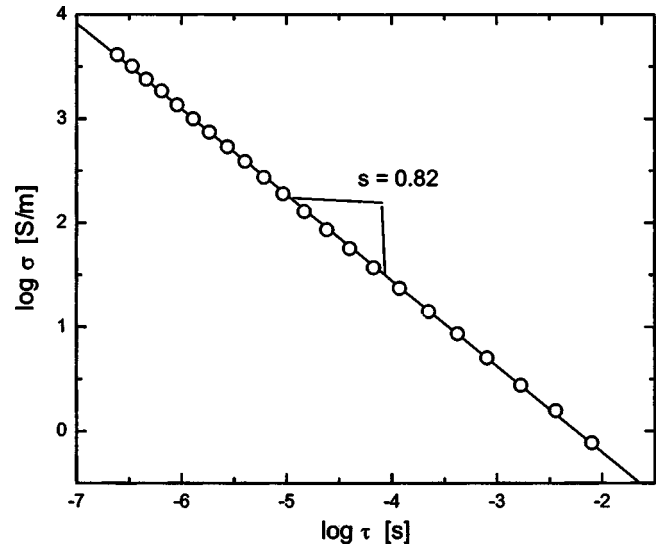
exerted via a piston and hydraulic press. During measurements, the sample was in contact only with the steel plates and Teflon insulation. The temperature was controlled within 0.1 K by means of liquid flow from a thermostatic bath.

III. RESULTS

A. Temperature dependence

Representative dielectric loss spectra of the main α relaxation at ambient pressure are shown in Fig. 1. At higher temperatures, a dc-conductivity contribution is evident at lower frequencies, while beyond the conductivity, there is the strong α-relaxation peak. Relaxation times for the α process τ_α are defined as the reciprocal of the maximum in the loss peak. For the α relaxation at lower temperatures, this requires subtraction of the ionic conductivity, the latter fitted using

$$\varepsilon''_{dc}(\omega) = \sigma_{dc}\omega^{-1}. \tag{1}$$

In Fig. 2, these σ_{dc} are plotted vs τ_α, the data conforming to a power law[9]

$$\sigma\tau^s = \text{const} \tag{2}$$

with $s=0.82$. This exponent reflects the degree of decoupling of the two quantities, so that for the BHPP we find τ_α and σ have somewhat different temperature dependences.

For the higher temperatures, a prominent "excess wing" is present in the loss spectra, appearing as a deviation of the α peak in Fig. 1 at higher frequencies from the Kohlrausch–Williams–Watts (KWW) form[10] of the relaxation function,

$$\varepsilon''(\omega) = \Delta\varepsilon \int_0^\infty dt \left[\frac{-d}{dt}\exp(-(t/\tau_K)^{\beta_K})\right]\sin(\omega t). \tag{3}$$

In Eq. (3), $\Delta\varepsilon$ is the dielectric strength, τ_K a characteristic relaxation time, ω the circular frequency, and β_K is the stretch exponent. Fits to the α peak using $\beta_K=0.55$ are shown in Fig. 1. (Note for this value of the stretch exponent, $\tau_K=0.76\tau_\alpha$.). The intensity at high frequencies in excess of
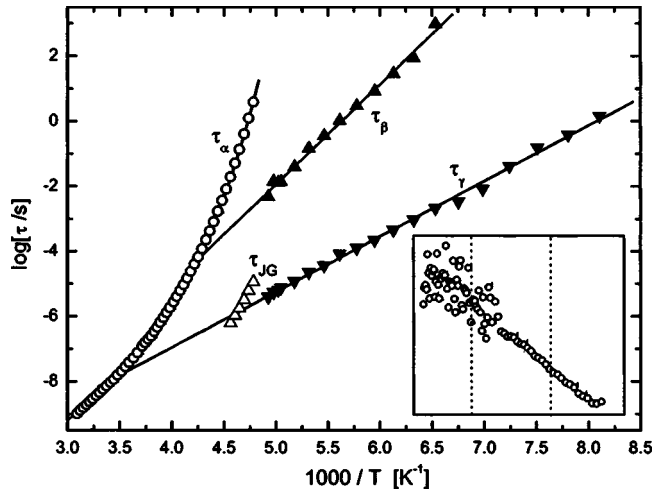
FIG. 3. Arrhenius plot of the relaxation times for the α ($\bigcirc$), β ($\blacktriangle$), and γ processes ($\blacktriangledown$). The solid lines are the fit of Eq. (4) to τ_α and linear fits (Arrhenius behavior) to the secondary relaxations, yielding E_β =58.8±1.3 kJ/mol and E_γ=32.6±0.4 kJ/mol. Extrapolations of the latter yield the intersections with τ_α at apparent merging temperatures, $T_{\alpha\beta}$ =233.2 and $T_{\alpha\gamma}$=281.6 K. The open triangles are τ_{JG} calculated from Eq. (10) assuming β_K=0.55. Inset shows the derivative (Stickel) plot of the α-relaxation times. The vertical dashed lines denote the merging temperatures.

the calculated KWW function constitutes the excess wing.

As temperature is reduced below ca. 207 K, the primary peak moves out of the experimental window, and a secondary process (β peak) becomes apparent toward higher frequencies. This reveals that the excess wing seen at lower temperatures is, in fact, just a submerged secondary relaxation. At still lower temperatures (<198 K), another secondary process becomes evident, which we refer to as the γ peak. Thus, at the higher temperatures in Fig. 1, the excess wing reflects contributions from two unresolved secondary processes.

Except at the highest measurement temperatures, the secondary peaks, although weak, are sufficiently isolated that no deconvolution from the α peak is necessary. The relaxation times for all three processes, defined from the peak maxima, are displayed in Fig. 3. Both secondary processes exhibit Arrhenius behavior, with activation energies equal to 58.8±1.3 and 32.6±0.4 kJ/mol for τ_β and τ_γ, respectively.

The α relaxation has a Vogel–Fulcher (VF) temperature dependence,

$$\log \tau_\alpha(T) = \log \tau_0 + \frac{B}{T - T_0} \tag{4}$$

with $\log \tau_0$ (s)=−12.97±0.01, B=649±3 K, and T_0 =161.3±0.1 K. Extrapolation to τ_α=100 s gives 204.7 K for the glass transition temperature T_g. From the VF parameters, we calculate the fragility (T_g-normalized temperature dependence),

$$m \equiv \left. \frac{d \log(\tau)}{d(T_g/T)} \right|_{T=T_K} = \frac{B \log(e)}{T_g(1 - T_0/T_g)^2}. \tag{5}$$

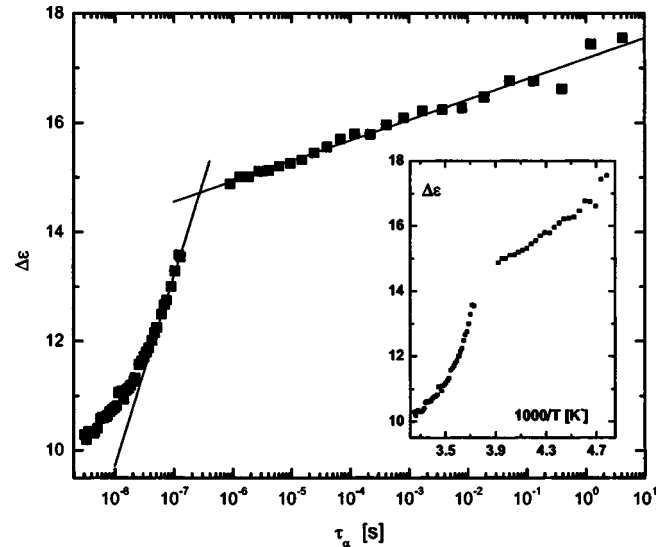The result, m=71, indicates that BHPP is a moderately fragile glass former.

FIG. 4. Dielectric strength of the α process as a function of the α-relaxation time. The solid lines, which are linear fits to the two regimes for $\tau_\alpha > 5 \times 10^{-8}$ s, intersect at $\tau_\alpha = 4 \pm 2 \times 10^{-7}$ s. The inset shows the same data plotted vs inverse temperature.

Equation (4) fits τ_α over the entire range, encompassing almost ten decades of time. It is unusual to be able to accurately describe relaxation times for the α process over such a broad range using a single VF equation. A Stickel plot[11] of the data, i.e., $(d \log \tau_\alpha/dT^{-1})^{-1/2}$ vs T^{-1}, is shown in the inset to Fig. 3. This yields a straight line, indicating absence of any marked change in dynamics, as commonly seen at a temperature $T_B \sim 1.2 T_g$.[11–15]

Although there is no evidence of a crossover in the relaxation time data, it has been found that the temperature variation of the dielectric strength of glass formers can exhibit two regimes, demarcating a change in dynamics in the liquid state.[16,17] In Fig. 4, $\Delta\varepsilon$ is plotted as a function of the α-relaxation time, where it can be seen that there is a clear break in the curve for τ_α=0.4±0.2 ms; thus, T_B=262±4 K. In the inset, the dielectric strength is plotted vs the reciprocal temperature. Classical theory predicts an inverse dependence of $\Delta\varepsilon$ on T, arising from orientation of the dipoles.[18] This is rarely observed, due to correlation of the dipoles. Instead, as seen in the inset to Fig. 4, there are the two regimes.[16,17] It is also interesting to note the curvature in $\Delta\varepsilon$ the towards higher temperatures. This may be caused by the presence of more than one dipole in the BHPP.

B. Pressure dependence

In Fig. 5 are shown spectra measured at 253 K for various pressures. The α peak exhibits a strong sensitivity to pressure, and beyond about 0.5 GPa, τ_α is too large to be observed within the available frequency range. At lower pressures, its shape is essentially unchanged from that at ambient pressure, β_K=0.55±0.03. The secondary relaxations, which were masked by the α peak at this temperature at ambient pressure (Fig. 1), appear as distinct peaks at elevated pressure. Thus, both temperature and pressure serve to transform the excess wing into a separated dispersion in the loss.
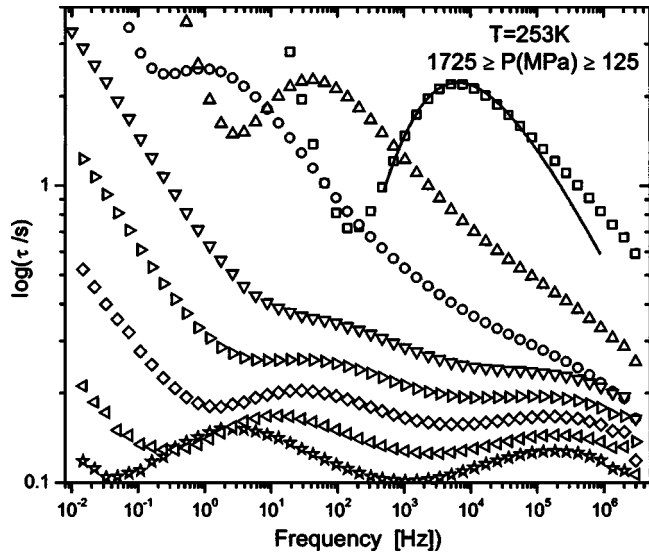
FIG. 5. Dielectric loss spectra measured at 253 K and pressures (in MPa) equal to 125 (□), 331 (△), 450 (○), 693 (▽), 843 (▷), 987 (◇), 1275 (◁), and 1725 (⋆). The solid line is Eq. (3) with $\beta_K=0.55$.

Similar to the α peak, the relaxation time for β process increases with increasing pressure. However, the faster γ peak does not change frequency over an almost threefold increase in P. The pressure dependence of the relaxation times are displayed in Fig. 6, from which an activation volume can be defined as $\Delta V_\alpha^\# = 2.303RT \lim_{P\to 0}(d\log\tau_\alpha/dP)$, with similar expressions for τ_β and τ_γ. While the variation of the relaxation time for the secondary processes is linear with pressure, there is some curvature in the plot of τ_α vs P in Fig. 6. A useful parametrization is[19,20]

$$\log \tau_\alpha(P) = \log \tau_P + \frac{CP}{P_0 - P}, \tag{6}$$

where τ_P, C, and P_0 are constants. Fitting the α-relaxation times in Fig. 6, we obtain $\log \tau_P$ (s)$=-5.85\pm-/05$, C
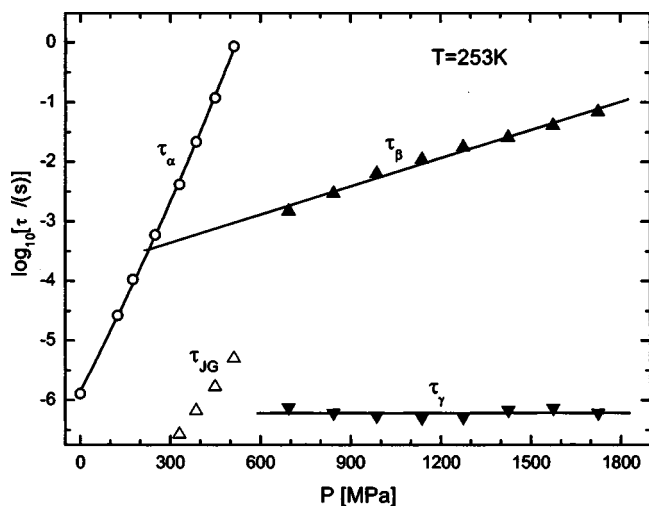

FIG. 6. Relaxation times as a function of pressure at 253 K. The lines are linear fits to the data, except for α-relaxation times, for which Eq. (6) was used. The corresponding activation volumes are listed in Table I. The open triangles are the τ_{JG} calculated using Eq. (10) with the assumption that $\beta_K=0.55$.

TABLE I. Activation parameters.

	E_a (kj/mol)	$\Delta V^\#$ (ml/mol)
α process	280[a]	47 ± 3
β process	58.8 ± 1.3	7.6 ± 0.2
γ process	32.6 ± 0.4	0.03 ± 0.03

[a]From Arrhenius slope at $T_g=204.7$ K.

$=41\pm12$, and $P_0=4180\pm1100$ MPa. In the limit of low pressure, $\Delta V_\alpha^\#=2.303RT(C/P_0)=47\pm3$ cm^3/mol. The activation volumes for all three processes are listed in Table I.

IV. DISCUSSION

The α relaxation of BHPP shows some interesting features. The liquid exhibits a moderate fragility, and in combination with the activation volume (Table I), the pressure coefficient of the glass temperature can be calculated as[21]

$$\frac{dT_g}{dP} = \frac{\Delta V_\alpha^\#}{2.303Rm}. \tag{7}$$

We obtain $dT_g/dP=35\pm2$ GPa^{-1}. This is substantially lower than for dibutyl phthalates,[22] and falls in the range of dT_g/dP values reported for H-bonding liquids.[23–25] The ester structures have less influence on the pressure variation of the glass temperature than do the hydroxyl groups, because of the dominant influence of hydrogen bonding.

Over a range covering more than nine decades of frequency, the temperature dependence of τ_α can be described by a single VF equation; that is, there is no evidence of a change of dynamics at $T_B>T_g$. The change in dynamics suggested by the dielectric strength data is also not seen in derivative plots of $\tau_\alpha(T)$. The latter behavior is usually found for glass formers having narrow relaxation functions. For example, glycerol and propylene glycol have large values of β_K (>0.7) and only very weak changes in the T dependence of τ_α above T_g.[26,27] However, fitting the α-relaxation peak of BHPP yields $\beta_K=0.55$, which is not an especially narrow relaxation function.

A confirmation of the obtained β_K can be obtained using the well-known correlation between the stretch exponent and the fragility, expressed as[28]

$$m = 250(\pm 30) - 320b_K \quad (30 < m < 200). \tag{8}$$

For $m=71$, this gives $\beta_K=0.56$, consistent with the value determined by fitting the loss spectra of BHPP to Eq. (3) (Fig. 1). There are notable exceptions to this general correlation,[29] and in particular, monohydric alcohols tend to have larger stretch exponents than Eq. (8) would suggest.[28] Thus, in Fig. 7 we plot (as open inverted triangles) the available literature data for alcohols, both monohydric and polyhydric.[7,28,30] The single solid symbol represents the values m and β_K obtained herein for BHPP. This datum lies within the range for the other alcohols, although the scatter is large.

Generally, glass formers may exhibit two types of secondary relaxations in their dielectric spectrum—processes involving all atoms in the molecule, which are referred to as JG relaxations, and (trivial) processes involving only in-
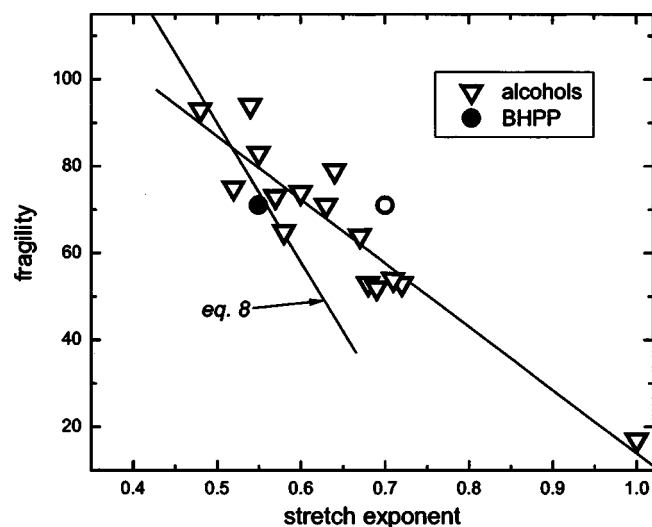
FIG. 7. T_g-normalized temperature dependence of τ_α for various alcohols ($\triangledown$) as a function of β_K (from Refs. 7, 28, and 30), along with the linear fit to the data (dashed line). Also included are the results herein for BHPP using the stretch exponent determined from fitting the loss peak ($\bullet$), and using the value of β_K deduced from the properties of the β relaxation ($\circ$). The solid line represents the correlation of these two quantities for all glass formers (not just alcohols) as reported by Bohmer et al. (Ref. 28).

tramolecular degrees of freedom.[1,2,31] When more than one secondary relaxation is present, the faster (smaller τ) cannot be the JG process, since motion involving only some atoms in the molecule is necessarily faster than intermolecular motion involving the entire molecule. This means that the γ relaxation in BHPP is not a JG process. It is not uncommon for associated liquids to exhibit a higher frequency, secondary peak, in addition to their JG relaxation (which may appear only as an excess wing at ambient pressure).[2,8] The question remains concerning the identity of the β process in BHPP—is it a JG relaxation or only intramolecular motion bearing no relationship to the glass transition? Various differences expected for these two types of secondary relaxations, with properties specific to the JG process described in the literature, are given below.

(i) The change in dynamics of the α process transpires at a temperature T_B, which is usually approximately equal the value of the temperature, T_β, at which the extrapolated JG relaxation times intersect τ_α. From Fig. 3, the secondary relaxation times for BHPP extrapolate to an intersection with the α process at $\log(\tau_\beta/s) = -4.3$ and $\log(\tau_\gamma/s) = -7.9$. An extrapolation of the pressure dependence (Fig. 6) yields similar results. The change in the dynamics inferred from Fig. 4 occurs at $\log(\tau_\alpha/s) = -6.4$, which is inconsistent with the identification of the β peak as a JG process.

(ii) The separation between the main α peak and the JG peak is also related to the magnitude of the stretch exponent, according to[7,32]

$$\tau_{JG} = t_c^{1-\beta_K} \tau_\alpha^{\beta_K}, \tag{9}$$

where $t_c \sim 2$ ps. The calculated values of the JG-relaxation time are displayed in Figs. 3 and 6 where it can be seen that they are at least three orders of magnitude smaller than τ_β. The separation of τ_α and τ_β is consistent with a 1.3-fold larger value of β_K. Indeed, glass formers exhibiting an ex-

cess wing are those having large values of the stretch exponent, $\beta_K \gtrsim 0.7$.[32]

(iii) A correlation has been proposed between the activation energy for the JG process and the glass transition temperature, $E_{JG} = 24RT_g$.[33] This relation has been generalized to[34]

$$E_{JG} = RT_g(31.6\beta_K - 26.9 - 2.303 \log \tau_0), \tag{10}$$

where the quantity in brackets equals about 24 for many glass formers, and =20.3 for BHPP. From Eq. (10) we calculate $E_{JG} = 35$ kJ/mol, which is about half the measured value of $E_\beta = 58.8 \pm 1.3$ kJ/mol. The latter suggests a value of β_K that is 1.2 times larger than measured.

There are two possible explanations for the behavior of the secondary β relaxation. First, it may not be a JG relaxation, and thus conditions (i)–(iii) above would not apply. However, this begs the question—where is the JG relaxation in BHPP? While it is often submerged under a dominant α peak, and thus appears only as an excess wing, the excess wing seen herein transforms into a distinct peak at lower T and higher P. In previous cases in which pressure or physical aging was used to deconvolute the primary α peak, the secondary peak arising from the excess wing was reported to be a JG relaxation.[8,24,35–38]

The second possibility is that the α-relaxation peak is inhomogeneously broadened, due to a complex structure having more than one dipole; consequently, the measured breadth would not be a true reflection of the intrinsic β_K for the α process. Such an effect has been observed previously in polymers, such as ethylene-propylene copolymer[39] and epoxidized polyisoprene,[40] in which local segmental motion originates with torsional motion of different repeat units, giving rise to an anomalously broadened relaxation function. The inference herein is that for a large molecule such as BHPP, having dipoles at both the ester moieties and the terminal hydroxyl groups, the α relaxation is broadened, whereby Eqs. (8)–(10) do not apply, at least using the directly measured peak breadth. This would account for the fact that there is no obvious change in the temperature dependence of the α relaxation in the vicinity of the extrapolated merging of τ_β and τ_α, since the usual change of dynamics is very weak in glass formers whose α relaxation has a large value of β_K. Conformance of the relaxation properties to Eqs. (9) and (10) implies $\beta_K \sim 0.7$. As seen in Fig. 7, the scatter in the correlation between fragility and β_K is sufficient to admit this larger value of the stretch exponent for BHPP. However, the activation volume measured for the β peak is too small, and this discrepancy would become *worse* for a larger value of β_K.

Finally, we note that for dibutylphthalate (DBP), $\beta_K = 0.65$.[22] Given the well-established inverse correlation between the magnitude of the stretch exponent and the capacity for intermolecular coupling,[41] it is not obvious how the local motion of the bulkier, more polar BHPP could be less intermolecularly cooperative than DBP. That is, we expect β_K for BHPP to be smaller than β_K for DBP; this argues in favor of the directly measured value of the stretch exponent, rather than the much larger one required for compliance with Eqs. (8)–(10).

V. SUMMARY

The slowest relaxation process in the dielectric spectrum of BHPP is the primary α relaxation. At higher temperatures and lower pressures, the α dispersion is obscured by dc conductivity toward lower frequencies, while exhibiting a prominent excess wing toward higher frequencies. As temperature decreases or pressure is elevated, this excess wing separates from the α peak, with two distinct secondary relaxations emerging in the loss spectrum. The faster secondary γ process reflects intramolecular dynamics (internal modes) and is of no import to the glass transition. Since, in principle at least, all glass formers have a JG process, involving all atoms in the molecule, we expect the lower frequency secondary peak in BHPP to be the JG relaxation. However, the properties of this β relaxation, including its relaxation time relative to τ_α, and the magnitude of both its activation energy and activation volume, are inconsistent with values predicted from the breadth of the α-relaxation peak. We conclude that the β process is indeed the JG relaxation, notwithstanding the departure from the predicted behavior [Eqs. (8)–(10)]. These predictions all rely on the shape of the α-relaxation function (value of β_K). The implication is the α peak is inhomogeneously broadened, as a result of the complex structure of the BHPP molecule, having multiple dipole moments. Consequently, the measured stretch exponent, =0.55, is misleadingly small. A value of $\beta_K \sim 0.7$, *apropos* of a narrower inherent α-relaxation function, would bring some of the measured relaxation properties into agreement with the theoretical predictions. However, so large a value seems unlikely, given that for DBP, which has a more compact molecule structure, $\beta_K = 0.65$. Thus, while other probes of the molecular motions in BHPP, especially NMR measurements, might be useful to unambiguously identify the nature of the β relaxation in BHPP, it does appears that its secondary dynamics are at odds with the correlation of the α and JG processes seen in glass formers with less complex molecular structures.

ACKNOWLEDGMENTS

[1] G. P. Johari and M. Goldstein, J. Chem. Phys. **53**, 2372 (1970); **55**, 4245 (1972).

[2] K. L. Ngai and M. Paluch, J. Chem. Phys. **120**, 857 (2004).

[3] C. Hansen, F. Stickel, T. Berger, R. Richert, and E. W. Fischer, J. Chem. Phys. **107**, 1086 (1997).

[4] G. Meier, B. Gerharz, D. Boese, and E. W. Fischer, J. Chem. Phys. **94**, 3050 (1991).

[5] S. Hensel-Bielowka, J. Ziolo, M. Paluch, and C. M. Roland, J. Chem. Phys. **117**, 2317 (2002).

[6] G. P. Johari and K. Pathmanathan, J. Chem. Phys. **85**, 6811 (1986).

[7] C. León, K. L. Ngai, and C. M. Roland, J. Chem. Phys. **110**, 11585 (1999).

[8] R. Casalini and C. M. Roland, Phys. Rev. Lett. **91**, 15702 (2003).

[9] S. Corezzi, E. Campani, P. A. Rolla, S. Capaccioli, and D. Fioretto, J. Chem. Phys. **111**, 9343 (1999).

[10] G. Williams and D. C. Watts, Trans. Faraday Soc. **66**, 80 (1970).

[11] F. Stickel, E. W. Fischer, and R. Richert, J. Chem. Phys. **102**, 6251 (1995).

[12] D. J. Plazek and J. H. Magill, J. Chem. Phys. **45**, 3038 (1966).

[13] E. Rossler, Phys. Rev. Lett. **65**, 1595 (1990).

[14] A. J. Barlow, J. Lamb, and A. J. Matheson, Proc. R. Soc. London, Ser. A **292**, 322 (1966).

[15] R. Casalini, K. L. Ngai, and C. M. Roland, Phys. Rev. B **68**, 14201 (2003).

[16] A. Schonhals, Europhys. Lett. **56**, 815 (2001).

[17] K. L. Ngai and C. M. Roland, Polymer **43**, 567 (2002).

[18] A. Schönhals and F. Kremer, in *Broadband Dielectric Spectroscopy*, edited by F. Kremer and A. Schonhals (Springer, New York, 2002).

[19] G. P. Johari and E. Whalley, Faraday Symp. Chem. Soc. **6**, 23 (1972).

[20] M. Paluch, S. J. Rzoska, P. Habdas, and J. Ziolo, J. Phys.: Condens. Matter **8**, 10885 (1996).

[21] M. Paluch, R. Casalini, S. Hensel-Bielowka, and C. M. Roland, J. Chem. Phys. **116**, 9839 (2002).

[22] M. Sekula, S. Pawlus, S. Hensel-Bielowka, J. Ziolo, M. Paluch, and C. M. Roland, J. Phys. Chem. B **108**, 4997 (2004).

[23] S. Hensel-Bielowka, M. Paluch, J. Ziolo, and C. M. Roland, J. Phys. Chem. B **106**, 12459 (2002).

[24] M. Paluch, R. Casalini, S. Hensel-Bielowka, and C. M. Roland, J. Chem. Phys. **116**, 9839 (2002).

[25] T. Atake and C. A. Angell, J. Phys. Chem. **83**, 3218 (1979).

[26] C. Leon and K. L. Ngai, J. Phys. Chem. B **103**, 4045 (1999).

[27] F. Stickel, Ph.D. thesis, Mainz University, Shaker, Aichen, Germany, 1995.

[28] R. Bohmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, J. Chem. Phys. **99**, 4201 (1993).

[29] C. M. Roland, M. Paluch, and S. J. Rzoska, J. Chem. Phys. **119**, 12439 (2003).

[30] A. Döß, M. Paluch, H. Sillescu, and G. Hinze, J. Chem. Phys. **117**, 6582 (2002).

[31] N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymer Solids* (Dover, New York, 1967).

[32] K. L. Ngai, Phys. Rev. E **57**, 7346 (1998).

[33] A. Kudlik, C. Tschirwitz, T. Blochowicz, S. Benkhof, and E. Rossler, J. Non-Cryst. Solids **235**, 406 (1998).

[34] K. L. Ngai and S. Capaccioli, Phys. Rev. E **69**, 031501 (2004).

[35] A. Döß, M. Paluch, H. Sillescu, and G. Hinze, Phys. Rev. Lett. **88**, 095701 (2002).

[36] U. Schneider, R. Brand, P. Lunkenheimer, and A. Loidl, Phys. Rev. Lett. **84**, 5560 (2000).

[37] T. Blochowicz and E. A. Rossler, Phys. Rev. Lett. **92**, 225701 (2004).

[38] J. Mattsson, R. Bergman, P. Jacobsson, and L. Börjesson, Phys. Rev. Lett. **90**, 075702 (2003).

[39] P. G. Santangelo, K. L. Ngai, and C. M. Roland, Macromolecules **29**, 3651 (1996).

[40] C. M. Roland, Macromolecules **25**, 7031 (1992).

[41] K. L. Ngai and C. M. Roland, Macromolecules **26**, 6824 (1993).