

Influence of molecular structure on the dynamics of supercooled van der Waals liquids

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Dielectric spectroscopy was carried out on the van der Waals liquid, 1,1'-di(4-methoxy-5-methylphenyl)cyclohexane (BMMPC) in the supercooled state at pressures up to 218 MPa. The excess wing in this type-A glass former exhibits a response to pressure and temperature changes that is identical to that of the primary structural relaxation peak, indicating that the two processes reflect correlated molecular motions. Under no conditions was a distinct secondary peak observed in BMMPC, unlike the structurally very similar BMPC [1,1'-bis(*p*-methoxyphenyl)cyclohexane]. However, the pressure dependences of both the glass temperature and fragility for the two materials are very close. The fragility is a decreasing function of pressure, although there is no concomitant narrowing of the relaxation peak. The pressure dependence of the relaxation times could be described as a simple volume-activated process, with the activation volume at the glass transition having the same magnitude as the molar volume.

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I. INTRODUCTION

The dynamics of molecules near their glass temperature T_g remains an intriguing problem in condensed matter physics. For practical reasons, most experimental investigations address the effects of temperature at ambient pressure; certain aspects of the behavior of supercooled liquids require measurements under conditions of elevated P . In fact, only by studying the dependence of the dynamics on both P and T can the relative contributions of thermal energy and volume to the glass transition be quantified. Recently, it has been found that a distinction can be made between van der Waals glass formers, for which thermal energy and density have a comparable effect on the structural relaxation times (e.g., phenylphthalein-dimethylether [1], cresylphthalein-dimethylether [2], diglycidylether of bisphenol A [3], *o*-terphenyl [4], and poly[(phenyl glycidyl ether)-co formaldehyde] [1]), and associated liquids, in which temperature is the dominant control variable (e.g., glycerol [5] and sorbitol [6]).

The use of pressure as an experimental variable also allows discrimination among close-lying dispersions. Since the primary α relaxation is strongly (intermolecularly) cooperative, it is more sensitive to pressure than secondary relaxations. This differing response to pressure can be utilized to resolve overlapping peaks [7]. Moreover, the degree to which secondary relaxation times depend on pressure reflects the extent to which the associated molecular motion is correlated with the motions of neighboring molecules. Thus, pressure dependences provide information about the inter- and intramolecular character of secondary relaxation processes [8,9]. This is particularly interesting considering the controversy in the literature regarding the nature of the excess contribution observed in the high frequency part of the α relaxation (the "excess wing"). The main debate is whether this process is an intimate part of the α relaxation [10,11] or a submerged β peak [12–15].

Two interesting glass formers are the van der Waals liq-

uids, 1,1'-di(4-methoxy-5-methylphenyl)cyclohexane (BMMPC) and 1,1'-bis(*p*-methoxyphenyl)cyclohexane (BMPC). Their chemical structures (shown in Fig. 1) are very similar, but their relaxation properties in the supercooled state are quite different. The dynamics in the supercooled state were first investigated at atmospheric pressure by Meier *et al.* [16]. They found that the breadth of the α relaxation of BMPC, as observed by dielectric (DS) and dynamic light scattering–photon correlation spectroscopy (DLS), was independent of temperature, while for BMMPC it increases with decreasing temperature. They attributed the differing behaviors to the presence of a second relaxation, which in the case of BMPC falls at higher frequencies than the α process (although not actually observed dielectrically by those authors [16]), while for BMMPC it was hypothesized to be close to, and thus masked by, the α relaxation. NMR measurements [16] identified a secondary relaxation process in BMPC, arising from the flipping of the methoxyphenol rings. These ring flips were not detected in BMMPC, presumably due to constraints from the neighboring methyl group.

Subsequently, Hansen *et al.* [17] observed a secondary dielectric relaxation in BMPC, at frequencies equivalent to those seen by NMR. This secondary relaxation exhibited characteristics generally attributed to a Johari-Goldstein (JG) [18] process; that is, a broad, weak dispersion, merging with the α relaxation above T_g [17,19]. However, since the under-

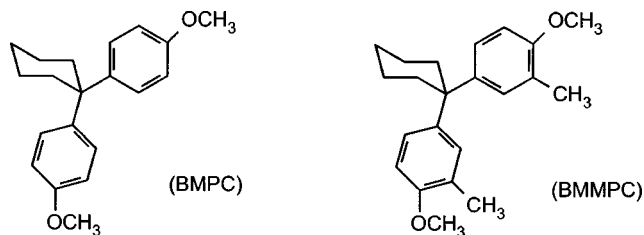


FIG. 1. Chemical structure of 1,1'-di(4-methoxy-5-methylphenyl)cyclohexane and [1,1'-bis(*p*-methoxyphenyl)cyclohexane].

lying motion involves intramolecular degrees of freedom (ring flipping [16]), this secondary process cannot be regarded as a JG process since the latter is intermolecular by definition [18].

Consistent with an intramolecular origin for the secondary process in BMPC, recent dielectric measurements at elevated pressure [20] showed its relaxation time to be insensitive to pressure, in contrast to the intermolecularly cooperative α relaxation. Interestingly, no dielectric measurements on BMPC beyond those of Meier *et al.* [16] have been reported in the literature; thus, the identity, or even the existence, of this secondary process in BMMPC is an open question. Note that it was undetected in either BMPC or BMMPC in the earlier work [16], due to instrumental limitations.

Herein, we present extensive dielectric measurements of BMMPC at both atmospheric and elevated pressure, directed to the behavior of the α relaxation, as well as the putative secondary relaxation. We compare these results to the properties of the structurally similar BMPC.

II. EXPERIMENT

Dielectric measurements were carried out over nine decades of frequency [$10^{-3} \leq f(\text{Hz}) \leq 10^6$], using an IMASS time domain dielectric analyzer [$10^{-3} \leq f(\text{Hz}) \leq 10^4$] and a Novocontrol Alpha Analyzer [$10^{-2} \leq f(\text{Hz}) \leq 10^6$].

The sample cell was a parallel plate capacitor, contained within a Manganin cell (Harwood Engineering). For measurements, the pressure vessel was placed in an environmental chamber (Tenney Engineering) having a nitrogen atmosphere, with the temperature controlled to ± 0.1 K. The capacitor (geometric capacitance ~ 35 pF) was isolated from the pressurizing fluid by means of a Teflon ring. Pressure was applied using a hydraulic pump (Enerpac), and measured with a Sensotec tensometric transducer (resolution = 150 kPa).

The BMMPC was synthesized in the laboratory of H. Sillescu at the Johannes Gutenberg University, Mainz, Germany. Note this compound is also referred to in the literature as bis-kresol-C-dimethylether (BKDE). Similarly, BMPC is also known as bis-phenol-C-dimethylether (BCDE).

III. RESULTS

A. Effect of pressure on structural relaxation

Figures 2–4 show the dielectric loss in the vicinity of the α dispersion for constant pressure ($P=0.1$ MPa) and constant temperature ($T=288.8$ and 307.5 K), respectively. At lower temperatures or higher pressures the peak moves to lower frequency, revealing an “excess wing” [21,22], observed as a change in the high frequency flank of the α relaxation from one power law $\varepsilon''(f) \sim f^{-\beta}$, to a second $\varepsilon''(f) \sim f^{-b}$, where β , the fractional exponent in the Kohlrausch function [23], is larger than b . However, under no measurement conditions, which *in toto* extended from 278.2 to 307.5 K at pressures up to 218 MPa, was a distinct secondary peak, or even a nascent shoulder, evident in the spectra. However, some curvature in the excess contribution is

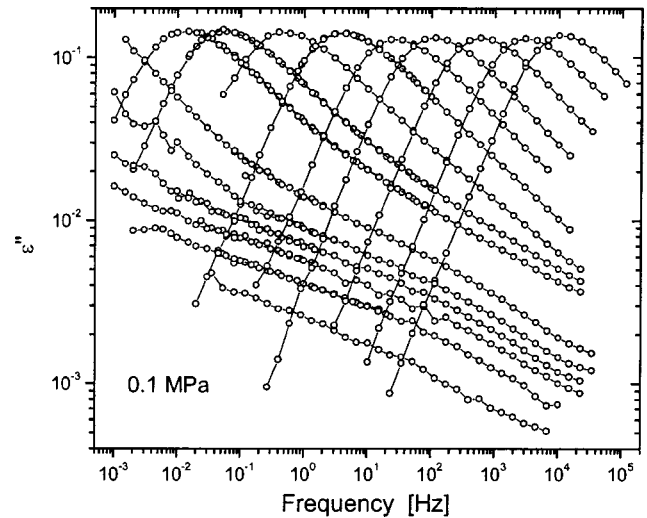


FIG. 2. Dielectric loss for BMMPC at ambient pressure and temperatures equal to 212.7 (lowest curve), 231.9, 241.5, 246.7, 251.2, 256.1, 263.6 ($f_{\text{max}}=0.014$ Hz), 266.6, 271.4, 277.0 ($f_{\text{max}}=4$ Hz), 283.5, 287.7, 292.8, 297.9, and 302.2 K (rightmost curve). Even for temperatures at which the peak frequency is too low to be observed, there is no indication of a secondary peak.

evident. This is similar to that observed for the glass formers salol and propylencarbonate [24].

The detailed shape of the α peak and the excess wing respond similarly to changes in temperature and pressure. This is illustrated in Fig. 5, which shows the α peak measured at three different temperatures and pressures, chosen such that the peak maxima almost coincide. The excess wing becomes evident on a logarithmic ordinate scale as a high-frequency deviation from the Kohlrausch function. Both the peak and the excess wing almost superimpose; thus, there is no clear indication of an underlying (“submerged”) β pro-

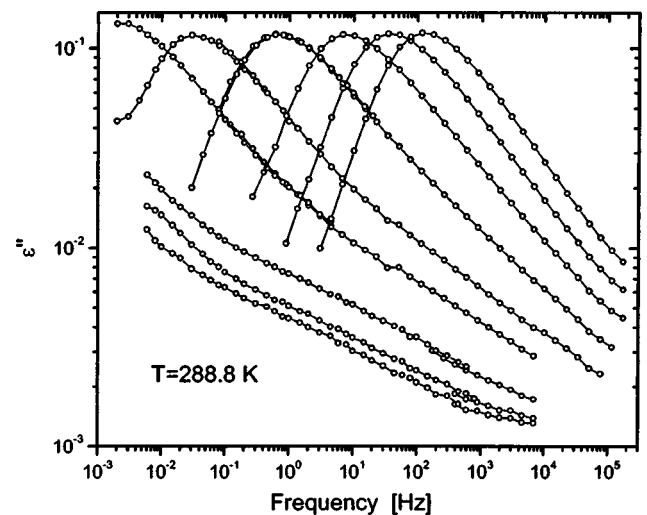


FIG. 3. Dielectric loss for BMMPC at 288.8 K at pressures equal to 0.1 (rightmost curve), 12.0, 27.9, 51.8, 80.9 ($f_{\text{max}}=0.03$ Hz), 101.7, 129.9, 185.5, and 218.7 MPa (lowest curve). Even at the higher pressures, for which the peak frequency is too low to be observed, there is no indication of a secondary peak.

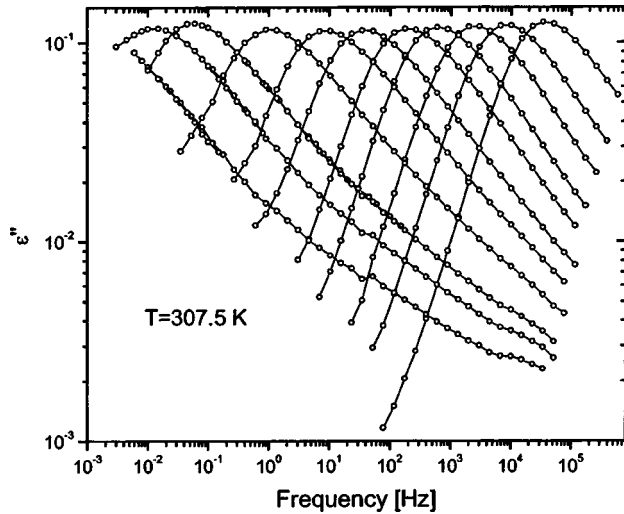


FIG. 4. Dielectric loss for BMMPC at 307.5 K and pressures equal to 0.1 (rightmost curve), 17.3, 31.6, 48.9, 63.0, 82.7 ($f_{\max} = 40$ Hz), 100.4, 124.5, 152.5 ($f_{\max} = 0.06$ Hz), 180.2, and 198.7 MPa (leftmost curve). At the highest pressures, for which the peak frequency falls below the measured range, no secondary peak is observed.

cess with a different pressure sensitivity. This superpositioning of the α peak and excess wing appears to be the rule for nonassociated (e.g., van der Waals) glass formers [8]. For larger values of the relaxation times τ_α ($= 1/[2\pi f_{\max}]$, where f_{\max} is the frequency of the peak maximum), there is a modest broadening of the peak with decreasing temperature at fixed P , and with increasing pressure at fixed T (Fig. 6).

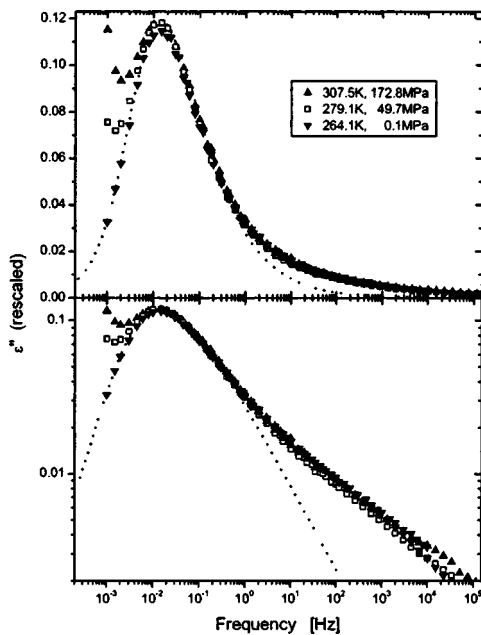


FIG. 5. Dielectric loss peak for BMMPC at the indicated temperatures and pressures. The data have been vertically scaled $\leq 20\%$ to account for the changing dielectric strength; the frequencies are as measured. The dotted line is the Kohlrausch function [23] with $\beta = 0.55$. The logarithmic ordinate scale in the lower panel makes evident the deviation to a second power law at higher frequencies.

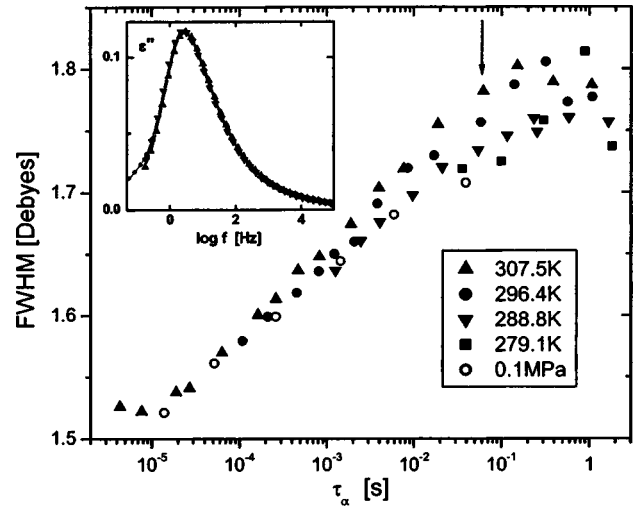


FIG. 6. The full width at half maxima for the α -relaxation peak of BMMPC measured at various pressures (solid symbols) at the indicated temperatures, and at various temperatures at atmospheric pressure (\circ). The inset shows the dispersion for three conditions (∇ , $T = 279.1$ K, $P = 0.9$ MPa; \bullet , $T = 288.8$ K, $P = 37.3$ MPa; \blacktriangle , $T = 307.5$ K, $P = 114.1$ MPa) for which the relaxation times are the same ($= 0.058$ s, indicated by the arrow).

However, any variation in peak breadth with T and P for a given τ_α is quite small, as seen in the inset to Fig. 6, showing measurements at three conditions for which τ_α is essentially constant. Similar results have been reported before for other materials [25,26].

The τ_α for BMMPC are displayed in Fig. 7 as a function of pressure. Defining a glass transition temperature as the temperature at which the relaxation time equals 100 s, we obtain the T_g results shown in Fig. 8. These can be described using the empirical equation [27]

$$T_g = a \left(1 + \frac{b}{c} P \right)^{1/b}, \quad (1)$$

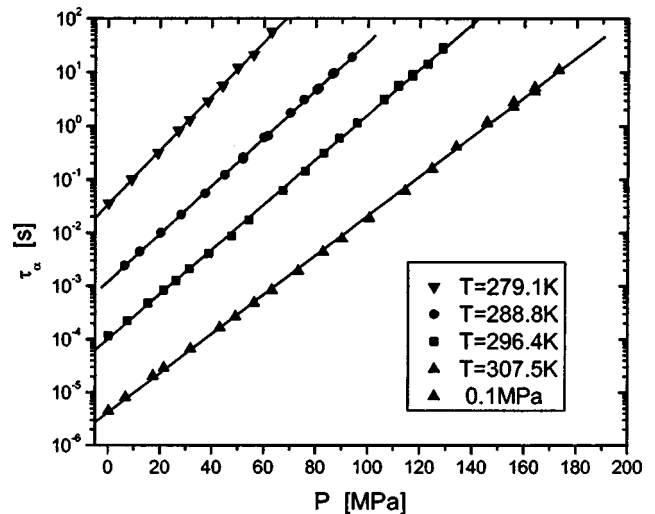


FIG. 7. Pressure dependence of the α relaxation times for BMMPC at the indicated temperatures. The linear fits to these data yield the activation volumes [Eq. (2)].

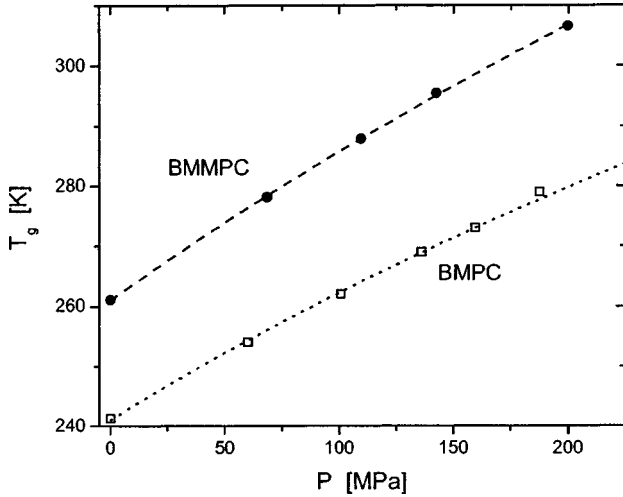


FIG. 8. The temperature at which $\tau_\alpha = 100$ s as a function of pressure. The lines through the data are the fits to Eq. (1).

yielding $a = 261$ K, $b = 2.99$, and $c = 962$ MPa. From this we obtain in the limit of zero pressure 0.27 K/MPa for the pressure coefficient of the transition temperature.

The pressure dependence of structural relaxation times can be described using various models [28–32]. However, for BMMPC the τ_α on the semilogarithmic scales of Fig. 7 appear linear over the range of measurements, and thus can be parametrized simply in terms of an activation volume

$$\Delta V(T, P) = \ln(10)RT \left(\frac{\partial \log_{10} \tau_\alpha}{\partial P} \right) \Bigg|_T, \quad (2)$$

where R is the gas constant. In a free volume description of structural relaxation, the activation volume reflects the unoccupied space necessary for the relaxation process to transpire. The ΔV obtained for BMMPC are displayed in Fig. 9,

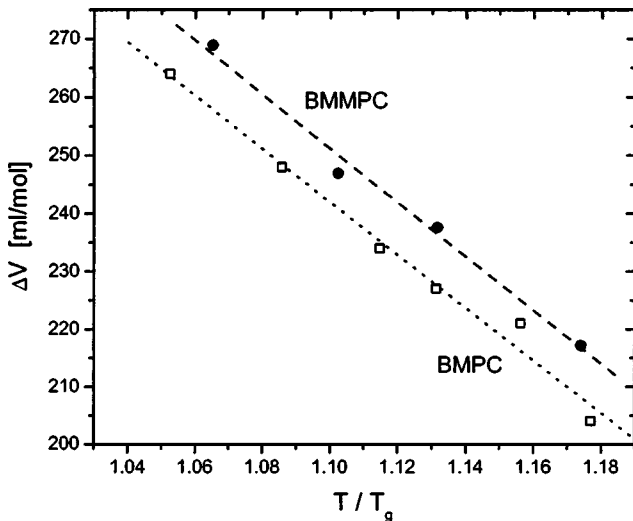


FIG. 9. Activation volume as a function of T_g normalized temperature. The data for BMPC were taken from Ref. [20]. The lines represent a linear fit.

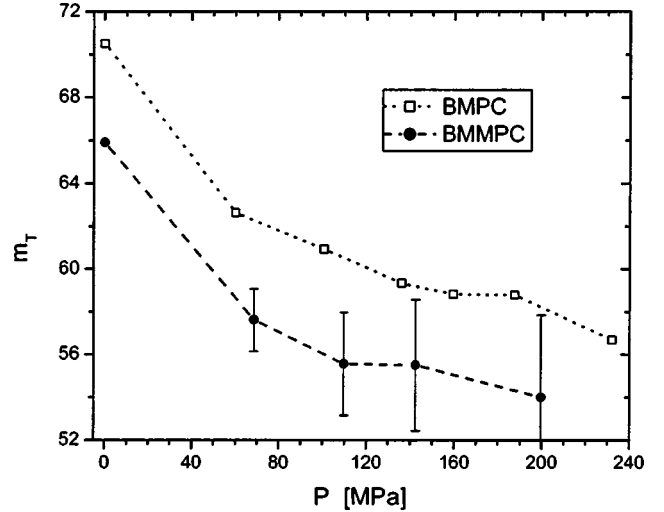


FIG. 10. Steepness index [Eq. (3)] as a function of pressure. The lines merely connect the points and are not a fit to the data.

as a function of temperature normalized by T_g (for $P = 0.1$ MPa).

The rapidity of the change in τ_α as T_g is approached from above is a common means to classify glass formers [33]. This temperature dependence is often expressed as the fragility, defined in terms of a steepness index, $m(P) \equiv (d \log_{10} \tau_\alpha / d(T_g/T))|_{T=T_g}^P$. The steepness index is proportional to the ratio of the activation volume and pressure coefficient of T_g

$$m(P) = \frac{\Delta V}{R \ln(10)} \Bigg/ \left(\frac{dT_g}{dP} \right). \quad (3)$$

From the data in Figs. 8 and 9, we calculate the steepness index for all measured pressures, with the results shown in Fig. 10.

From the decrease in fragility with pressure, we anticipate a concomitant narrowing of the relaxation function, given the phenomenological correlation between the two quantities [34]. In fact, the breadth of the α peak *increases* with both increasing pressure and (at $P = 0.1$ MPa) decreasing temperature (although, as shown by Figs. 5 and 6 above, the breadth is almost a unique function of the relaxation time). Recent light scattering measurements similarly found that the fragility of BMMPC decreased with pressure, although the peak breadth in those experiments increased slightly [35].

B. Comparison to BMPC

The principle difference between the dynamics of BMPC and BMPC is that only the latter exhibits a distinct secondary relaxation peak in its dielectric loss spectrum. As seen in Figs. 3–6, application of hydrostatic pressure to BMPC does not cause any underlying peak to separate out from the main α peak. This result corroborates interpretation of the secondary process in BMPC as due to phenyl ring flips, and the suggestion that such motion is precluded in

TABLE I. Comparison of properties for BMPC and BMMPC.

	T_g ($\tau_\alpha = 100$ s)	dT_g/dP (K/MPa)	ΔV at T_g (ml/mol)	$\Delta V/V_m$ at T_g	dm/dP^b (MPa $^{-1}$)
BMPC ^a	241 K	0.24±0.01	288	1.12±0.07	-0.033±0.005
BMMPC	261 K	0.27±0.01	298	1.04±0.05	-0.029±0.015

^aFrom data in Ref. [20].^b $P \geq 60$ MPa.

BMMPC by steric hindrance due to the methyl group adjacent to the ether moiety [16].

In Table I we list various results for the two glass formers. The respective temperatures at which $\tau_\alpha = 100$ s differ by 20° (note both values are within one degree of the glass temperature determined by differential scanning calorimetry at an “infinitely” slow heating rate [36]). T_g for BMMPC exhibits a slightly greater dependence on pressure, a consequence of its moderately larger activation volume (Fig. 8). When compared at T_g ($P = 0.1$ MPa), $\Delta V = 288$ ml/mol for BMPC versus 298 ml/mol for BMMPC. We can compare these activation volumes to the molar volumes V_m of the two liquids. From the molar volumes for BMPC and BMMPC at their glass temperatures, $V_m = 257$ and 287 ml/mol, respectively [37], we find that the ratio $\Delta V/V_m$ (listed in Table I) is about the same for the two liquids, within the experimental error.

These similarities in the response to pressure extend also to the fragility, as seen from the parallel nature of the curves in Fig. 10. Since there is a gap between the ambient pressure results and those obtained herein at elevated pressure (due to limitations of the experimental apparatus), the detailed dependence of the steepness index on pressure is uncertain. However, a rough estimate gives $dm/dP \sim 0.12$ MPa $^{-1}$ at atmospheric pressure for both BMMPC and BMPC.

IV. SUMMARY

For BMMPC, the shape of the α relaxation, including the excess wing, is essentially independent of temperature and pressure, when the dielectric loss peaks are compared at a constant value of τ_α . There is no change in the spectrum, in particular the emergence of any secondary relaxation, when high pressure is applied. Thus, the high frequency secondary peak seen in BMPC is absent in BMMPC for all measured conditions. This exemplifies the utility of pressure in identifying secondary processes in glass formers.

The absence of a secondary peak in BMMPC is likely due to steric hindrance from the methyl group, adjacent to the ether moiety, as was previously proposed by Meier *et al.* [16]. The constraint on the phenyl ring in BMMPC would cause its motion to be more coupled to the structural relaxation, and hence exhibit a stronger pressure dependence. From this point of view, the secondary relaxations of BMPC and BMMPC reflect similar motions, differing only in the angle subtended by the flipping of the phenyl ring. In fact,

²H NMR measurements [38] have been interpreted to suggest that secondary relaxations in general are due to spatially restricted reorientation of all molecules over a small angle. An unresolved secondary peak would then simply be motion restricted to even smaller angles. However, such simple structure-property relations may not hold generally. For example, toluene [22,38] and 2-picoline [39] have very similar molecular structures, yet only the former has a resolved secondary peak. Correlations between unresolved secondary relaxations and the primary structural relaxation have been adduced [8,12,15], although moving this discussion beyond speculation requires further experimental investigation.

The pressure dependence of T_g is nonlinear, with a variation at low pressure equal to 0.27 K/MPa. This is quite close to the value obtained by light scattering measurements on BMMPC [35], and a few percent larger than dT_g/dP for BMPC [20]. Since the logarithm of the relaxation times is proportional to pressure over the range of our measurements, the pressure dependence for BMMPC can be treated as a simple volume-activated process, similar to results for BMPC [20]. For both liquids at T_g , the activation volume, representing the local excess volume necessary for relaxation, is only slightly larger than the molar volume. At ambient pressure, the relaxation time for BMMPC equals 100 s at a temperature, 261 K, which is the same as the DSC transition temperature determined for an infinitely slow heating rate [36].

Finally, the steepness index, describing the T_g -normalized temperature dependence of τ_α , decreases with pressure. Such a result has been reported previously for poly(methyltolylsiloxane) [40], polystyrene [41], poly(vinylchloride) [41], poly(methylacrilate) [41], salol [42], as well as BMPC [20]. In fact, for the latter, the pressure coefficient of the m , equal to about 0.12 MPa $^{-1}$ at atmospheric pressure, is equal within experimental error to that for BMMPC. More usually, fragility is found to be independent of P [3,41,43–50], or even, as in the case of glycerol [51], increasing with increasing pressure.

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